Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.979329

57 (2016) 738–746
January

Taylor & Francis
Taylor & Francis Group

The optimization study of direct red 81 and methylene blue adsorption on NaOH-modified rice husk

S.D. Ashrafi[a], H. Kamani[b], A.H. Mahvi[a,c,d,*]

[a]*Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Science, Tehran, Iran, Tel. +98 2144729729; Fax: +98 2188950188; email: d_ashrafi @yahoo.com (S.D. Ashrafi), Tel. +98 2188954914; Fax: +98 2188950188; email: ahmahvi@yahoo.com (A.H. Mahvi)*
[b]*Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran, Tel. +98 5412428797; Fax: +98 2166662267; email: hossein_kamani@yahoo.com (H. Kamani)*
[c]*National Institute of Health Research, Tehran University of Medical Science, Tehran, Iran*
[d]*Center for Solid Waste Research, Institute for Environmental Research, Tehran University of Medical Science, Tehran, Iran*

Received 23 July 2014; Accepted 27 September 2014

ABSTRACT

The objectives of this investigation are to obtain optimal adsorption conditions for direct red 81 (DR81) and methylene blue (MB) from aqueous solution on NaOH-modified rice husk (NaOH-RH) using response surface methodology (RSM). A Box–Behnken design (BBD) statistical experimental design was used to investigate the adsorption of DR81 and MB on NaOH-RH. For DR81, pH (4–7), initial concentration of dye (25–125 mg/l), adsorbent dose (2–6 g/l) and for MB pH (7–10), initial concentration of dye (25–125 mg/l) and adsorbent dose (0.25–0.75 g/l) were selected as independent variables. The results showed that the predicted values for both dye adsorptions were close to the experimental values and were in a good agreement, on the other hand, the R^2 values for DR81 ($R^2 = 0.9685$) and MB ($R^2 = 0.9832$) indicated that the regression is able to give a good predict of response for the adsorption process in the range studied. From the BBD predictions, the optimal conditions in the adsorption process for removing 54.04% of DR81 were found to be 25 mg/l initial dye concentration and 6 g/l adsorbent dose at pH 4. Also, removing 97.66% of MB was found to be 25 mg/l initial dye concentration and 0.595 g/l adsorbent dosage at pH 8.89.

Keywords: NaOH-modified rice husk; Direct red 81; Methylene blue; Adsorption

1. Introduction

Many industries such as food, textile, paper, pharmaceutical, plastic, and several other industries may have been using a lot of types of dyes in their processing and manufacturing operations. The majority of these industries use large volumes of water. Therefore, they generate effluent that may have a large amount of different types of dyes and enter into the environment [1–3]. For example, some of these dyes like direct red 81 (DR81) and methylene blue (MB) may cause adverse effects such as aesthetic, carcinogenic, and toxicity consequently can harmful on human beings, animals, and plants [4–9]. The existence of benzene rings in the dye compounds makes them toxic. MB and DR81 are hazardous pollutant on the environment and have toxic effects on the human

*Corresponding author.

being and animals [5,7,10]. One of the major problems about the removal of dyes from some industries wastewater such as textile is the non-biodegradability of the most of dyes due to the aromatic structure of them and the quality of wastewater, so in many treatment plants that use biological methods, they do not have efficiency for degradation and decolorization for them [10].

A lot of methods and techniques such as precipitation, filtration, reverse osmosis, coagulation, adsorption, chemical degradation, biological, and enzymatic treatment have been used in wastewater treatment [11–14]. One of the most important points in selection of techniques is low-cost, availability, and feasibility applications of methods for removal of hazardous pollutant from aqueous solution [15–17]. Among these methods, dye adsorption is comparatively a cost-effective method [18–20]. Several adsorbents have been suggested for the adsorption of dye from aqueous solution, such as perlite [21], montmorillonite clay [22], activated carbon [23], carbon nanotubes [24], peanut husk [20,25], hen feather [26,27], and bottom ash [28]. So investigators always put effort to find a better adsorbent or modify them for enhancing their dye adsorption efficiency, one of them can be rice husk, whether natural or modified.

Many uses of rice husk and rice husk ash have been suggested in the papers for adsorption of pollutants, such as ammonia nitrogen [29], oil or oil product [30], humic acids [31], dyes [32–34], and heavy metals ions removal from aqueous solution [35,36], also removal of dibenzothiophenes in kerosene [37].

Rice husk consists of cellulose, hemicelluloses, crude proteins, lignin, and silica. Since the hydrolyzing hemicellulose, de-polymerizing lignin, and breaking the covalent association between lignocellulose components by NaOH solution, it can affect the molecular, supramolecular, and morphological characteristics of cellulose and changes crystallinity, accessibility, pore structure, and hardness. NaOH also modify chemical and mechanical properties of rice husk and clean natural dirties such as fats and waxes from the surfaces and consequently revealing functional groups like –OH. Therefore, this modifying technique can be useful for the surface modification of rice husk for increasing the capacity of adsorption [38–41].

