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Response surface analysis of removal of a textile dye by a Turkish coal powder

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Abstract. In the present study, an experimental design methodology was used to optimize the adsorptive removal of Basic Yellow 13 (BY13) using Turkish coal powder. A central composite design (CCD) consisting of 31 experiments was employed to evaluate the simple and combined effects of the four independent variables, initial dye concentration (mg/L), adsorbent dosage (g/L), temperature (°C) and contact time (min) on the color removal (CR) efficiency (%) and optimizing the process response. Analysis of variance (ANOVA) showed a high coefficient of determination value (R^2 = 0.947) and satisfactory prediction of the polynomial regression model was derived. Results indicated that the CR efficiency was not significantly affected by temperature in the range of 12-60°C. While all other variables significantly influenced response. The highest CR (95.14%), estimated by multivariate experimental design, was found at the optimal experimental conditions of initial dye concentration 30 mg/L, adsorbent dosage 1.5 g/L, temperature 25°C and contact time 10 min.

Keywords: adsorption; coal; organic dye; experimental design; optimization

1. Introduction

The dye effluents are considered to be harmful to aquatic environments and interfere with light penetration in the receiving water bodies which ultimately disturb the biological processes (Garg *et al*. 2004). To treat dye-containing effluents, several physical and chemical processes, such as coagulation/flocculation, biosorption, photocatalytic degradation, ultrafiltration and advanced oxidation processes (AOPs) have been applied (Sadri Moghaddam *et al*. 2010, Kousha *et al*. 2012, Mozia *et al*. 2008, Dong *et al*. 2011, Khataee *et al*. 2011, Modirshahla *et al*. 2011, Chen *et al*. 2005). The literature indicates that in the recent years adsorption techniques have received much attention for this purpose, offering significant reduction of expenses and efficient removal of dyes. Since the adsorption of dye by an adsorbent is strongly influenced by many factors, including adsorbent dosage, initial effluent pH, initial concentration of dye, temperature and the contact time of adsorbent with dye, it is crucial to search for the key influencing factor(s) and discover the experimental conditions in which the best possible response can be obtained. Performing such

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work by using conventional and classical techniques involves changing one variable at a time and keeping the others constant at an unspecified level. These techniques are extremely laborious and time-consuming and do not depict the combined effect of all factors involved. In contrast, statistical design of experiments using response surface methodology (RSM) can significantly reduce the number of experiments, maximize the extractable complex information and save both time and cost (Chen *et al*. 2005, Karacan *et al*. 2007).

RSM is a collection of mathematical and statistical techniques based on the multivariate non-linear model, which is useful for designing experiments, developing a mathematical model and determining the optimal value of the independent variables that produces a maximum or minimum response (Myers and Montgomery 2002). RSM has been widely used for studying the optimization of the treatment process of simulated dye wastewater using various adsorbents (Hameed *et al*. 2008, Ravikumar *et al*. 2007, Chatterjee *et al*. 2012, Arulkumar *et al*. 2011Khayet *et al*. 2011, Singh *et al*. 2011).

Although activated carbons are highly efficient adsorbents for most of environmental contaminants due to their elevated surface areas, their price often limits their possible applications. Coal, not being a pure material, is a major component of the geo-polymers in the environment which its composition varies with source materials and formation conditions (Allen-King *et al*. 2012, Nishikiori *et al*. 2003). The porous structure and abundant various functional groups on the coal surface makes its application a useful means for controlling the extent of water pollution due to dyes and metallic species (Karaca *et al*. 2004, McKay *et al*. 1999).

The present investigation has been designed to explore the efficiency of coal as a low-cost adsorbent for removal of a basic dye, BY13, from aqueous solution. The effect of operational parameters including initial dye concentration, adsorbent dosage, temperature and contact time has been studied. RSM with a rotatable CCD was used to design experiments and develop a mathematical relationship between color removal efficiency (%) and selected operational variables, providing quantitative evaluation and optimization of the process response.

2. Experimental

2.1 Materials

The used model dye, BY13, was purchased from Shimi Boyakhsaz Company, Iran and used without any purification. BY13 is a cationic dye and chemically lies in methin class. Fig. 1 shows chemical structure of BY13 with molecular formula of $C_{20}H_{23}ClN_2O$, color index number = 48056, λ_{max} = 412 nm and molecular weight = 342.86 g/mol. The coal was supplied from Aşkale coal mines in Turkey and air dried as received. The dried sample was ground and sieved to – 180 + 400 mesh size fraction using ASTM standard sieves. All other chemicals used in this study were analytical grade and provided by Merck Co. Solutions were prepared using distilled water.

2.2 Physico-chemical characterization of coal

Analysis of chemical composition of the coal (e.g., moisture, ash yield, volatile matter and fixed carbon content (%) as well as elemental analyses) was performed using ASTM standards and the mean values of duplicate tests are reported. The BET surface area of the coal was determined by N_2 adsorption at 77 K in the relative pressure range from 0.05 to 0.4 using automatic surface

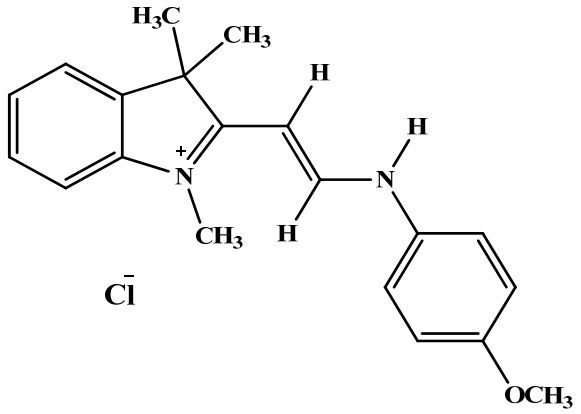

Fig. 1 Chemical structure of Basic Yellow 13

analyzer (Belsorp mini II Bel instrument, Japan). The total pore volume, defined as the volume of liquid nitrogen corresponding to the adsorbed amount, was measured from the amount of N_2 adsorbed at the relative pressure close to unity (0.987). The pore size distribution was derived from the BET using the Barrett-Joyner-Halenda (BJH) method (Tseng and Tsent 2006). Prior to measurements, the sample was degassed at 100°C in the degas port of the adsorption analyzer for 15 h. The surface morphology of the coal was characterized by Quanta 400 F field emission scanning electron microscopy (FE-SEM) (FEI Company, USA). Functional groups of coal surface, before and after dye adsorption process (in optimum conditions), were analyzed by Bruker Tensor 27, Germany spectrometer instrument with potassium bromide (KBr) pellets, within the wave range 400-4000 cm^{-1}.

