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Investigation of affecting operational parameters in photocatalytic degradation of Reactive Red 198 with TiO_2: optimization through response surface methodology

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A B S T R A C T

This research investigated the photocatalytic decolorization and degradation of an azo dye, reactive red 198 (RR198), in an aqueous solution with TiO_2-P25 (Degussa) as the photocatalyst in a slurry form using UV light. There was a significant difference in the adsorption of the dye on the TiO_2 surface with the change in the solution pH. The effect of various parameters such as catalyst loading, pH and the initial concentration of the dye on decolorization and degradation were determined. The optimum conditions of the reactor were acquired at a dye concentration of 62 mg/L, a pH of 3.7, and a catalyst concentration of 2.25 g/L; the dye removal efficiency was 98%. According to the ANOVA equation, the catalyst loading relevant coefficient = 19.25 and the pH relevant coefficient = −2.62 were determined to be the most and least effective parameters on the dye removal, respectively.

1. Introduction

A number of colored effluents that contain dyes are discharged in the wastewater of textile, food, leather, pharmaceutical, paper, and ink industries [1,2]. Different organic pollutants have been introduced into natural water resources and land by the residual dyes from the discharge of these effluents [3]. The textile industry is one of the largest producers of effluents contaminated with dyes. Azo dyes, which are the most important class of synthetic organic dyes used in the textile industry and therefore the most common industrial pollutants, are produced in large amounts and enter the environment during manufacturing processes [4]. The dispersion of these toxic substances in the environment, even at low concentrations, not only cause cancer [5] but also decreases the influence of sunlight in deep waters and reduces the ecosystem optical activity, which consequently lowers the level of dissolved oxygen in the water and increases temperature [6]. Therefore, dye effluents must be removed completely before entering the environment.

Traditional physical techniques such as adsorption on activated carbon, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc. have the ability to remove the dye in a short time, but they have shortcomings such as high energy consumption, high costs, and the necessity of a second treatment method due to the transferring of contaminants from one phase to another [7,8,9]. Also, conventional biological treatment methods are ineffective for decolorization and degradation due to the large degree of aromatics present in the dye molecules and the stability of modern dyes. Furthermore, the majority of dyes are only adsorbed on the sludge and are not degraded [10,11]. In recent years, an advanced oxidation process based on heterogeneous photocatalysts, notably titanium dioxide (TiO_2), has been introduced as an efficient method due to its availability, low cost, chemical stability, and ability to remove a variety of contaminants up to the mineralization stage in environmental conditions

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[7,12,13,14,15,16,17]. Also, based on the characteristics of catalysts, these materials remain unused at the end of the process and have the potential to be recycled. The optimization of the processes by the traditional method involves changing one independent parameter and maintaining all others at a constant level [18]. The main downside of this technique is that it does not contain the interaction effects among the variables and does not explain the effects of various factors on the process [19]. In order to overcoming this problem, optimization studies can be carried out using response surface methodology (RSM), which is a combination of mathematical and statistical techniques arising from experimental methodology [20]. The aim of RSM is the optimization and interpolation of other unexamined points and a correct estimation of the probable response at those points [21,22]. The novelty of this paper was the use of the photocatalyst process for treating reactive red 198 in which the simultaneous effects of three operating variables (dye concentration, pH and the amount of catalyst) on dye removal were considered and analyzed by RSM. Thus, the interaction of the three independently selected operational parameters was precisely examined and investigated to determine their clear relationship and effect, those of which had not been previously considered for RR198 by TiO_2. There are various references concerning the removal of RR198 with TiO_2, but they differ from our research. *Kumar Anupam et al.* treated RR198 by TiO_2, but they did not use UV light; their process was only an adsorption process, not a degradation one. Also, they selected operational parameters that were different from our work [23]. *Sumandeep Kaur and Vasundhara Singh, Niyaz Mohammad Mahmoodi* degraded RR198 via the photocatalyst process, but they did not use design of experiment software to determine the precise interaction of the various operational parameters [24,25].