The objective of this work was to study the potential of NaOH-modified rice husk as a low-cost adsorbent for the adsorption of DR81 and MB from aqueous solutions. Several operating conditions may be influence the adsorption efficiency. Therefore, in this study, the effects of pH, initial concentration of dyes, and adsorbent dose on DR81 and MB adsorption rate have been investigated. The response surface methodology (RSM) is one of the best methods to investigate the main and interaction effects of independent variables on dependent variables that require a few numbers of experiments to determine optimum condition of operating parameters, so it is relatively a time-saving method that reduce the cost of classical one [42]. Thus, to find the optimum conditions of sorption process of these dyes on NaOH-modified rice husk and introducing a mathematical model for it, RSM based on Box–Behnken Design (BBD) had been used that shows the influence of each variable and their interactions.

2. Materials and methods

2.1. Chemicals

Sodium hydroxide (NaOH) was purchased from Merck (Darmstadt, Germany). Synthetic dyes were provided by Alvan Sabet Co. (Tehran, Iran). The chemical structure of DR81 and MB is shown in Fig. 1. All other reagents and chemicals were of the highest purity available.

2.2. Preparation of NaOH-RH adsorbent

The rice (Hashemi) husk was collected from a local rice mill of Guilan province of Iran. First, rice husk was passed through 2-mm sieve size to clean the dust. Then, biomass treated and washed repeatedly by distilled water to eliminate dust and other impurities, until to obtained clear effluent. After that, it was dried in oven 60°C for 24 h. The rice husk obtained from this stage was immersed in the 5% solution of sodium hydroxide (NaOH), and the mixture was autoclaved at 121°C for 15 min at 10 psi. Then, it kept in room temperature for 24 h. After this time, it was filtered and washed many times with distilled water until color was removed and clear water with neutral pH obtained in the effluent. Then, the rice husk was dried at 40°C for 24 h. Finally, it was labeled as NaOH-RH and stored to use in all experiments.

2.3. Preparation of dye solution

The stock solution of DR81 and MB at a concentration of 1,000 mg/l was prepared by dissolving in deionized water. The required dye concentration was prepared from the stock solution by dilution. The three levels of pH were adjusted by 0.1 N NaOH or 0.1 N HCl and were measured by pH meter (metrohm, 827 pH lab). The concentration of dyes was measured photometrically using UV–Vis

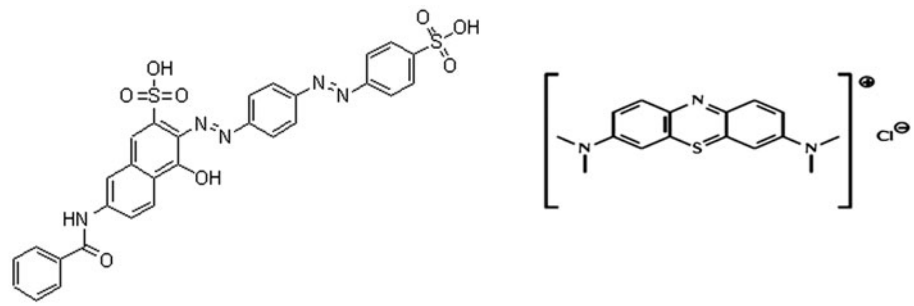

Fig. 1. Chemical structure of dyes DR81 (left) and MB (right).

spectrophotometer (Shimadzu UV 1700, Japan) at the maximum absorbance wavelength for each dye, 509 nm for DR81 and 665 nm for MB.

2.4. Batch adsorption studies

The adsorption study conducted by shaking 50 ml of each dye solution in a 100-ml Erlenmeyer flask according to the pH, concentrations of dyes, and adsorbent dose in Table 2. After keeping the solution flask under agitation rate 150 rpm on rotary shaker for 3 h, the adsorbent was separated by keeping the solution under settling condition for 15 min and the samples were analyzed for dye concentration.

2.5. Box–Behnken factorial design of experiments

In this study, the RSM was used to determine the effects of operating conditions in the removal of DR81 and MB from aqueous solutions through adsorption process by NaOH-RH. One of the most important advantages of RSM is the need to less number of runs, so it is a time- and money-saving method. The other benefit of this method is the capability of illustrating variables that shows more impact and influences the variation of one variable on the other variables.

To investigate the effect of three factors on removal efficiency of dyes, Box–Behnken factorial design method was used. As shown in Table 1, three factors at three different levels (−1, 0, +1) selected for the determination of optimal conditions were designated as A, B, and C, corresponding to pH, initial concentration of dyes, and adsorbent dose.

The results of the experimental design were analyzed and interpreted using the software MINITAB 14 (PA, USA) and Design-expert version 7.0.0 (Stat-Ease, trial version), and along with the main effects, the interactions of all factors were determined. The coded mathematical model for these designs can be given by the following quadratic (Eq. (1)):

$$R = X_0 + X_1A + X_2B + X_3C + X_4AB + X_5AC + X_6BC + X_7AA + X_8BB + X_9CC \quad (1)$$

where R is the predicted percentage removal of each dye; X_0 is the intercept; $X_{1\text{–}9}$ are the estimated regression coefficients of the linear, square, and interaction effects; and A, B, and C are the coded factors (Table 1).

3. Results and discussion

3.1. Design of experiments

According to the Table 2, the experimental, predicted, and residual results accomplished with variable matrix which adapted from BBD were shown in the studies of combined effects of factors (pH, initial concentration of dyes, and adsorbent dose) in three levels (−1, 0, +1), based on RSM for removal of DR81 and MB. There were 15 runs for studying the process of each dye removal, which three of them are repetitive in center points (0, 0, 0).