2.3 Experimental procedure for BY13 adsorption

The dye adsorption experiments were carried out in batch system. Dye solutions with different concentrations were prepared by diluting the stock solution (1000 mg/L) with appropriate volume of distilled water. Certain amount of adsorbent was added into the 250 mL glass erlenmeyer flask containing 100 mL of dye solution. Flasks were shaken for a given time in a shaking incubator (ISH 554 D, Fanavaran SahandAzar Co., Iran) with constant frequency of 150 rpm at different temperatures. At the end, suspension was centrifuged at 6000 rpm for 10 min and residual dye concentration was determined using a UV-Vis spectrophotometer (WPA light wave S2000, UK) at dye maximum wavelength. The CR efficiency (%) was calculated through Eq. (1)

$$CR(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 and C are the initial and final concentrations of dye (mg/L), respectively.

2.4 Design of experiments

In this study, rotatable CCD was chosen for designing experiments and exploring the effect of

independent process variables on the response within the range of investigation. Initial concentration of dye (mg/L) (X_1), adsorbent dose (g/L) (X_2), temperature (°C) (X_3) and contact time (min) (X_4) were selected as independent variables and the percentage of CR was used as process response. The ranges and levels of each independent variable are shown in Table 1 as coded and actual values. The coded values were obtained using the following dimensionless equation

$$x_i = \frac{X_i - X_0}{\Delta X_i} \tag{2}$$

where X_0 is the value of X_i at the center point, and ΔX_i presents the step with maximum and minimum values of variable X_i.

This design involved 31 experiments, including 16 experiments at factorial points, 8 experiments at axial point and 7 replications at central points. Replicates were used to estimate the pure error of the model. To make the design rotatable, the value of α was taken as 2 ($\alpha = (nF)^{1/4}$, where nF is the number of factorial points). Experimental set was carried out in a random order to minimize the effects of variability in the observed responses due to external factors. The least square method was used to develop a polynomial model associated with the central composite matrix, which correlates the response to the four process variables. This model is presented in Eq. (3) (Myers and Montgomery 2002).

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{i \neq j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{3}$$

where, y is the response, β_0 is the constant, β_i is the linear coefficient, β_{ii} represents the quadratic coefficient, β_{ij} is the interaction coefficient, x_i is the coded variable level, k is the number of independent variables and ε is the residual term.

2.5 Evaluation of the model fitness

To evaluate the adequacy of the proposed model, the diagnostic checking tests provided by ANOVA was used. The quality of the fit for the polynomial model was expressed by the coefficient of determination (R^2 and Adjusted-R^2) and model statistical significance was checked by the Fisher's variance ratio test, known as the F-test, at 95% confidence level. This test compares the residual variance with the replication variance and the value of F can be calculated by the following equation

$$F = \frac{\dfrac{SSreg.}{q-1}}{\dfrac{SSres.}{N-q-1}} \tag{4}$$

where, SS_{reg} and SS_{res} represent the sum of squares of regression and residuals, respectively. q is the number of model terms including the intercept and N is the number of observations (Brown *et al*. 2009).

The analysis of residuals (difference between the predicted and experimental responses) is another important diagnostic tool for judging adequacy of the fitted model for predicting the

Table 1 Process variables and their experimental levels

Variables (factors)	Ranges and actual values of coded levels					Standard deviation
	-2	-1	0	+1	+2	
X_1: $[Dye]_0$ (mg/L)	10	20	30	40	50	8.80
X_2: Adsorbent dosage (g/L)	0.4	0.8	1.2	1.6	2.0	0.04
X_3: Temperature (°C)	12	24	36	48	60	10.56
X_4: Time (min)	5	15	25	35	45	8.80

Table 2 Physico-chemical characteristics of the coal

Proximate analyses (wt.%)				Elemental analyses (wt.%)				
Moisture	Ash yield	Volatile matter	Fixed carbon	C	H	S	N	O
4.46	29.64	34.28	31.62	70.86	4.28	4.76	2.20	17.90

response. We also analyzed the residuals through normal probability and residual plots to explain the normal distribution and constant variance of errors and to detect the possible systematic departures from the assumption.

A multiple regression analysis was performed on the experimental data to estimate the regression coefficients of the model. The significance of the regression coefficients was tested by Student's *t* tests at 95% confidence level.

3. Results and discussion

3.1 Chemical and physical characteristics of the coal

Table 2 shows the content of coal moisture, ash yield, volatile matter and fixed carbon, as well as its elemental analyses.

3.1.1 BET and SEM analyses

Fig. 2 shows the N_2 adsorption/desorption isotherm and pore size distribution curve of coal. The coal BET surface area was determined at 77 K. Fig. 2(a) shows the type II isotherm with type-H4 hysteresis loop, which can be attributed to the mesoporous structure of coal containing open slit-shaped capillaries with wide bodies and narrow short necks. The calculated BET surface area and monolayer adsorption capacity of coal was found to be 38.34 m^2/g and 8.81 cm^3/g, respectively. The pore size distribution of coal was determined according to the BJH model. The total pore volume and mean pore diameter were found to be 36.14 cm^3/g and 3.77 nm, respectively. BET surface area and total pore volume of coal sample show that the coal sample is predominantly microporous which is in agreement with the results of SEM analysis. Fig. 3 represents the SEM micrograph of coal. As can be seen, coal has a porous and rough surface and thus there is a good possibility for dye sorption into its pores.