2. Materials and methods

2.1. Characteristics of materials

For the present study, commercial diazo dye reactive red 198 with a molecular formula of – $C_{27}H_{18}ClN_7Na_4S_5O_{15}$ and a molecular weight of 863.70 was used (Figure 1 shows the molecular structure of diazo dye). The catalyst employed was a technical grade TiO_2 Degussa P-25. The TiO_2-P25 contained anatase 80% and rutile 20% with a mean particle size of 30 nm and a BET surface area of 50 m^2/g.

2.2. Photocatalytic reactor

The photochemical reactions were carried out in a specially designed rectangular batch reactor (dimensions: diameter=25 cm and height=43 cm) made of stainless steel and is shown in Figure 2. The light source was provided using 8 UV-C 16-watt lamps manufactured by the Philips Company and were installed in the reactor using 8 holders made of quartz.

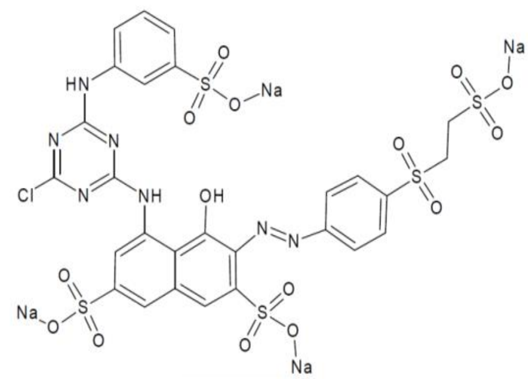

Fig. 1. Molecular structure of reactive red 198

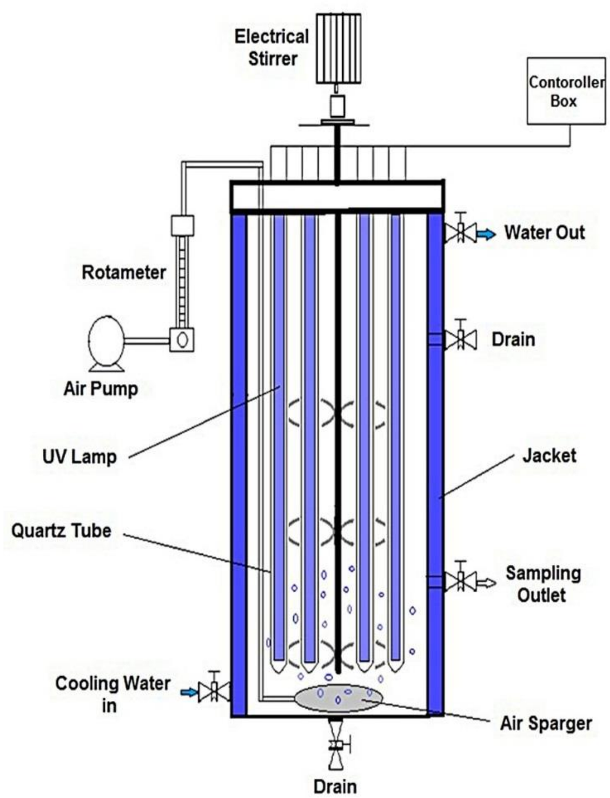

Fig. 2. Schematic diagram of the photocatalytic reactor set up

2.3. Experimental procedure

In all runs, 750 ml of the dye solution containing the appropriate quantity of the TiO_2 suspension was used. The suspension was stirred for 30 min in a dark place in order to attain adsorption equilibrium. After this period, the lights and aeration pump were turned on for one hour. All the experiments were done at room temperature, atmospheric pressure and in batch operation. 10 ml samples were collected at specified time intervals and analyzed after centrifugation.

