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Optimization of Reactive Black 5 removal by adsorption process using Box–Behnken design

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ABSTRACT

Optimization of process parameters is an important part of any process development. Maximum efficiency of any process is achievable when it runs at optimum condition. In this paper, optimization of Reactive Black 5 adsorption on TiO_2 surface was carried out. Adsorption of dye depends on many process parameters like pH, adsorbent dose, initial dye concentration, and adsorption time. In this study, adsorption efficiency has been optimized based on those process parameters. Response surface methodology has been used for optimization as it has many advantages over classical optimization methods. Box–Behnken design was employed to design the experiment. For regression analysis and ANOVA study, software MINITAB 15 was used. All factors in regression equation are not equally important. Pareto analysis has been employed to find the most influential process parameters. The analysis shows that pH is the dominating factor during dye adsorption. This study confirms that more than 98% dye removal is possible at the optimum condition.

Keywords: Reactive Black 5; Adsorption; Process optimization; RSM; Box–Behnken; Pareto analysis

1. Introduction

Process optimization is a vital part of any process development. Process characteristics and process dynamics are very much required for process modeling and optimization. The dynamic characteristics of adsorption process are very complicated; a number of attempts have been taken for developing an experimental-based optimization methodology which may help to provide a better understanding of the process in terms of the effects of independent process variables and their effects on the dependent variable. In this study, adsorption of Reactive Black 5 (RB5) has been optimized using response surface methodology (RSM). Removal efficiency of reactive dye by adsorption depends on initial dye concentration, adsorbent dose, pH of the solution, and batch time. The initial concentration of solute depends on the source of the effluent; this parameter cannot be optimized. So, the process has been optimized against three independent process parameters (viz. pH, adsorbent dose, and batch time). Wastewater containing reactive dyes is harmful for human and aquatic life. This wastewater needs proper treatment before discharge to the surface water bodies. Many physical and chemical methods including adsorption, coagulation, precipitation, filtration, and oxidation have been used for the treatment of azo dye-contaminated effluents [1]; adsorption is one of the most suitable treatment methods for this purpose. Nevertheless many advantages, the main disadvantage of adsorption process is disposal or regeneration of spent adsorbent. TiO_2 photocatalyst can be used as adsorbent for reactive dye removal. Our previous study [2] shows that regeneration and recycling of spent TiO_2 is possible, so there is no sludge disposal problem. Study shows that dye degradation by photocatalytic reaction strongly depends on the adsorption capacity of TiO_2 powder, because the substances that are adsorbed strongly degrade faster [3]. With this connection, finding the optimum operating condition for adsorption is essential to get the optimum dye removal efficiency. Research shows that adsorption of heavy metals can be optimized by RSM [4]. Several works have proved that RSM is a powerful statistical tool for optimization of adsorption and photocatalytic oxidation processes [5–7]. RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes [8]. This method was initially developed and described by Box and Wilson [9]. This method has some advantages over the classical optimization methods; classical methods of optimization involve the change of one variable at a time, which is quite time consuming especially when a large number of variables are considered [10]. RSM is a very practical, economical, and useful tool for modeling and analysis of any process using polynomials as local approximations to the true input/output relationship [11]. In this study, Pareto analysis has been carried out to check the influence of each parameter.

2. Experimental methodology

2.1. Materials

Reactive dye used for this study is RB5 (λ_{max} = 592 nm) supplied from a dyehouse near Kolkata (India). The molecular structure is given in Fig. 1. TiO_2 powder (Hombikat UV—100; 99% anatase; surface area >250 m^2/g; primary crystal size <10 nm diameter) supplied by Sachtleben Chemie GmbH was used as adsorbent.

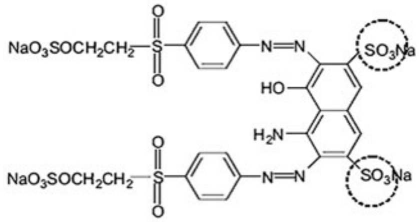

Fig. 1. Molecular structure of RB5.