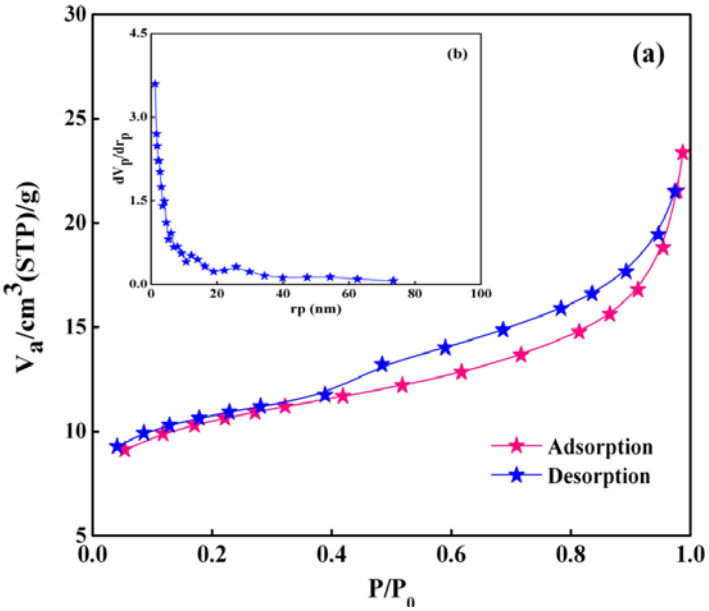

Fig. 2 N_2 Adsorption/desorption isotherm (a) of coal and the BJH plot (b)

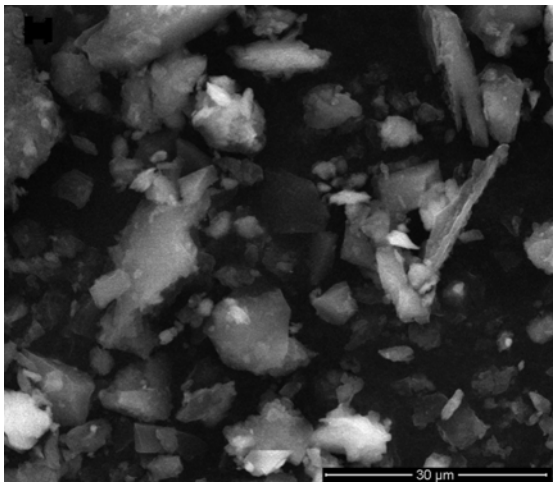

Fig. 3 Scanning electron micrograph of coal surface

3.1.2 FT-IR spectroscopic analysis

The surface of coal has wide variety of functional groups which are responsible for adsorption of dye molecules. To identify the various functional groups present on the coal surface and their relative influence on the dye adsorption, FT-IR spectra of coal, before and after adsorption of dye has been measured and shown in Fig. 4. We compared the absorption peaks with the standard patterns to assign the FT-IR spectra (Cooke *et al*. 1986, Das 2001, Grigoriew 1990, Speight 1972). The characteristic peaks of coal before dye adsorption (Fig. 4(a)) are located around as follows:

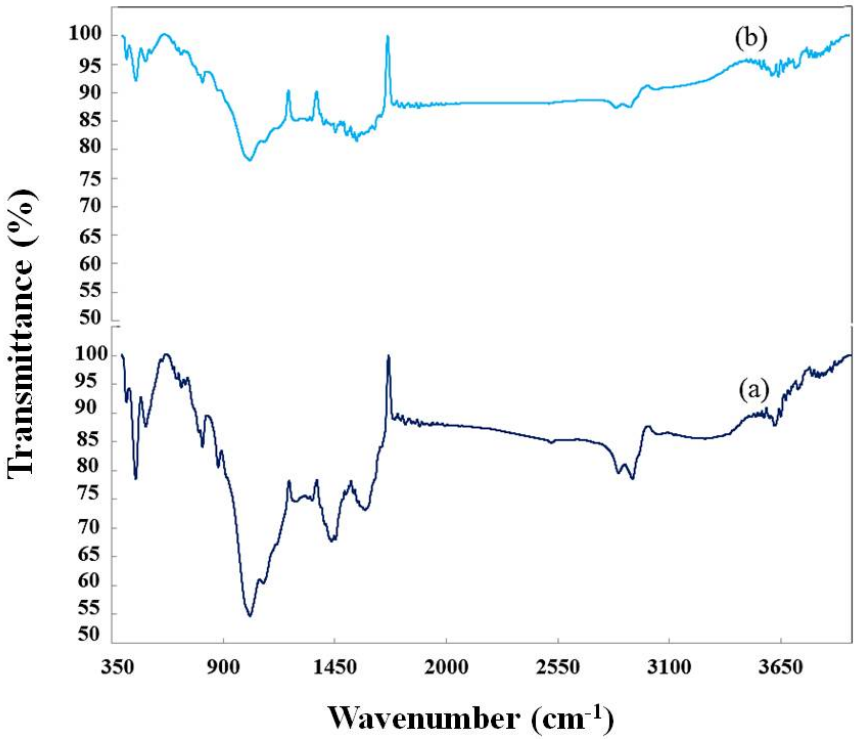

Fig. 4 FT-IR spectrum of coal before (a) and after (b) adsorption of dye at optimum conditions (dye initial concentration = 30 mg/L, adsorbent dosage = 1.5 g/L, temperature = 25°C, contact time = 10 min)

the peak at 1600.05 cm^{-1} was attributed to the presence of *C* = *C* groups and possibly due to other oxygen-containing groups. The broad peaks about 3619.17 and 3275.45 cm^{-1} correspond to -OH and -NH stretching vibrations, respectively. The peaks at 2915.31 and 2850.45 $cm^{-1}$are ascribed to stretching vibration of the aliphatic and alicyclic CH_3, CH_2 and CH groups, where the main contribution is dedicated to the CH_2 groups. A strong peak observed at 1433.39 $cm^{-1}$is mainly due to the presence of CH_3 asymmetric stretch and CH_2 group at the bridges or may also be partially due to hydrogen bonded O–H groups of carboxylic acids in the coal structure. The presence of siloxan (Si-O-Si) bond was confirmed by a strong peak appeared at 1030.96 cm^{-1}. The peaks in region 1100-400 $cm^{-1}$are suggested to be due to the clay minerals and silicon-containing groups.