2.4. Response surface methodology

In the present work, the Design Expert ® (7.3.1) software was used for statistical analysis of the data. The response surface method based on Box-Behnken was used to examine the effect of the parameters and their interactions; it also determined the optimum condition for the decolorization of the dye. Seventeen experiments were conducted based on the same design. The dye concentration, pH and TiO_2 concentration were selected as operational factors in order to evaluate dye removal which was chosen as a response variable by photocatalytic reaction after one hour. The values and levels of the chosen factors are shown in Table 1. Each factor was altered at three levels, whereas the other parameters were kept constant.

Table 1. Values and levels of chosen variables for Box- Behnken

Variable	symbol	Coded levels		
		-1	0	+1
dye concentration (mg/L)	A	50	100	200
initial pH	B	3	5	7
TiO_2 concentration (g/L)	C	0.2	1.6	3

3. Result and Discussion

3.1. Designed model and ANOVA analysis

The values of the parameters for seventeen runs and their responses are shown in Table 2.

Based on the results of the experiments in Table 2, a modified equation (Equation 1) was presented by the software to predict the experiments. This equation includes a set of coefficients and coded factors described as follows:

$$\text{Decolorization} = +82.40 - 16.88A - 2.62B + 19.25C + 3.00AC + 2.50BC - 3.33A^2 - 4.82B^2 - 14.07C^2 \quad (1)$$

Variables A, B, C are the operating parameters for dye concentration, initial pH, and the concentration of catalyst, respectively. It also can be seen that there was an interaction between (A, C) and (B, C), but there was no interaction between (A, B). Figure 3 shows the actual results obtained from testing against the prediction of the software, and it can be said that the designed equation covered a large area of the experiments well.The success and proportion of the model examined by variance analysis is shown in Table 3. A p-value < 0.0001 implied that the model was significant. There was only a 0.01% chance of occurrence of model F-value due to noise. The lack of Fit F-value of 0.98 was not significant relative to the pure error. For a model to be successfully used for prediction, the lack of fit should not be significant. The "Pred R-Squared" of 0.9809 was in reasonable agreement with the "Adj R-Squared" of 0.9943, which confirmed the adaptability of this model [26]. Therefore, it can be concluded that the obtained model was adequate to describe the relationship between the decolorization efficiency and operational factors for the degradation of RR198 by the photocatalytic process.

Table 2. Experimental design matrix and the value of response based on experiment runs

Run	A	B	C	Decolorization (%)
1	50	3	1.60	92
2	200	5	0.2	26
3	125	5	1.6	84
4	200	7	1.6	55
5	125	7	3	82
6	125	3	0.2	50
7	125	7	0.2	38
8	125	5	1.6	83
9	50	7	1.6	90
10	125	3	3	84
11	50	5	0.2	66
12	125	5	1.6	83
13	200	5	3	70
14	50	5	3	98
15	125	5	1.6	80
16	200	3	1.6	60
17	125	5	1.6	82