Other chemicals used for this study were HCl, NaOH, etc. Ultra-pure deionised water used in this study was obtained from Arium 611DI ultrapure water system (Sartorius A.G., Göttingen, Germany). The feed to this Arium 611DI was taken from usual laboratory distillation unit.

2.2. Design of experiment

Design of experiment (DOE) is an approach for finding cause and effect relationships. The purpose of statistically designing an experiment is to collect the maximum amount of relevant information with a minimum expenditure of time and resources. It is also important to remember that the DOE should be as simple as possible and consistent with the requirements of the problem.

To determine the effect of various operating parameters such as pH of the solution, adsorbent dose and contact time, Box–Behnken design has been used. Different studies show [12,13] that Box–Behnken design is very useful for optimizing adsorption process. The main advantage of Box–Behnken design over CCRD is that it requires less number of experimental design points which reduces the experimental cost, consequently cost of optimization process. The values of the independent parameters were converted in coded form. The experimental points and the levels for all parameters are given in Table 1. Table 1 also shows the range of different variables.

For this present study, the number of independent variables is three. So, number of experiment required is given by the following equation.

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

where N is total number of experiment, k is number of variables and p is replicate number of the central point.

The relationship between the coded and un-coded form of the variables is

$$\text{Coded value} = X_i = \frac{(x_i - \overline{x}_i)}{\Delta x} \quad (2)$$

Table 1
Values of independent variables at different levels of Box–Behnken design

Independent variable	Symbol	Levels		
		−1	0	+1
pH	X_1	3.318	5	6.682
TiO_2 dose ($g.L^{-1}$)	X_2	0.977	3.5	6.023
Contact time (min)	X_3	2.452	26	49.548

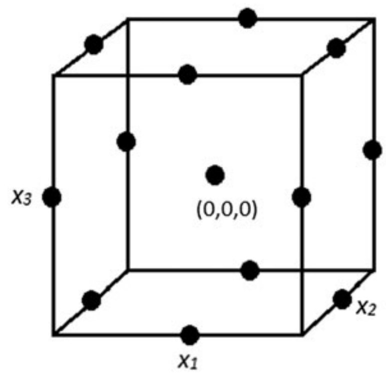

Fig. 2. Distribution of design points for Box–Behnken Design.

where x_i is the actual value of the ith factor in the uncoded units, $\overline{x}_i$ is the average of the low and high values for the ith factor, and Δx is the step change. Fig. 2 shows the various design points.

2.3. Experimental

2.3.1. Experimental setup

A jar tester manufactured by Phipps and Bird, Virginia, USA was used for this experimental purpose. The jar tester comprises six glass jars with six stirrers (uniform speed). To maintain the uniform speed, jars are connected with a motor through a common chain.

The volume of each jar is 1 litre. Stirrers of this jar tester consist of two flat bladed rectangular paddles with an area $1.9 \times 10^{-3}\,\mathrm{m}^2$. A uniform speed of 150 rpm was maintained by using a control panel with digital display. The schematic diagram of the jar tester is shown in Fig. 3.

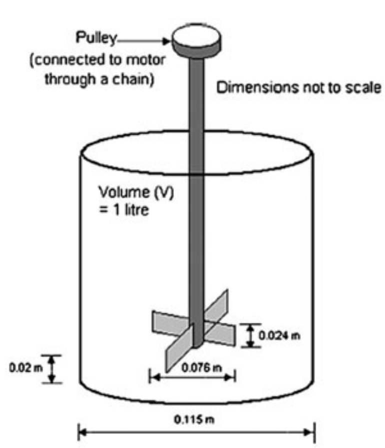

Fig. 3. Schematic diagram of jar tester.