The remarkable changes in FT-IR spectra of coal were observed after adsorption of dye (Fig. 4(b)). In particular, the shift and reduction in the Si-O-Si bond peak from 1030.90 cm^{-1} (T = 54.5%) to 1022.22 cm^{-1} (T = 77.59%) highlights the major role of siloxan group in the adsorption of basic dyes onto the coal. The Si-O-Si groups with oxygen atoms on the surface play an important role in adsorption of dye molecules through interaction between the n-π and π systems of the dye and the electron lone pairs of the oxygen atoms of siloxane group on the surface of coal. On the other hand, the shift and significant reduction in the peaks at 2915.31 cm^{-1} (T = 73%) and 2850.45 cm^{-1} (T = 67.6%) to 2885 (T = 87.99%) and 2821 (T = 88.2%) reflect the high effect of CH_3, CH_2 and CH groups upon binding of the dye onto the coal.

Table 3 The 4-factor central composite design matrix and corresponding responses and residual values

Run	Variables				CR (%)		Residuals
	x_1	x_2	x_3	x_4	Exp.	Pred.	
1	0	0	0	0	91.80	93.33	-1.533
2	-2	0	0	0	91.96	94.37	-1.440
3	1	-1	1	-1	80.51	82.78	-2.045
4	0	-2	0	0	85.76	86.32	-0.593
5	-1	1	-1	-1	95.55	96.77	-1.123
6	-1	1	-1	1	97.77	95.21	2.286
7	-1	-1	-1	1	93.26	93.63	-0.273
8	-1	-1	1	1	93.05	92.78	-0.012
9	0	0	-2	0	92.12	92.85	-0.760
10	1	-1	-1	-1	83.18	83.75	0.018
11	1	-1	1	-1	88.79	88.02	1.067
12	1	1	1	-1	92.59	92.67	0.217
13	0	0	0	0	93.59	93.33	0.757
14	0	0	0	0	93.59	93.33	0.397
15	2	0	0	0	88.18	85.60	1.255
16	-1	-1	-1	-1	96.28	94.10	1.310
17	1	1	-1	1	93.18	94.54	-1.065
18	0	0	0	0	93.59	93.33	-0.163
19	-1	1	1	1	95.38	95.25	-0.075
20	0	0	0	2	95.02	95.18	-0.486
21	-1	1	1	-1	94.66	94.44	-0.057
22	1	1	-1	-1	92.79	92.76	0.253
23	0	0	0	-2	91.83	91.50	0.302
24	0	0	2	0	92.82	91.92	0.575
25	0	0	0	0	93.59	93.33	0.257
26	0	0	0	0	93.59	93.33	0.317
27	0	0	0	0	93.59	93.33	-0.033
28	1	1	1	1	94.94	96.82	-1.069
29	1	-1	-1	1	86.70	86.62	0.298
30	0	2	0	0	98.53	97.79	0.409
31	-1	-1	1	-1	91.80	90.88	1.008

3.2 Model fitting and statistical analysis

A systematic study using RSM has been performed to examine the individual and combined effects of dye initial concentration, adsorbent dosage, temperature and contact time on the dye adsorption efficiency. The experimental and predicted values of CR efficiency (%) with

corresponding residual values for different combination of selected variables are presented in Table 3.

The experimental data obtained under varying reaction conditions were processed by the Design Expert® software and second order polynomial regression model was established in terms of the process independent variables (based on coded values) to describe the CR efficiency (%) as follow

$$y = 93.3329 - 2.3687_{x1} + 2.9421_{x2} - 0.1588_{x3} + 0.9946_{x4} + 1.1677_{x1}^{2} - 0.2739_{x2}^{2} - 01927_{x3}^{2} + 0.0461_{x4}^{2} + 1.4731_{x1x2} + 0.4481_{x1x3} + 0.7244_{x1x4} + 0.1106_{x2x3} - 0.3831_{x2x4} + 0.4819_{x3x4} \quad (5)$$

The calculated F-value (20.40) was greater than tabulated $F_{14,16,\ 0.01}$ value (3.45), so we conclude that at least one of the terms in the regression equation is non-zero and the model is statistically significant at 99% confidence level (P-value < 0.0001) (see Table 4). It means that the obtained model very accurately describes the response variations. The high values of R^2 and Adj-

Table 4 Analysis of variance (ANOVA) for response surface quadratic models

Source of variation	Degree of freedom	Sum of squares	F-value	P-value
Model	14	460.119	20.40	0.000
Residuals	16	25.780		
Total	30	485.899		

R^2 = 0.947, Adjusted-R^2 = 0.901

Table 5 Estimated coefficients and corresponding standard error, t and P-values

Term	Coefficient	Estimated value	Standard error	Student t	P-value
Constant	b_0	93.3329	0.4798	194.537	0.000
[BY13]	b_1	-2.3687	0.2591	-9.142	0.000
[Ads.]	b_2	2.9421	0.2591	11.355	0.000
Temp.	b_3	-0.1588	0.2591	-0.613	0.549
Time	b_4	0.9946	0.2591	3.839	0.001
[BY13] × [BY13]	b_{11}	-1.1677	0.2374	-4.919	0.000
[Ads.] × [Ads.]	b_{22}	-0.2739	0.2374	-1.154	0.265
Temp. × Temp.	b_{33}	-0.1927	0.2374	-0.812	0.429
Time × Time	b_{44}	0.0461	0.2374	0.194	0.849
[BY13] ×[Ads.]	b_{12}	1.4731	0.3173	4.642	0.000
[BY13] × Temp.	b_{13}	0.4481	0.3173	1.412	0.177
[BY13] × Time	b_{14}	0.7244	0.3173	2.283	0.036
[Ads.] × Temp.	b_{23}	0.1106	0.3173	0.349	0.732
[Ads.] × Time	b_{24}	-0.3831	0.3173	-1.207	0.245
Temp. × Time	b_{34}	0.4819	0.3173	1.518	0.148