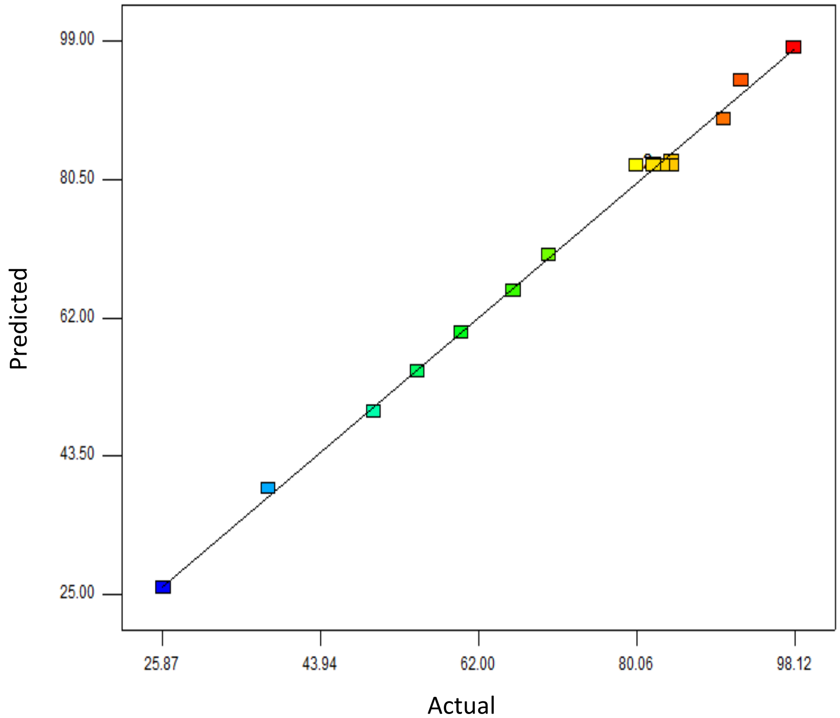

Fig. 3. Actual results against the prediction of the software

Table 3. ANOVA table for the response surface modified model

Source	Sum of Squares	df	Mean Squares	F-value	p-value Prob>F	
Model	6404.74	8	800.59	351.91	< 0.0001	significant
A: dye concentration	2278.12	1	2278.12	1001.37	< 0.0001	
B: pH	55.13	1	55.13	24.23	0.0012	
C: catalyst concentration	2964.50	1	2964.50	1303.08	< 0.0001	
AC	36.00	1	36.00	15.82	0.0041	
BC	25.00	1	25.00	10.99	0.0106	
A^2	46.55		46.55	20.46	0.0019	
B^2	98.02	1	98.02	43.09	0.0002	
C^2	834.13	1	834.13	366.65	< 0.0001	
Residual	18.20	8	2.28			
Lack of Fit	9.00	4	2.25	0.98	0.5082	not significant
Pure Error	*9.20*	4	2.30			
Cor Total	6422.94	16				
R-Squared	0.9975					
Adj R-Squared	0.9943					

3.2. Effect of dye concentrations

The pollutant concentration is a very important parameter in wastewater treatment. The effect of various initial dye concentrations on the photocatalytic decolorization were investigated from 50 to 200 mg/L. The results are shown in Figure 4. It was found that the increase of the dye concentration decreased the removal rate. As the concentration of dye increased, the amount of UV light that permeated decreased, so the amount of light which was needed to activate the catalyst decreased and consequently, the removal rate declined.