2.3.2. Experimental procedure

A series of experiments were conducted at the design points. All of these experiments were carried out in presence of infrared light to prevent any decolorization of dyes by photocatalytic reaction. These tests were performed with different TiO_2 doses and at different pH. A simulated dye solution of $100\,\mathrm{mg.L^{-1}}$ was used as feed solution. The pH of the test solution (mixture of dye solution and TiO_2 adsorbent) was controlled using 10 M HCl and 10 M NaOH solution. After starting the experimental run, samples were collected from the jar tester from time to time. Then the collected samples were filtered using 0.45 μm polyethersulfone microfiltration membranes (Pall, Gelman Laboratory, Michigan) to separate the TiO_2 particles. After filtration, the concentration of dyes was measured using a spectrophotometer (Jenway 6505 UV–Vis spectrophotometer; Dunmow, Essex, UK) at a wavelength of 592 nm.

3. Results and discussion

3.1. Building empirical model

In the first step of RSM, a suitable approximation is introduced to find true relationship between the dependent variables (responses) and the set of independent variables (factors). Second-order designs are used in practice in situations when the linear model is insufficient for a mathematical description of a research subject with an adequate precision. In this study, a first-order (linear) model was formed to fit the experimental data. The linear model shows high error value. Then a mathematical model in the form of a second-order polynomial is formed. The behavior of the system is explained by the following quadratic equation.

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_{ii}^2 + \sum b_{ij} X_i X_j + e \tag{3}$$

where b_0 is the constant coefficient, b_i, b_{ii} and b_{ij} are coefficients of linear, quadratic, and the second-order terms, respectively, e is the error, Y is dependent variable (response), and X is independent variable in codified form. The values of all these coefficients are calculated from the experimental data. Software MINITAB 15 was used for finding regression coefficients and statistical analysis. The design matrix used for regression analysis is given in Table 2. Calculated values of the coefficients are given in Table 3. The regression equations are given below.

Table 2
Matrix of Box–Behnken design

No of experiment	Coded value of independent variable			Response (% dye removal)
	pH	TiO_2	Time	
1	1	0	−1	2.4
2	0	0	0	58.4
3	1	1	0	33.1
4	0	−1	−1	7.18
5	0	−1	1	16.58
6	−1	−1	0	60.85
7	0	0	0	58.4
8	1	0	1	17.15
9	0	1	1	67.78
10	0	1	−1	37.74
11	−1	0	−1	66.14
12	1	−1	0	2.1
13	−1	0	1	90.81
14	−1	1	0	85.9
15	0	0	0	58.4

Table 3
Estimated regression coefficients for percentage dye removal

Term	Coef	SE coef	*T*	*P*
Constant	58.4000	3.328	17.547	0.000
pH	−31.1275	2.038	−15.273	0.000
TiO_2	17.2175	2.038	8.448	0.000
Time	9.8575	2.038	4.837	0.005
pH × pH	*−0.5625*	*3.000*	*−0.188*	*0.859*
$TiO_2 \times TiO_2$	−12.3675	3.000	−4.123	0.009
Time × time	−13.7125	3.000	−4.571	0.006
pH × TiO_2	*1.4700*	*2.882*	*0.510*	*0.632*
pH × time	*−2.4800*	*2.882*	*−0.860*	*0.429*
TiO_2 *× time*	*5.1600*	*2.882*	*1.790*	*0.133*

$S = 5.76458$, $R^2 = 98.66\%$, $R^2(\text{pred}) = 78.53\%$, $R^2(\text{adj}) = 96.24\%$.