3.2. Normal probability

One of the ways to investigation of model adequacy is examination of residuals. The normal probability plot of the residuals can indicate to the normality of data that obtained from experiments. If the data points fall fairly close to a straight line, that is, the data are normally distributed, and data are reliable [43]. The normal probability plot of the residuals with a 95% confidence for DR81 and MB was shown in Fig. 2(a) and (b), respectively. It can be seen from these figures that for both dyes, the points fall fairly close to the straight line. Consequently, we can say that the data from the experiments come from a normally distributed population and they were reliable.

Table 1
Experimental ranges and levels using BBD of independent variables for DR81 and MB adsorption

Independent variables	Coded symbol	Code levels					
		DR81			MB		
		−1	0	1	−1	0	1
pH	*A*	4	5.5	7	7	8.5	10
Initial concentration of dye (mg/l)	*B*	25	75	125	25	75	125
Adsorbent dose (g/l)	*C*	2	4	6	0.25	0.5	0.75

Table 2
Experimental and predicted results and variable matrix from BBD for DR81 and MB removal

	Values of independent variables			Adsorption efficiency (%)					
				DR81				MB	
Run	*A*	*B*	*C*	Experimental	Predicted	Residual	Experimental	Predicted	Residual
1	0	−1	−1	33.33	32.48	0.84	87.68	86.38	1.29
2	1	−1	0	28.38	27.21	1.16	95.70	94.61	1.08
3	−1	0	−1	30.01	28.51	1.50	61.00	60.88	0.11
4	0	1	1	32.52	33.36	−0.84	78.92	80.21	−1.29
5	0	−1	1	41.68	41.34	0.34	94.80	95.77	−0.97
6	0	0	0	25.55	25.63	−0.09	85.56	85.42	0.14
7	1	0	−1	18.44	20.45	−2.00	74.90	77.27	−2.37
8	−1	−1	0	41.84	44.19	−2.34	85.20	86.60	−1.40
9	−1	1	0	32.11	33.27	−1.16	65.70	66.78	−1.08
10	0	0	0	25.66	25.63	0.02	85.50	85.42	0.08
11	0	0	0	25.70	25.63	0.06	85.20	85.42	−0.22
12	−1	0	1	45.87	43.86	2.00	80.10	77.72	2.37
13	1	0	1	21.82	23.33	−1.50	82.44	82.55	−0.11
14	1	1	0	24.01	21.66	2.34	81.40	79.99	1.40
15	0	1	−1	23.64	23.98	−0.34	68.46	67.49	0.97

Fig. 3(a) and (b) shows the parity plot comparing the adsorption efficiency of model predicted values for DR81 and MB vs. the experimental values, respectively. As it can be realized, the predicted values for both dye adsorptions were close to the experimental values and were in good agreement, on the other hand, the R^2 values for DR81 ($R^2 = 0.9685$) and MB ($R^2 = 0.9832$) indicate that the regression is able to give a good predict of response for the adsorption process in the range studied. This judgment is in agreement with normal probability plots of residuals (Fig. 2).

3.3. Analysis of variance (ANOVA)

The effect of a factor is defined as the change in response produced by a change in the level of the factor, and it was statistically significant at $p < 0.05$ [44]. As shown in Table 3, the main effects *A*, *B*, and *C* and interactions *AC*, and B^2 are significant for DR81, and for MB, the main effects *A*, *B*, and *C* and interactions *AC*, A^2 and C^2 are high significant.

The following simplified second-order polynomial equations have been given from the Analysis of variance (ANOVA) output by substituting the coefficients X_i in Eq. (1) by their values for each dye:

$$(\%)R_{DR81} = +25.64 - 7.15\,A - 4.12\,B + 4.56\,C - 3.12\,AC + 4.85\,B^2 \tag{2}$$

$$(\%)R_{MB} = +85.42 + 5.30A - 8.61B + 5.53C - 2.89AC - 5.64A^2 - 5.17C^2 \tag{3}$$

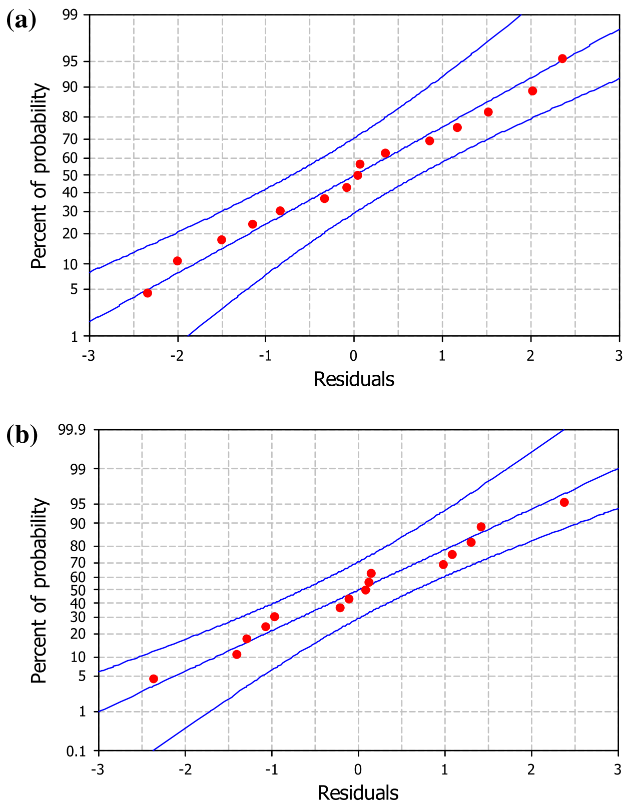

Fig. 2. Normal plots of residuals for (a) DR81 and (b) MB.