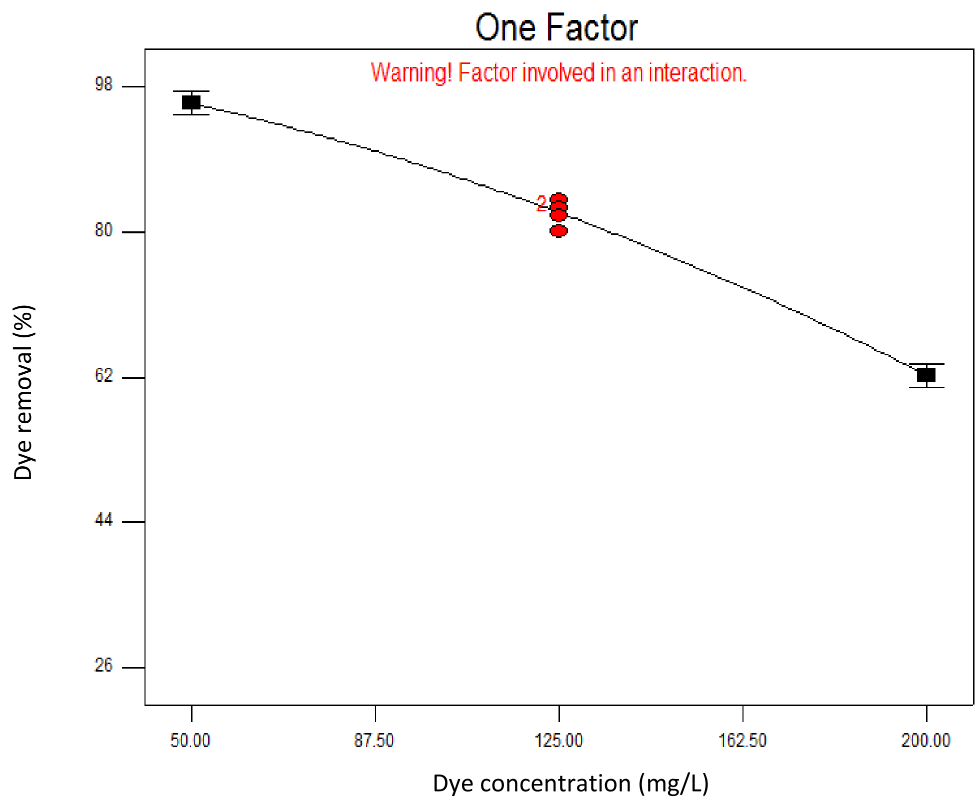

Fig. 4. Effect of dye concentration on dye removal

3.3. Effect of pH

As seen earlier, the photocatalytic degradation efficiency was affected by the surface charge property of TiO_2, charge of dye molecule, adsorption of dye on TiO_2 surface, and hydroxyl radical concentration. As these properties are pH dependent, pH played an important role in the degradation of RR198. The effect of pH from 3 to 7 on the decolorization and degradation are shown in Figure 5. An increase of pH of the dye solution from 3 to 7 decreased the efficiency of decolorization from 80% to 72 %.

3.4. Effect of catalyst loading

For economic removal of dye effluent from wastewater, it is necessary to find the optimum amount of catalyst needed for efficient degradation. Several authors have investigated the reaction rate as a function of catalyst loading in the photocatalytic oxidation process [27,28]. The effect of photocatalyst (TiO_2) concentration on the degradation of RR198 was investigated from 0.2 to 3 g/L. The effect of TiO_2 loading on the initial rate of removal for decolorization and degradation is shown in Figure 6. As the concentration of the catalyst increased from 0.2 to 1.6 g/L, the initial rate of dye removal of increased sharply from 50% to 80% for decolorization. This was due to the increase of TiO_2 particles, which increased the number of photons absorbed and the dye molecules adsorbed. The increase of the catalyst loading beyond 1.6 g/L may cause light scattering and screening effects. These reduced the specific activity of the catalyst [29]. At high concentrations of catalysts, particle aggregation may also reduce the catalytic activity. The optimum amount of catalyst loading was found to be 1.6 g/L for the degradation and decolorization of RR198. Hence, 1.6 g/L was used as the catalyst dosage for the photocatalytic reactions.