The regression equation for RB5 is

$$\begin{aligned}\text{Dye removal }(\%) = {} & 58.40 - 31.128(\text{pH}) + 17.218(\text{TiO}_2) \\ & + 9.858(\text{Time}) - 0.563(\text{pH})^2 \\ & - 12.367(\text{TiO}_2)^2 - 13.713(\text{Time})^2 \\ & + 1.47(\text{pH})(\text{TiO}_2) - 2.48(\text{pH})(\text{Time}) \\ & + 5.16(\text{Time})(\text{TiO}_2) \end{aligned} \quad (4)$$

Values of the parameters in the above equation are in coded form. The response surfaces developed for RB5 are shown in Figs. 4–6. The value of error (*e*) can be calculated using Eqs. (3) and (4). The difference between calculated value (from Eq. (4)) and actual value (from experimental result) is the error (*e*). The error value should be within acceptable range for any reliable regression equation.

3.2. Analysis of variance study

The analysis of variance (ANOVA) is employed for the determination of significant variables. ANOVA consists of classifying and cross-classifying statistical results and tested by the means of a specified classification difference, which was carried out by Fisher's statistical test (*F*-test). The F-value represents the significance of each controlled variable on the tested model. The correlation coefficients R^2 and R^2_{adj} have been calculated to check the adequacy of the model. A large value of R^2 does not imply that the regression model is a good one. However, R^2_{adj} preferred to be

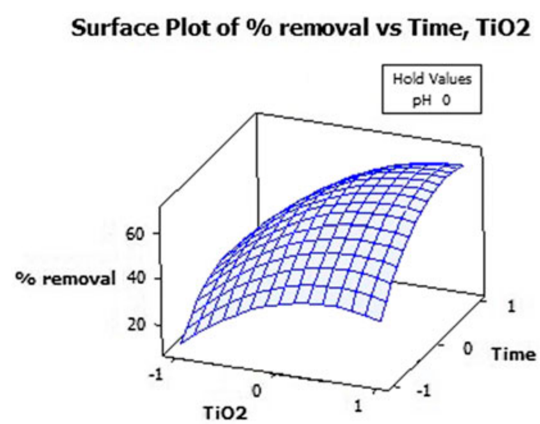

Fig. 4. Response surface for RB5 removal by adsorption at constant pH 5.

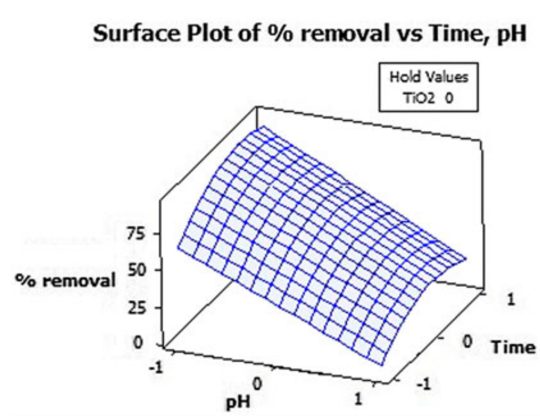

Fig. 5. Response surface for RB5 removal by adsorption at constant TiO_2 dose 3.5 g.L^{-1}.

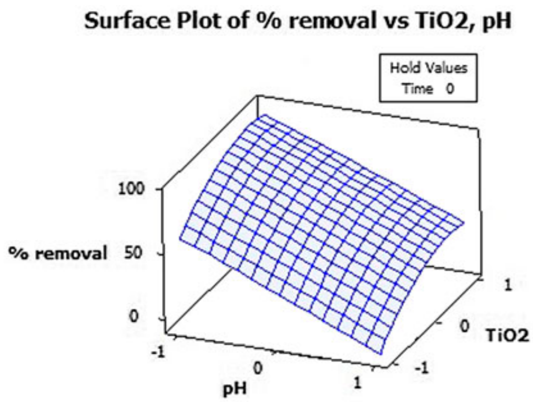

Fig. 6. Response surface for RB5 removal by adsorption at constant time 26 min.

used to determine the fit of a regression model as it does not always increase when variables are added [14]. Statistical analysis was carried out to check if the regression models comply with experimental data.