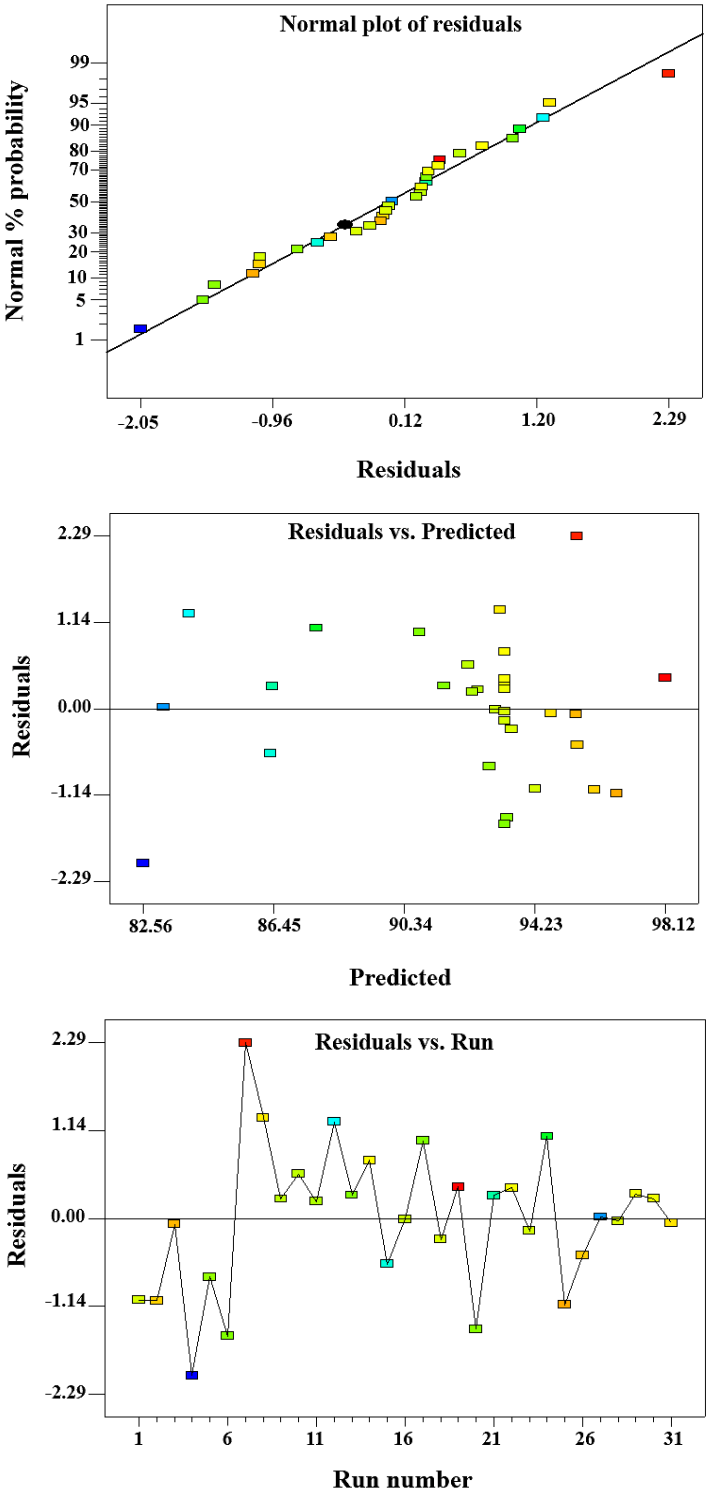

Fig. 5 Residuals plots for removal efficiency of BY13

R^2 (0.947 and 0.901, respectively) also confirm the suitability of the model and implying that the model can explain a high percentage of the variations occurred in the responses.

Analysis of residuals was performed by normal probability, residuals vs. predicted responses and residuals vs. run plots and results are shown in Fig. 5. The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line (Alidokht *et al*. 2011). As can be seen from Fig. 5, residuals are aligned in the plot then the normality assumption is satisfied. Visually, the residuals scatter randomly on the residuals vs. predicted responses and residuals vs. run plots, suggesting that the variance of original observations is constant for all values of response.

The hypothesis of any individual regression coefficient nullity and its statistical significance was tested using Student's *t* test. Table 5 represents the estimated regression coefficients together with their standard errors, *t* statistics and corresponding *P*-values. Smaller *P*-values show a higher significance level for the corresponding coefficients (Wu *et al*. 2009). The effect of coefficients b_1, b_2 and b_3 as well as the quadratic coefficient b_{11}were significant at confidence level of 95%. The interaction coefficient b_{14} is also significant at the same level. Therefore, the linear effect of initial concentration of dye, adsorbent dosage and contact time, quadratic effect of initial concentration of dye and the interaction effect of dye initial concentration and contact time were found to be the most influential parameters.