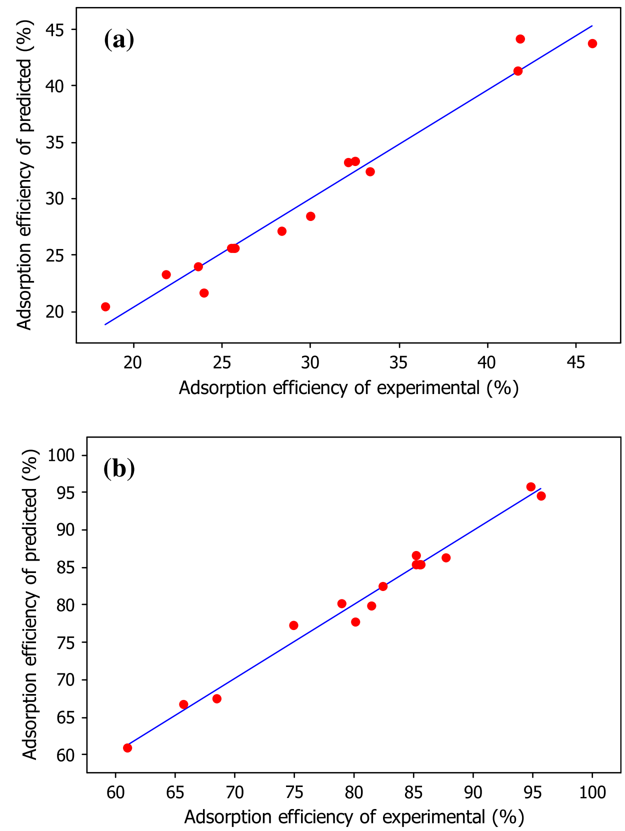

Fig. 3. Parity plot comparing the adsorption of (a) DR81 and (b) MB data with the model predictions by Eqs. (2) and (3), respectively.

where R is the percent adsorption efficiency of DR81 and MB; A, B, and C are the coded values of the operational variables pH, initial dye concentration, and adsorbent dose, respectively.

As shown in Table 3, the results revealed that the second-order polynomial models, Eqs. (2) and (3), were statistically significant and sufficient to represent the actual relationship between the efficiency of adsorption and the significant variables, with p value 0.0030 and 0.0007, and satisfactory coefficient of determination $R^2 = 0.9685$ and $R^2 = 0.832$ for DR81 and MB, respectively.

3.4. Main and interaction effects of variables

Table 3 for DR81 shows that the main effect of all three variables is statically significant, and the pH of solution was found to have the greatest effect on the response, with the highest F value of 73.06, while the initial concentration of dye and adsorbent dose showed lower effect than pH about the adsorption efficiency. According to Table 3, the interaction effects between pH and adsorbent dose are significant due to the lower values of p (0.0461). In addition, the quadric effect of initial concentration of dye with low p value 0.0109 is statically significant. However, the other variables interactions due to their higher values of p were insignificant. The response surface graphs in Fig. 4(a)–(c) shows the effects of the all variables on the adsorption efficiency of DR81. According to the coefficient of pH (−7.15) in Eq. (2), and Fig. 4(a) and (b), it has been found that the pH has negative effect on the adsorption efficiency of DR81 by NaOH-RH. Therefore, with the increase in pH values, the adsorption percentage decreases, this may be due to the DR81 that is anionic dye and will be hardly adsorbed onto the surface of NaOH-RH under neutral or alkaline conditions, which has –OH functional groups. This observation is in agreement with those reported previously by other researchers for adsorption of DR81 by chitosan that have amino functional groups [45]. It has been found that (Fig. 4(a) and (c)) with the increases of the initial concentration of DR81, the adsorption percentage decreases, while the amount of dye removed at equilibrium (14.77 mg/g) is more than when the initial concentration of DR81 is low. This is consequence the driving

Table 3
ANOVA for experimental responses of DR81 and MB adsorption

	DR81					MB				
Source	DF	Sum of squares	Mean square	*F* value	Prob. > *F*	DF	Sum of squares	Mean square	*F* value	Prob. > *F*
A	1	408.63	408.63	73.06	0.0004	1	225.14	225.14	49.06	0.0009
B	1	135.66	135.66	24.25	0.0044	1	593.40	593.40	129.30	<0.0001
C	1	166.24	166.24	29.72	0.0028	1	244.43	244.43	53.26	0.0008
AB	1	7.17	7.17	1.28	0.3088	1	6.76	6.76	1.47	0.2791
AC	1	38.90	38.90	6.95	0.0461	1	33.41	33.41	7.28	0.0429
BC	1	0.070	0.070	0.013	0.9151	1	2.79	2.79	0.61	0.4709
A^2	1	4.44	4.44	0.79	0.4139	1	117.35	117.35	25.57	0.0039
B^2	1	86.90	86.90	15.54	0.0109	1	18.16	18.16	3.96	0.1034
C^2	1	19.62	19.62	3.51	0.1200	1	98.79	98.79	21.53	0.0056
Model	9	858.72	95.41	17.06	0.0030	9	1,340.05	148.89	32.44	0.0007
Residual error	5	27.97	5.59			5	22.95	4.59		
Lac of fit	3	27.95	9.32	1,489.36	0.0007	3	22.87	7.62	204.95	0.0049
Pure error	2	0.013	0.006			2	0.074	0.037		
Total	14	886.68				14	1,363.00			