All terms in the regression models are not equally important. The significance of each coefficient was determined by student's *t*-test and *p* values, which are listed below. The *t* value represents the ratio of the estimated parameter effect to the estimated parameter standard deviation. Moreover, the *p* value is used as a tool to check the significance of each of the coefficients. The larger the magnitude of the *t* value and the smaller the *p* value, the more significant is the corresponding parameter in the regression model [15]. The results of ANOVA studies for RB5 are given in Table 4. Results show that interaction terms have less influence in the regression equations. Table 3 shows that *p* values are high for the highlighted terms. So, excluding those terms from the regression equation, we get the final equations. The final regression equations for RB5 (Eq. (5)) are given below. The parameters in Eq. (5) are in coded form.

$$\begin{aligned}\text{Dye removal } (\%) = {} & 58.40 - 31.128(\text{pH}) \\ & + 17.218(\text{TiO}_2) + 9.858(\text{Time}) \\ & - 12.367(\text{TiO}_2)^2 - 13.713(\text{Time})^2\end{aligned} \tag{5}$$

Fig. 7 shows calculated results using Eq. (5) against the experimental results. It is clear from these graphs that the regression equations follow the experimental results with a good accuracy ($R^2 = 0.9866$).

The Pareto analysis was carried out to check the percentage effect of each factor. This analysis gives more significant information to interpret the results. This analysis calculates the effect of each factor according to Eq. (6) [16].

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

Adsorption process is a surface phenomenon which depends on the characteristics of adsorbent surface. The surface property largely depends on pH of the solution. Fig. 8 depicts that all factors are not equally

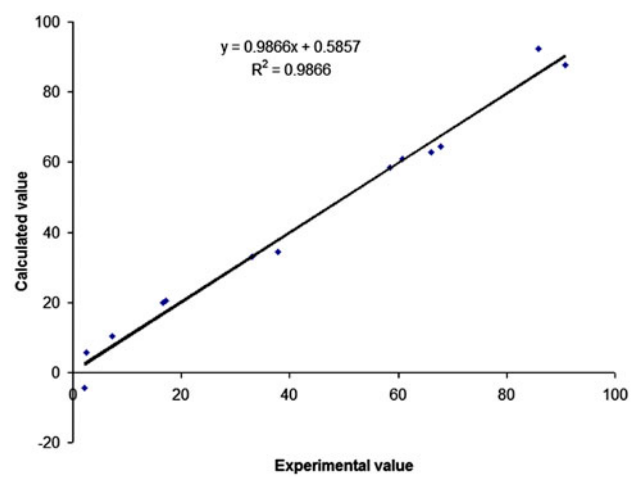

Fig. 7. Experimental results vs. calculated results for RB5.

Table 4
ANOVA for percentage dye removal

Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Regression	9	12215.9	12215.9	1357.33	40.85	0.000
Linear	3	10900.3	10900.3	3633.42	109.34	0.000
Square	3	1175.9	1175.9	391.98	11.80	0.010
Interaction	3	139.7	139.7	46.58	1.40	0.345
Residual error	5	166.2	166.2	33.23		
Lack-of-fit	3	166.2	166.2	55.38		
Pure error	2	0.0	0.0	0.00		
Total	14	12382.1				

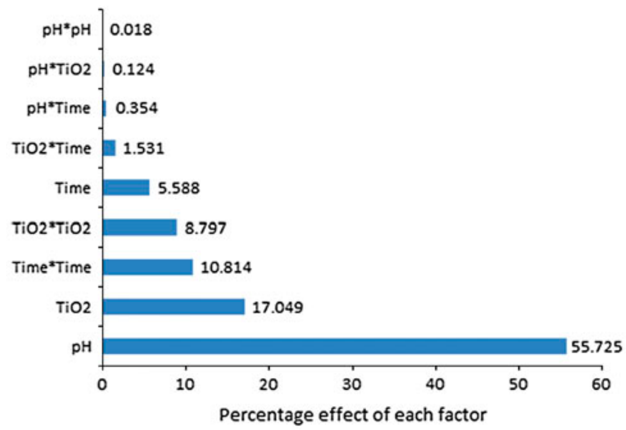

Fig. 8. Pareto graph for RB5 removal by adsorption.

important; solution pH is the most dominating factor during dye removal. This result can also be used for controlling the batch adsorption process.