To visualize the percentage effect of the regression parameters on the process response, all parameters are depicted in rank order in the form of Pareto chart and are shown in Fig. 6. The

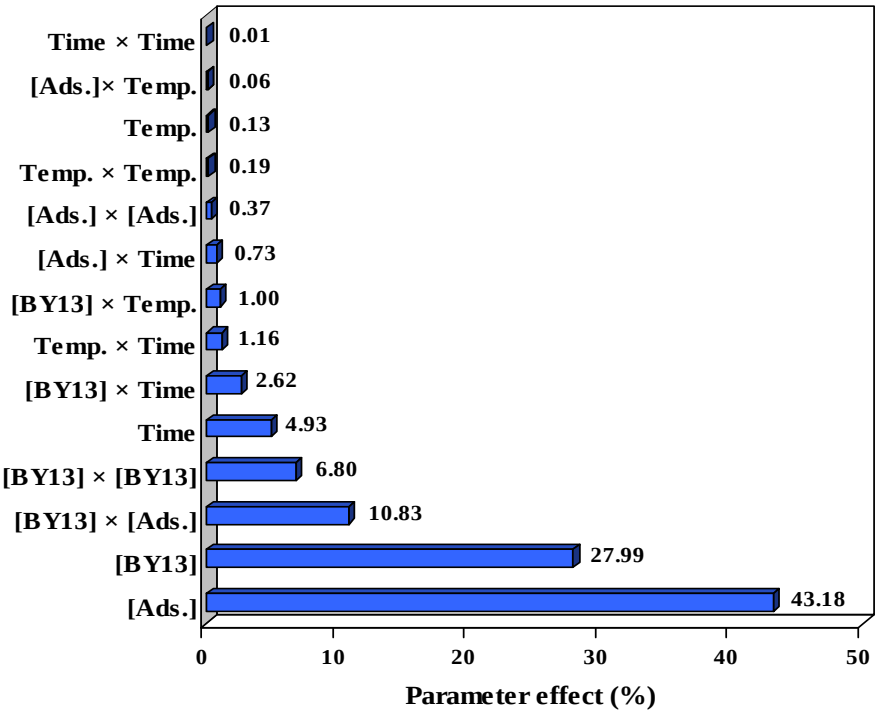

Fig. 6 Pareto graphic analysis

percentage effect of each parameter was calculated using the following equation

$$p_i = \left(\frac{b_i^2}{\sum b_i^2} \right) \times 100 \qquad i \neq 0 \tag{6}$$

where, b is the related regression coefficient of the parameter. As can be seen from this figure, the most important parameters for the BY13 removal are the linear effect of adsorbent dosage (43.18%) and dye initial concentration (27.99%), followed by interaction effect of adsorbent dosage and initial concentration of dye (10.83%).

3.3 Effect of variables and response surface analysis

The influence of all the single factors were considered and drawn wherein the lines indicate the estimated change in response as factors level is changed at experimental range. Fig. 7 shows the influence of single factors while maintaining all other factors constant at central level.

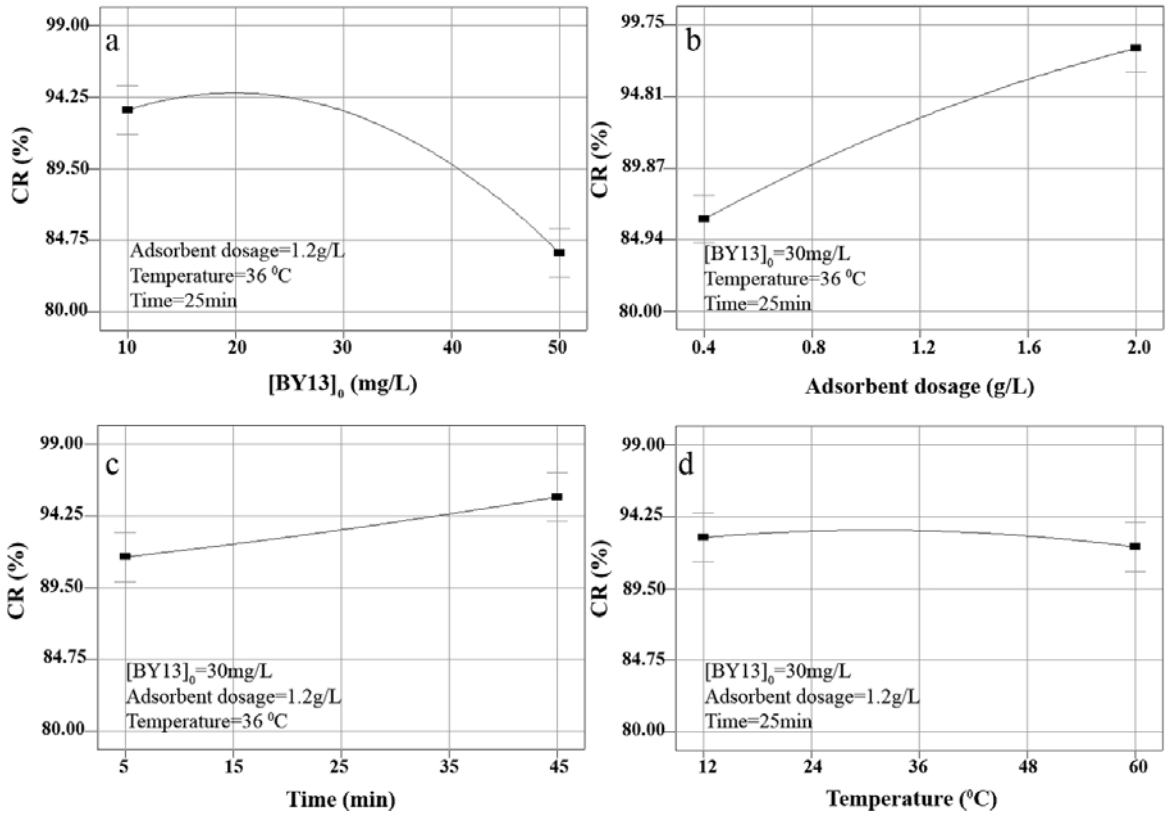

Fig. 7 Graphical presentation of the individual effects of (a) initial dye concentration; (b) adsorbent dosage; (c) contact time; and (d) temperature on the color removal efficiency (%)

During dye initial concentration enhancement the percentage of color removal showed significant decrease (Fig. 7(a)). Increasing the dye initial concentration from 10 to 50 mg/L decreased the CR efficiency form 93.40% to 83.92%. The results clearly indicated that the adsorption of BY13 from aqueous solution is significantly dependent on its initial concentration. From the quadratic equation established for percent CR efficiency, it can be concluded that the adsorbent dosage has the most significant impact on the process response. As expected, adsorbent dosage showed a positive effect on the CR efficiency (%) (see Fig. 7(b)).