Notes: DR81: R^2 = 0.9685; MB: R^2 = 0.9832.

force of high concentration of dye to the mass transfer between the aqueous and solid phase. This is in agreement with our previous study of DR81 adsorption on pumice [7]. The results showed that, because of the greater surface area can provide more availability of adsorption sites, with increase in adsorbent dosage of NaOH-RH, the adsorption efficiency of DR81 was increased. It can be seen from Fig. 4(b) and (c).

In the case of MB, like DR81 adsorption, the main effect of all three variables is statically significant, but the initial concentration of dye solution was found to have the greatest effect on the response, with the highest *F* value of 129.30, while the pH and adsorbent dose showed lower effect than initial concentration of dye regarding the adsorption efficiency. In the case of interaction effects, according to Table 3, the interaction effects between pH and adsorbent dose are statically significant due to the lower values of *p* (0.0429). Additionally, the quadric effects of pH and adsorbent dosage with low *p* values 0.0039 and 0.0056, respectively, are statically significant. Nevertheless, the other variables interactions due to their *p* values, which are higher than 0.05, were insignificant. The response surfaces graphs in Fig. 5(a)–(c) shows the effects of the all variables on the adsorption efficiency of MB. According to the coefficient of pH (5.3) in Eq. (3) and Fig. 5(a) and (b), it revealed that the pH has positive effect on the adsorption efficiency of MB on the NaOH-RH. Consequently, with the increase in pH values, the adsorption percentage increased, this is due to that the MB is cationic dye and will be easily adsorbed on the surface of NaOH-RH under alkaline conditions, which has –OH functional groups. This observation is similar to other studies results [5,39]. It has been found that (Fig. 5(a) and (c)) with the increases in concentration of the initial concentration of MB, the adsorption efficiency decreases, while the amount of dye removed at equilibrium (342.3 mg/g) is more than when the initial concentration of MB is low. This is in agreement with other studies of dye adsorption [38,39]. Fig. 5(b) and (c) shows the adsorption efficiency of MB as a function of NaOH-RH dosage. Similar to the DR81 adsorption, the results revealed in Fig. 5(b) and (c) demonstrate that the adsorption efficiency of MB increases with increasing adsorbent dose. The increase may be explained by an increase in the surface area of the NaOH-RH samples.

3.5. Optimization

To be aware of the optimum values of variables for dye adsorption, using a numerical technique with the software Design-expert version 7.0.0 (Stat-Ease, trial version), the accurate optimal values of the variables were obtained to find the specific point that maximizes the efficiency. The main objective of optimization was to maximize adsorption efficiency of both dyes. The results showed that the optimal pH,

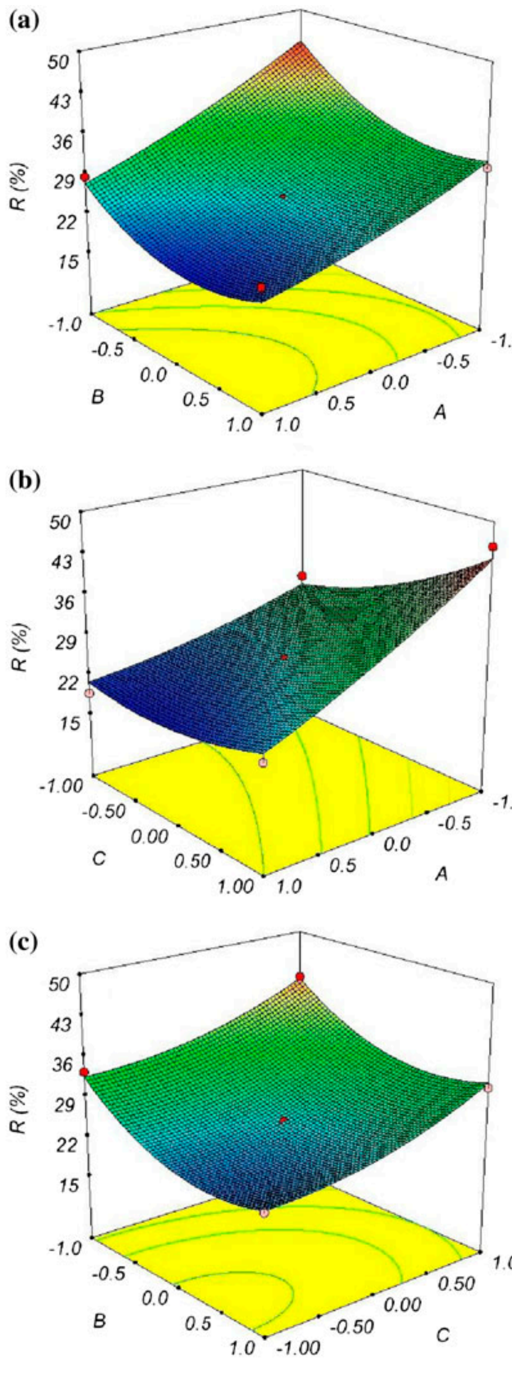

Fig. 4. Response surfaces from BBD showing the effects of (a) pH and initial concentration of dye, (b) pH and adsorbent dose, and (c) initial concentration of dye and adsorbent dose on adsorption of DR81.