3.3. Optimization of parametric condition

Contour plots for dye removal are shown in Figs. 9–11. It is clear from Figs. 9 and 11 that the dye removal is favorable with high TiO_2 dose. Chakraborty et al. [17] found a similar result which shows adsorption dose is an important parameter. But high TiO_2 concentration increases the solution turbidity and consequently reduces the UV ray penetration during regeneration. At the same time it increases the cost of TiO_2 separation from the treated water. So, optimization of TiO_2 concentration is required for economic plant operation. Figs. 10 and 11 show that dye removal increases with decreasing pH because at low pH, TiO_2 surface becomes positively charged which attracts negatively charged dye molecules [2]. Each factor and the response have been optimized using software MINITAB 15. Fig. 12 shows the graphical representation of numerical optimization. This

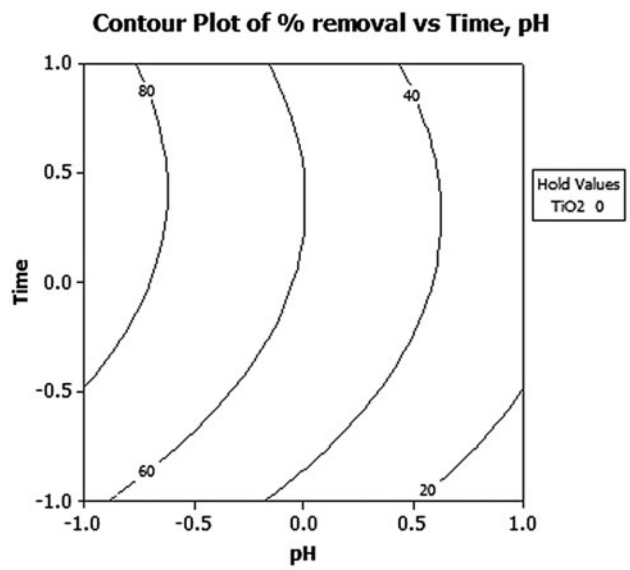

Fig. 10. Contour plots for RB5 removal by adsorption at constant TiO_2 dose 3.5 g.L^{-1}.

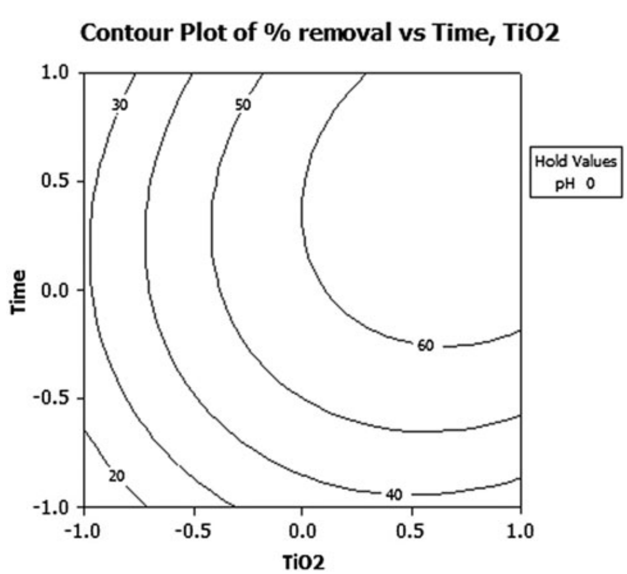

Fig. 9. Contour plots for RB5 removal by adsorption at constant pH 5.