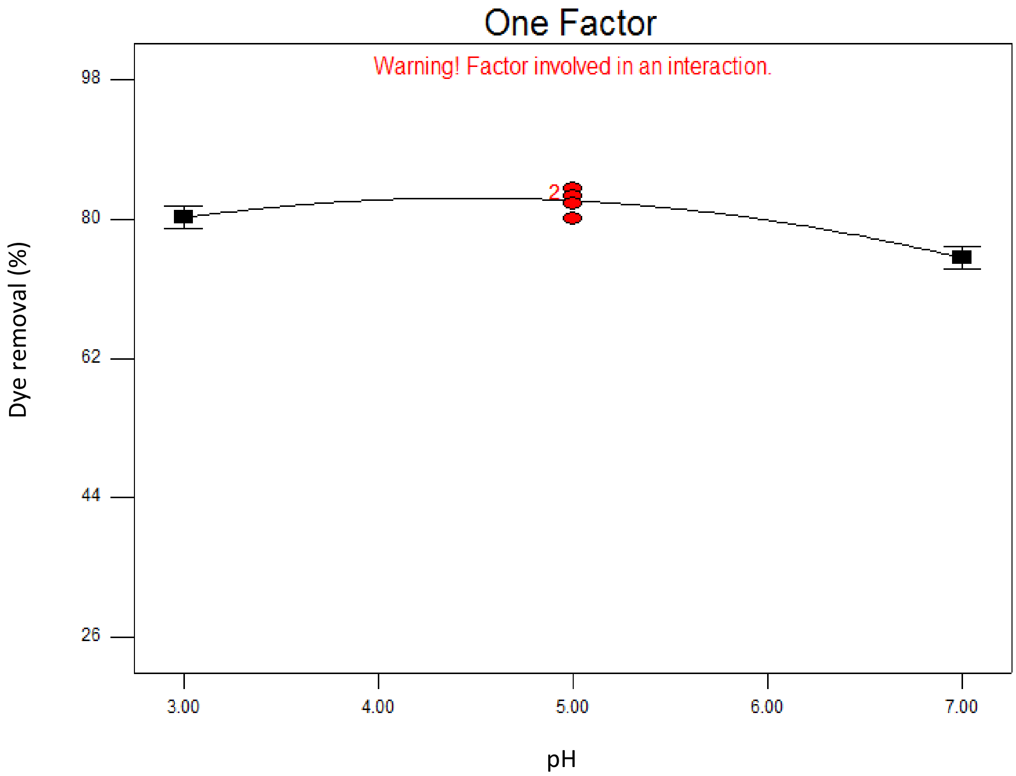

Fig. 5. Effect of pH on dye removal

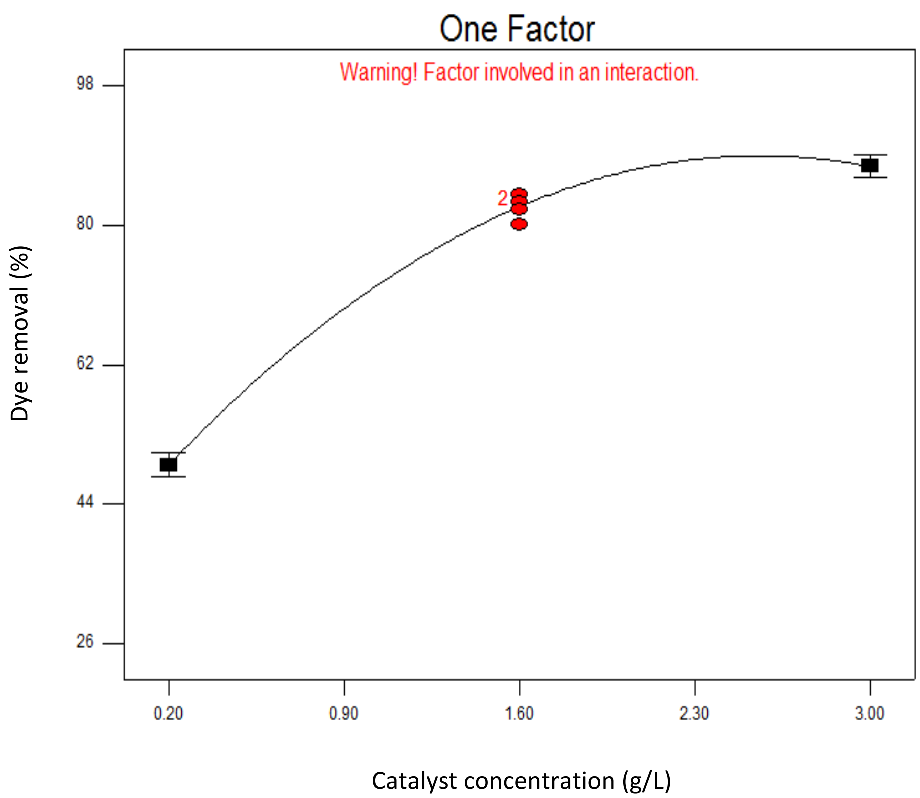

Fig. 6. Effect of catalyst loading on dye removal

3.5. Interaction between pH and concentration of TiO_2

As it can be observed from Figure 7, an increase of pH from 3 to 5 led to the enhancement of dye removal, but with an increase in pH from 5 to 7, the percentages of dye removal faced reversed mode. It was noticeable that the variation of dye removal in high concentrations of catalyst was much more than in low concentrations. Furthermore, at a constant pH, increasing the catalyst concentration from 0.2 up to 2.30 caused the enhancement of dye removal which met a reversed trend for a higher amount of pH. Studies have indicated that pH can affect the photocatalytic process in several ways. First, charged dye molecules with ionizable functional groups and the catalyst surface charge are dependent on pH; therefore, changing the pH can influence the dye molecules absorption on the catalyst surface, which is an important step for the photocatalytic process. Second, due to the reaction of the hydroxide ion (OH^-) and positive hole, hydroxyl radicals can be produced. Thus, alkaline conditions could favor the formation of hydroxyl radicals and degradation increases. Third, TiO_2 particles tend to aggregate in acidic conditions and the usable surface for dye and photon absorption decreases [30]. The coefficients of both the pH and catalyst concentration parameters in dye removal correlation in the ANOVA table