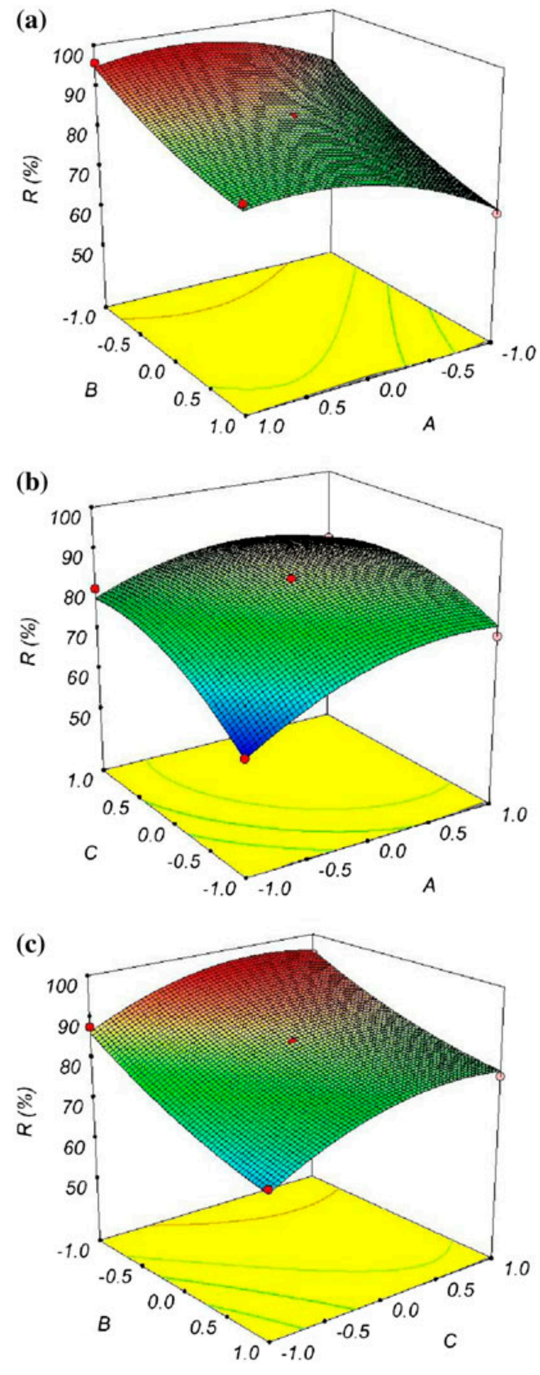

Fig. 5. Response surfaces from BBD showing the effects of (a) pH and initial concentration of dye, (b) pH and adsorbent dose, and (c) initial concentration of dye and adsorbent dose on adsorption of MB.

initial concentration of dye, and adsorbent dosage for DR81 adsorption are 4, 25 mg/l, and 6 g/l, respectively, which results to the highest efficiency (54.04%) of adsorption. While in the case of MB, the optimal pH, initial concentration of dye, and adsorbent dosage are 8.89, 25 mg/l, and 0.595 g/l, respectively, which results to the highest efficiency (97.66%) of adsorption.

4. Conclusions

The Box–Behnken is a good design for RSM. It can be employed to develop mathematical models for predicting DR81 and MB adsorption on NaOH-RH. This study investigated the optimization of DR81 and MB on NaOH-RH applying the Box–Behnken experimental design methodology. The results showed that pH and adsorbent dose were important factors in the adsorption efficiencies for both dyes. The adsorption efficiencies for DR81 decrease with increasing pH but for MB it increase with increasing the pH. The adsorption efficiency decreases with increasing initial concentration of both dyes, and it increases with increasing the adsorbent dose for both dye. The optimal conditions for the maximum adsorption of DR81 (54.04% from prediction) were 25 mg/l initial dye concentration and 6 g/l adsorbent dosage at pH 4. In the case of MB, the optimal conditions for the maximum adsorption (97.66% from prediction) were 25 mg/l initial dye concentration and 0.595 g/l adsorbent dosage at pH 8.89.

The NaOH-RH adsorption capacity was 14.77 and 342.43 mg/g, respectively, for the DR81 and MB. So it can be realized that NaOH-RH has excellent adsorptive characteristics for the removal of MB as cationic dye from aqueous solution. However, it may not be a very good adsorbent for DR81 as anionic dye.

Acknowledgment

This work was supported by Department of Environmental Health Engineering at School of Public Health, Tehran University of Medical Sciences, Tehran, Iran.

References

[1] S. Sadaf, H.N. Bhatti, S. Nausheen, S. Noreen, Potential use of low-cost lignocellulosic waste for the removal of direct violet 51 from aqueous solution: Equilibrium and breakthrough studies, Arch. Environ. Contam. Toxicol. 66 (2014) 557–571.