It can be seen in Fig. 7(c) that the variation of the CR (%) is linear as a function of contact time and no quadratic effect is associated with it. Increasing the contact time from 5 to 45 min led to an slight increase of the CR(%) from 91.53% to 95.51%. Results imply the rapid adsorption of BY13 using coal, where more than 90% of dye removal occurred at first 5 minutes (when other factors lie at their central values). The rapid removal of dye is mainly due to the electrostatic interactions between adsorbent and adsorbate at the external adsorption sites on the coal surface. The efficiency of color removal was not significantly influenced by temperature at the studied experimental range as it is evident from the coefficient for this parameter (b_3) in Eq. (5). Fig. 7(d) confirms this finding well. As can be seen, the removal of BY13 was not changed considerably with increasing the temperature in the range of 12 to 60°C when other variables are kept constant at their central values. Tanyildizi (2011) reported similar results in the adsorption of reactive dye 5 using peanut hull as the adsorbent. However, our findings of insignificant effect of temperature on basic dye removal is inconsistent with Aravindhan et al. findings in adsorption of Basic Yellow dye (Sandocryl golden yellow C-2G) on green alga *Caulerpa scalpelliformis* (Aravindhan *et al*. 2007).

Response surfaces and contour plots of CR(%) as a function of two independent variables varying in the experimental space (between –2 and +2), while the other variables have been set at their central level, are given in Figs. 8-10. Examination of the CR (%) as a function of initial dye concentration and adsorbent dosage (Fig. 8) revealed an interaction behavior with a negative main effect of dye initial concentration and a positive main effect of adsorbent dosage. The significance of the observed interaction between mentioned variables has been proven by statistical analyses.

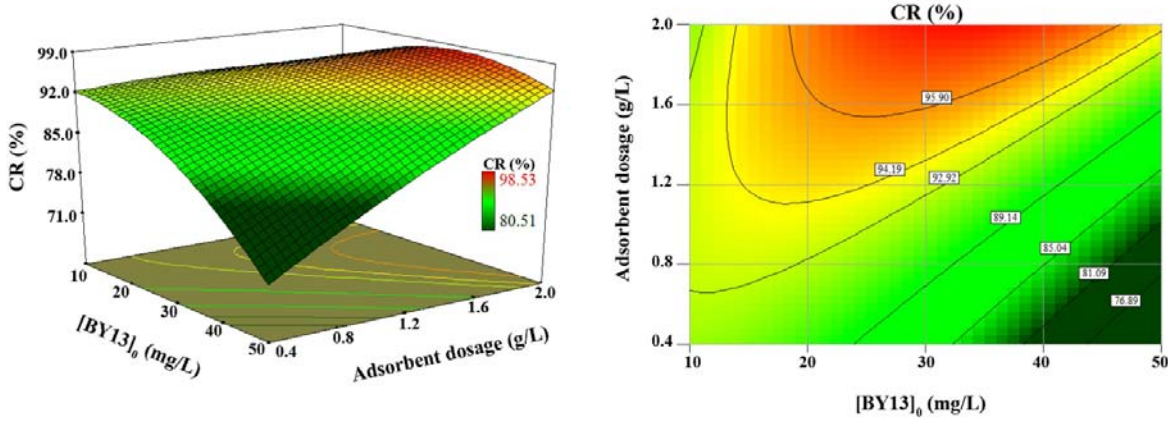

Fig. 8 The response surface and contour plots of the color removal efficiency (%) as the function of dye initial concentration and adsorbent dosage (Temperature = 36°C, contact time = 25 min)

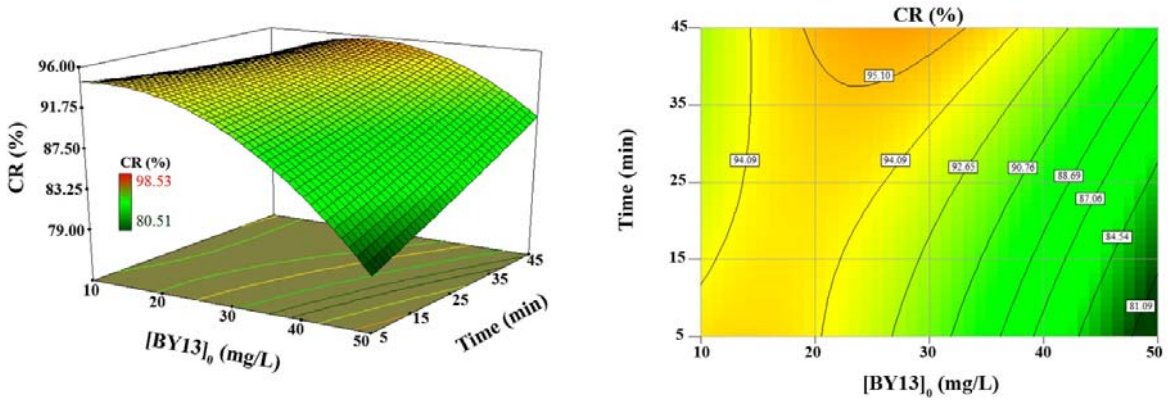

Fig. 9 The response surface and contour plots of the color removal efficiency (%) as the function of adsorbent dosage and contact time (Temperature = 36°C, dye initial concentration = 30 mg/L)

The dye initial concentration variable is also involved in a two-way interaction with contact time (Fig. 9). From this figure it can be deduced that contact time has a smaller effect on CR (%) in comparison whit the effect of dye concentration. Although the maximum CR (95.69%) was achieved at contact time 45 min and dye concentration 26.50 mg/L, considerably high CR efficiency (92.65%) can be achieved only after 5 min at the same concentration of dye. These findings confirm extremely rapid removal of dye in first 5 min using coal powder. This rapid adsorption process normally is being controlled by the diffusion process from the bulk to the adsorbent pores (interior surface) and led to the subsequent slow adsorption rate.