were respectively -262 and 19.25, which emphasized the fact that the catalyst concentration had a higher impact on dye removal in contrast with pH. The interaction of pH and catalyst concentration (relevant coefficient=2.5) in the correlation of dye removal confirmed the significant interaction between the factors mentioned.

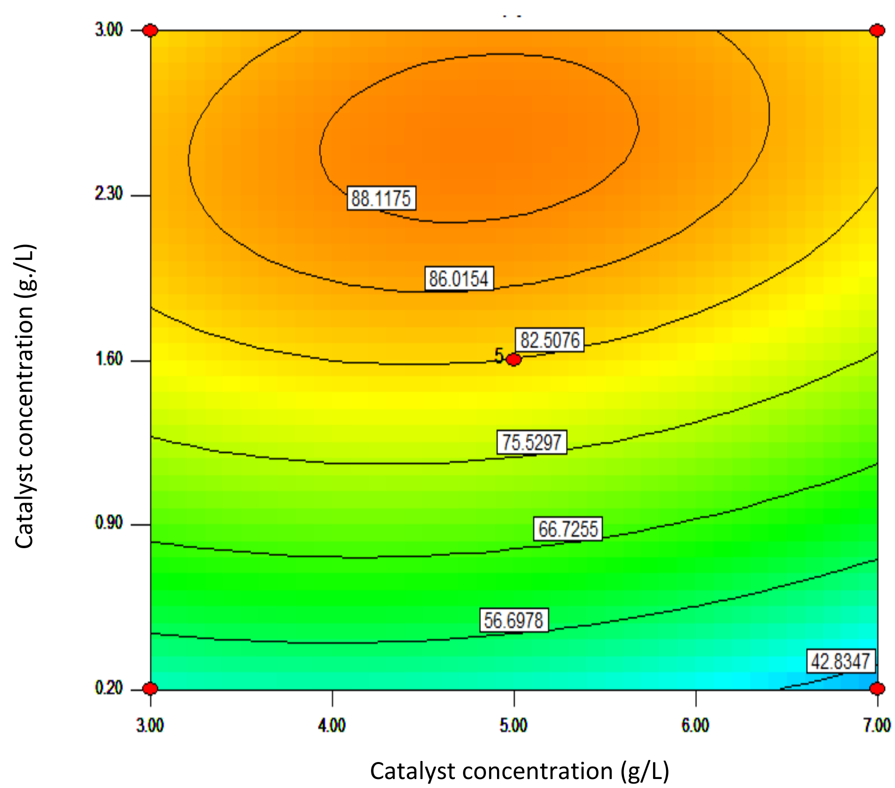

Fig. 7. Interaction between pH and concentration of TiO_2 on dye removal

3.6. Interaction between dye concentration and concentration of TiO_2

The effects of dye concentration and TiO_2 concentration are presented in Figure 8. It was apparent that at a constant catalyst concentration and with an increase of dye concentration, the value of dye removal showed a decreasing trend. Furthermore, when the TiO_2 concentration was increased in a constant value of dye concentration, the amount of dye removal increased in early TiO_2 concentration. However, the trend of dye removal was met with a decline in higher TiO_2 concentration. As a result, the graph reveals that an optimum TiO_2 concentration could be exerted for each dye concentration; thereby, maximum dye removal would occur for those certain conditions. According to the presented results in the dye removal equation (Eq.1), the coefficients of dye concentration and TiO_2 concentration were −16.88 and 19.25, respectively, which emphasized the same effect of these operational parameters on dye removal. The coefficient of interactive between them was 3, which expressed the significance of their interactions.