[2] S. Noreen, H.N. Bhatti, Fitting of equilibrium and kinetic data for the removal of Novacron Orange P-2R by sugarcane bagasse, J. Ind. Eng. Chem. 20 (2014) 1684–1692.

[3] G. Sharma, M. Naushad, D. Pathania, A. Mittal, G.E. El-desoky, Modification of *Hibiscus cannabinus* fiber by graft copolymerization: Application for dye removal, Desalin. Water Treat. (2014) 1–8.

[4] A.M.M. Vargas, A.L. Cazetta, M.H. Kunita, T.L. Silva, V.C. Almeida, Adsorption of methylene blue on activated carbon produced from flamboyant pods (*Delonix regia*): Study of adsorption isotherms and kinetic models, Chem. Eng. J. 168 (2011) 722–730.

[5] H. Deng, J. Lu, G. Li, G. Zhang, X. Wang, Adsorption of methylene blue on adsorbent materials produced from cotton stalk, Chem. Eng. J. 172 (2011) 326–334.

[6] A.H. Mahvi, M. Ghanbarian, S. Nasseri, A. Khairi, Mineralization and discoloration of textile wastewater by TiO_2 nanoparticles, Desalination 239 (2009) 309–316.

[7] A.H. Mahvi, B. Heibati, Removal of reactive red 120 and direct red 81 dyes from aqueous solutions by pumice, Res. J. Chem. Environ. 16 (2012) 62–68.

[8] S.D. Ashrafi, S. Rezaei, H. Forootanfar, A.H. Mahvi, M.A. Faramarzi, The enzymatic decolorization and detoxification of synthetic dyes by the laccase from a soil-isolated ascomycete, *Paraconiothyrium variabile*, Int. Biodeterior. Biodegrad. 85 (2013) 173–181.

[9] A. Mittal, L. Kurup, Column operations for the removal and recovery of a hazardous dye 'Acid Red-27' from aqueous solutions, using waste materials—Bottom ash and de-oiled soya, Ecol. Environ. Conserv. 12 (2006) 181–186.

[10] I. Maghri, A. Kenz, M. Elkouali, O. Tanane, M. Talbi, Textile dyes removal from industrial waste water by mytilus edulis shells, J. Mater. Environ. Sci. 3 (2012) 121–136.

[11] F. Gholami-Borujeni, A.H. Mahvi, S. Nasseri, M.A. Faramarzi, R. Nabizadeh, M. Alimohammadi, Enzymatic treatment and detoxification of acid orange 7 from textile wastewater, Appl. Biochem. Biotechnol. 165 (2011) 1274–1284.

[12] M.A. Zanjanchi, H. Golmojdeh, M. Arvand, Enhanced adsorptive and photocatalytic achievements in removal of methylene blue by incorporating tungstophosphoric acid–TiO_2 into MCM-41, J. Hazard. Mater. 169 (2009) 233–239.

[13] E. Kurt, D.Y. Koseoglu-Imer, N. Dizge, S. Chellam, I. Koyuncu, Pilot-scale evaluation of nanofiltration and reverse osmosis for process reuse of segregated textile dyewash wastewater, Desalination 302 (2012) 24–32.

[14] F. Gholami-Borujeni, A.H. Mahvi, S. Nasseri, M.A. Faramarzi, R. Nabizadeh, M. Alimohammadi, Application of immobilized horseradish peroxidase for removal and detoxification of azo dye from aqueous solution, Res. J. Chem. Environ. 15 (2011) 217–222.

[15] H. Daraei, A. Mittal, M. Noorisepehr, F. Daraei, Kinetic and equilibrium studies of adsorptive removal of phenol onto eggshell waste, Environ. Sci. Pollut. Res. 20 (2013) 4603–4611.

[16] H. Daraei, A. Mittal, M. Noorisepehr, J. Mittal, Separation of chromium from water samples using eggshell powder as a low-cost sorbent: Kinetic and thermodynamic studies, Desalin. Water Treat. (2013) 1–7.

[17] H. Daraei, A. Mittal, J. Mittal, H. Kamali, Optimization of Cr(VI) removal onto biosorbent eggshell membrane: Experimental and theoretical approaches, Desalin. Water Treat. 52 (2013) 1307–1315.

[18] S. Nawaz, H.N. Bhatti, T.H. Bokhari, S. Sadaf, Removal of Novacron Golden Yellow dye from aqueous solutions by low-cost agricultural waste: Batch and fixed bed study, Chem. Ecol. 30 (2013) 52–65.

[19] S. Noreen, H.N. Bhatti, S. Nausheen, S. Sadaf, M. Ashfaq, Batch and fixed bed adsorption study for the removal of Drimarine Black CL-B dye from aqueous solution using a lignocellulosic waste: A cost affective adsorbent, Ind. Crops Prod. 50 (2013) 568–579.