Combined effect of on BY13 removal efficiency at 30 mg/L of dye and contact time 25 min is represented in Fig. 10. From this figure it can be seen that there is no pronounced interaction between adsorbent dosage and temperature.

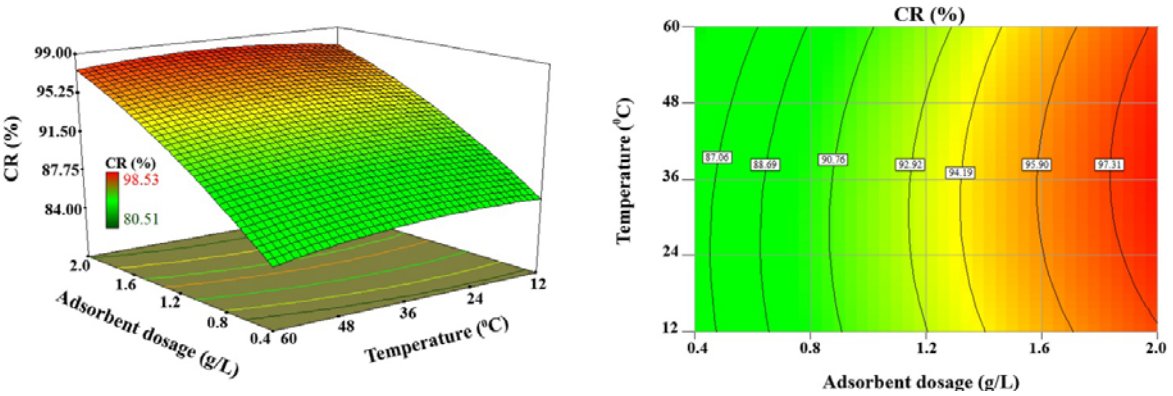

Fig. 10 The response surface and contour plots of the color removal efficiency (%) as the function of adsorbent dosage and temperature (dye initial concentration = 30 mg/L, contact time = 25 min)

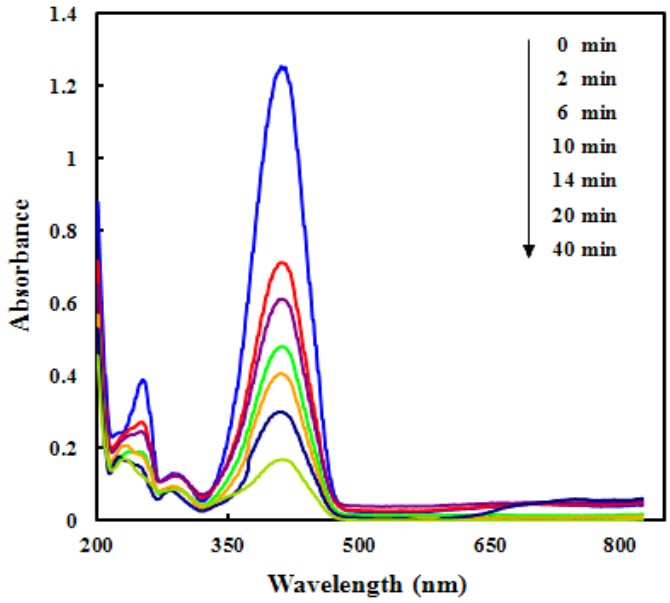

Fig. 11 UV–Vis spectra changes during different contact time at optimum conditions

4. Process optimization

4.1 Sensitivity analysis

The final objective of this study was to optimize the process variables and predict the response at the optimal settings. The numerical optimization of the software was chosen in order to locate the specific points that optimize both response and desirability function. This technique allows us to enter levels for each variable into the current model. The software then calculates the expected response using the method of canonical and ridge analyses of the obtained second-order equation (Hoerl 1959, 1964). From the ANOVA results (Table 4), it has been seen that the main effects of initial dye concentration, adsorbent dosage and contact time on the CR efficiency was significant. We assigned these factors respectively as target values 30 mg/L, 1.5 g/L and 10 min and the value of temperature variable was set equal to 25°C (ambient temperature). By using all above described settings, the software predicted 95.14% removal of BY13 (desirability function = 1) by solving Eq. (5).

For validation of predicted response, duplicate confirmatory experiments were performed at the same conditions and result was compared with the prediction. Experimentally obtained response (mean value) was 94.43% which is very close to the predicted value, indicating that the developed empirical model is robust and insensitive to external noises. Therefore, CCD design could be effectively used for optimization of removal efficiency of basic dye BY13 from aqueous solution.

The changes in the UV–Vis spectra of BY13 concentration during the removal process as a function of contact time and under the optimized conditions are displayed in Fig. 11. The spectrum of BY13 in visible region exhibits a main peak with a maximum wavelength at 412 nm which is

related to the chromophore groups of the dye molecules. The bands appeared in the UV region are characteristic of aromatic ring structures. The continuous decrease in the intensity of dye absorption peaks indicates removal of BY13 as contact time increases.

5. Conclusions

The adsorptive removal of basic dye BY13 using coal, as a cost-effective adsorbent, was investigated focusing on the influence of four independent variables (initial concentration of dye, adsorbent dosage, temperature and contact time). To consider the combined effects of studied process variables, five-level central composite experimental design, as the most popular design in RSM, was applied. Analysis of variance showed a high coefficient of determination value (R^2 = 0.947) between experimental and predicted responses by the model, confirming the model reliability for response predicting and multivariate optimization through sequential experiment-ation. By using RSM, 95.14% of CR was possible under optimal conditions of process parameters, such as, initial concentration of dye, 30 mg/L, adsorbent dosage, 1.5 g/L, temperature, 25°C and contact time, 10 min. Regression analysis revealed that linear effect of adsorbent dosage and initial concentration of dye as well as interactive effect of adsorbent dosage and initial concentration of dye have the highest impact on the CR efficiency, respectively.

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