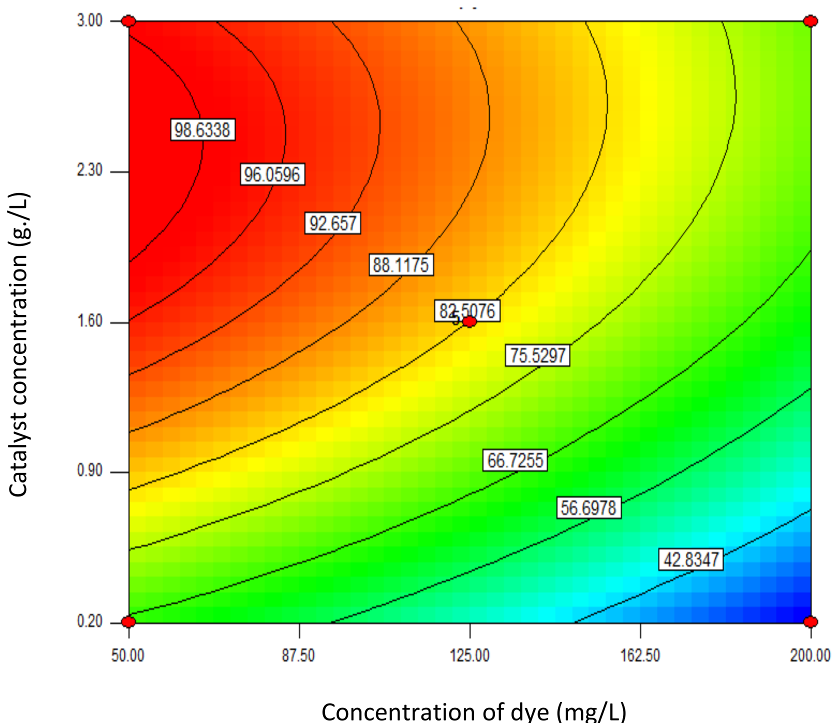

Fig. 8. Interaction between dye concentration and TiO_2 concentration on dye removal

3.7. Maximum dye removal

The optimum conditions of the process were obtained regarding the main target (maximum dye removal) by analyzing the data: dye concentration=62mg/L, pH=3.7 and TiO_2 concentration=2.25 g/L. An experiment under optimized conditions was performed in order to survey the accuracy of the fitted correlations at the 95 % confidence interval, and the results are shown in Table 4. The confidence interval achieved (number=95 %) was validated based on the reported outcomes of the experiments conducted at optimum conditions and the predicted values from the fitted correlations.

Table 4. Verification experiment results at the optimum conditions

Response	Target	Correlation predicted	Confirmation experiment	Confidence interval (95 %)	
				Low	High
Dye removal (%)	Maximize	98	96	94	102

4. Conclusions

In the current study, the successful implementation of a photocatalytic reactor in treating wastewater containing reactive red dye 198 was shown. The simultaneous effects of dye concentration, pH and catalyst concentration on the efficiency of dye removal was explored. According to the fitted correlations from RSM and the associated coefficients of operational factors, TiO_2 concentration (relevant coefficient = 19.25) and pH (relevant coefficient = −2.62) had the maximum and minimum impact on dye removal, respectively. The achieved results illustrated that under optimum conditions (dye concentration=62mg/L, pH=3.7, TiO_2 concentration=2.25 g/L), the dye removal efficiency was at 98%.

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