[20] S. Sadaf, H.N. Bhatti, Batch and fixed bed column studies for the removal of Indosol Yellow BG dye by peanut husk, J. Taiwan Inst. Chem. Eng. 45 (2014) 541–553.
[21] B. Acemioglu, Batch kinetic study of sorption of methylene blue by perlite, Chem. Eng. J. 106 (2005) 73–81.
[22] C.A.P. Almeida, N.A. Debacher, A.J. Downs, L. Cottet, C.A.D. Mello, Removal of methylene blue from colored effluents by adsorption on montmorillonite clay, J. Colloid Interface Sci. 332 (2009) 46–53.
[23] A.H. Mahvi, B. Heibati, A.R. Yari, N. Vaezi, Efficiency of Reactive Black 5 dye removals and determination of isotherm models in aqueous solution by use of activated carbon made of walnut wood, Res. J. Chem. Environ. 16 (2012) 26–30.
[24] E. Bazrafshan, F.K. Mostafapour, A.R. Hosseini, A. Raksh Khorshid, A.H. Mahvi, Decolorisation of reactive red 120 dye by using single-walled carbon nanotubes in aqueous solutions, J. Chem. (2013) 1–8, doi: http://dx.doi.org/10.1155/2013/938374.
[25] S. Sadaf, H.N. Bhatti, Evaluation of peanut husk as a novel, low cost biosorbent for the removal of Indosol Orange RSN dye from aqueous solutions: Batch and fixed bed studies, Clean Technol. Environ. Policy 16 (2014) 527–544.
[26] J. Mittal, V. Thakur, A. Mittal, Batch removal of hazardous azo dye Bismark Brown R using waste material hen feather, Ecol. Eng. 60 (2013) 249–253.
[27] A. Mittal, V. Thakur, J. Mittal, H. Vardhan, Process development for the removal of hazardous anionic azo dye Congo red from wastewater by using hen feather as potential adsorbent, Desalin. Water Treat. 52 (2013) 227–237.
[28] J. Mittal, D. Jhare, H. Vardhan, A. Mittal, Utilization of bottom ash as a low-cost sorbent for the removal and recovery of a toxic halogen containing dye eosin yellow, Desalin. Water Treat. 52 (2014) 4508–4519.
[29] K. Zhu, H. Fu, J. Zhang, X. Lv, J. Tang, X. Xu, Studies on removal of $NH4^+$-N from aqueous solution by using the activated carbons derived from rice husk, Biomass Bioenergy 43 (2012) 18–25.
[30] D. Angelova, I. Uzunov, S. Uzunova, A. Gigova, L. Minchev, Kinetics of oil and oil products adsorption by carbonized rice husks, Chem. Eng. J. 172 (2011) 306–311.
[31] A. Imyim, E. Prapalimrungsi, Humic acids removal from water by aminopropyl functionalized rice husk ash, J. Hazard. Mater. 184 (2010) 775–781.
[32] Y. Safa, H.N. Bhatti, Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk, Desalination 272 (2011) 313–322.
[33] S.T. Ong, C.K. Lee, Z. Zainal, Removal of basic and reactive dyes using ethylenediamine modified rice hull, Bioresour. Technol. 98 (2007) 2792–2799.
[34] V.S. Mane, I. Deo Mall, V. Chandra Srivastava, Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash, J. Environ. Manage. 84 (2007) 390–400.
[35] S.A. Abo-El-Enein, M.A. Eissa, A.A. Diafullah, M.A. Rizk, F.M. Mohamed, Removal of some heavy metals ions from wastewater by copolymer of iron and aluminum impregnated with active silica derived from rice husk ash, J. Hazard. Mater. 172 (2009) 574–579.
[36] H. Ye, Q. Zhu, D. Du, Adsorptive removal of Cd(II) from aqueous solution using natural and modified rice husk, Bioresour. Technol. 101 (2010) 5175–5179.
[37] S. Kumagai, Y. Shimizu, Y. Toida, Y. Enda, Removal of dibenzothiophenes in kerosene by adsorption on rice husk activated carbon, Fuel 88 (2009) 1975–1982.
[38] S. Chakraborty, S. Chowdhury, P. Das Saha, Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk, Carbohydr. Polym. 86 (2011) 1533–1541.
[39] P. Sharma, R. Kaur, C. Baskar, W.-J. Chung, Removal of methylene blue from aqueous waste using rice husk and rice husk ash, Desalination 259 (2010) 249–257.
[40] S.-T. Hsu, L.-C. Chen, C.-C. Lee, T.-C. Pan, B.-X. You, Q.-F. Yan, Preparation of methacrylic acid-modified rice husk improved by an experimental design and application for paraquat adsorption, J. Hazard. Mater. 171 (2009) 465–470.
[41] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol. 97 (2006) 104–109.
[42] P. Sharma, L. Singh, N. Dilbaghi, Optimization of process variables for decolorization of Disperse Yellow 211 by *Bacillus subtilis* using Box–Behnken design, J. Hazard. Mater. 164 (2009) 1024–1029.
[43] X.S. Yi, W.X. Shi, S.L. Yu, X.H. Li, N. Sun, C. He, Factorial design applied to flux decline of anionic polyacrylamide removal from water by modified polyvinylidene fluoride ultrafiltration membranes, Desalination 274 (2011) 7–12.
[44] R. Gottipati, S. Mishra, Process optimization of adsorption of Cr(VI) on activated carbons prepared from plant precursors by a two-level full factorial design, Chem. Eng. J. 160 (2010) 99–107.
[45] M.-S. Chiou, P.-Y. Ho, H.-Y. Li, Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads, Dyes Pigm. 60 (2004) 69–84.