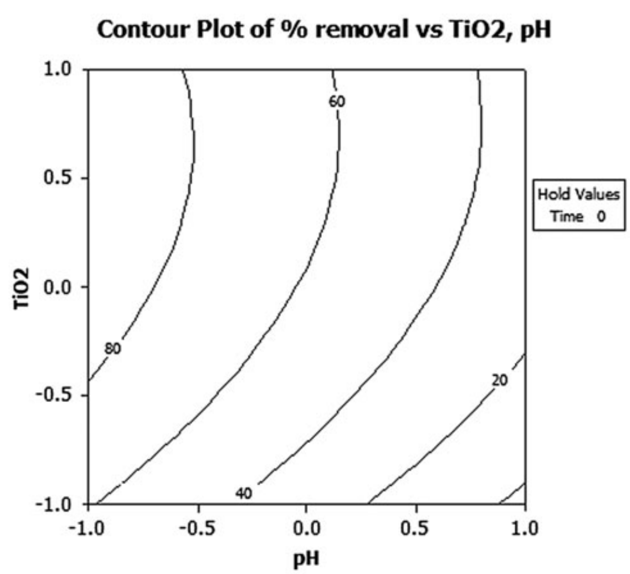

Fig. 11. Contour plots for RB5 removal by adsorption at constant time 26 min.

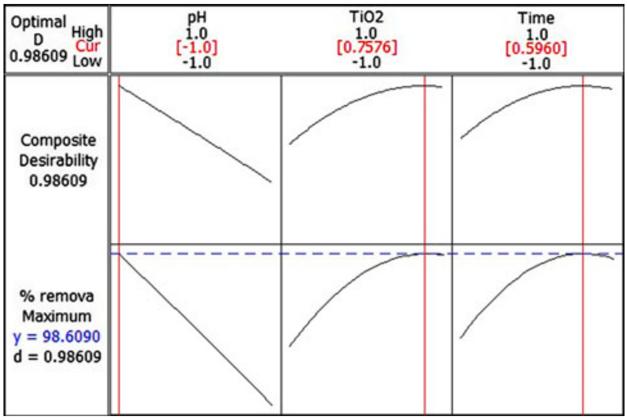

Fig. 12. Graphical representation of numerical optimization of all factors and responses.

figure suggests that pH value should be kept as low as possible, as dye removal increases monotonically with decreasing pH. The optimum values of pH, TiO_2 dose, and time are 3.32, 5.4 g.L^{-1}, and 40.0 min, respectively. Dye removal at this optimum condition is 98.61%.

4. Conclusions

The present study shows that adsorption of RB5 TiO_2 surface is favorable at low pH. The regression model equation follows the experimental data with a good accuracy ($R^2 = 0.957$). This study confirms that Box–Behnken design can be used for experimental design of dye adsorption on TiO_2 surface. Time required for optimum dye adsorption is 40 min and optimum TiO_2 concentration is 5.4 g.L^{-1}. Under optimal values of the process parameters, almost 98.6% removal of RB5 was possible. ANOVA study shows that interaction terms are not important for regression model. Pareto analysis shows that pH is the most influential factor for dye adsorption on TiO_2 surface; it has 63.48% effect on the overall response.

Abbreviation

ANOVA	—	analysis of variance
DOE	—	design of experiment
RB5	—	reactive black 5
RSM	—	response surface methodology

Nomenclature

b_0	—	constant coefficient
b_i, b_{ii}, b_{ij}	—	coefficients of linear, quadratic and the second-order terms
e	—	error
k	—	number of variables
N	—	total number of experiment
P_i	—	percentage effect of each term
p	—	replicate number of the central point
X	—	independent variable in codified form
X_i	—	coded value of the ith factor
x_i	—	actual value of the ith factor in the uncoded units
$\bar{x}_i$	—	average of the low and high values for the ith factor
Δx	—	step change
Y	—	dependent variable (response)

Greek letters

λ_{max}	—	wavelength

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