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Enhanced photocatalytic decolorization of reactive red by sonocatalysis using TiO_2 catalyst: factorial design of experiments

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ABSTRACT

The sonocatalysis, photocatalysis, and sonocatalysis followed by photocatalytic process has been studied to treat the decolorization of reactive red dye using heterogeneous TiO_2 catalysts. Effects of various operating parameters such as reactor system, reaction time, amount of catalyst, and pH on sonocatalysis and photocatalytic treatment were investigated. The ultrasonication of dye was enhanced by the addition of catalyst, which results an increase in the color removal of the photocatalytic process. The results of sonocatalysis followed by photocatalytic color removal of reactive dye showed 98.23% that it could be used as an efficient and environmentally friendly technique for the wastewater treatment. Factorial deign has been used for the experiment to optimize the process variables and to study the interaction of variables for the color removal. The color removal has been modeled and it follows the pseudo-second-order adsorption kinetics for the sonocatalysis followed by photocatalytic process.

Keywords: Sonocatalysis; Photocatalysis; TiO_2 catalyst; Factorial design; Adsorption model

1. Introduction

Effluents from textile industry are highly colored due to colored dyes, which are used for fabrics. The effluent discharged to the environment, pollute the water bodies such as river, underground water, etc. Hence, the treatment of effluent is mandatory before letting out to the environment.

Various treatment methods used for decolorization of dyes are based on physicochemical methods. They include membrane filtration, adsorption, precipitation, chemical degradation, and photo degradation. The limitations of the physicochemical process are cost intensive and difficult to dispose the sludge. Another type of process is an activated sludge process for the decolorization of dye. But this process is failed to remove the color and other micro-pollutants present in textile effluents [1–4]. Hence, the development of new and inexpensive methods for the treatment of effluent is needed. In this aspect, researchers are attempting various treatment processes such as electrochemical techniques [5–9], ozonization [10], photocatalytic methods [11,12], sonication [13], and enzymatic treatment [14] of effluents.

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Among this method, advanced oxidation process of heterogeneous photocatalytic treatment process is used widely for the treatment of effluent. In this process, UV light irradiation generates positive holes on the surface of the catalyst particles that react with water and liquid to produce OH radical. This OH radical is used for the degradation of the pollutant [15,16]. The advantage of the photocatalytic process is low cost as well as it works at room temperature, and it uses UV light sources and TiO_2 as a catalyst. Another alternative for the pollutant degradation is ultrasonication method. In this method, the formation, growth, and collapse of micro bubbles or cavities are generating high temperatures. The collapse of bubbles results in the formation of reactive hydrogen atoms and hydroxyl radicals which are mainly used for the degradation of the pollutant. But, in sonocatalysis the efficiency is much lower than the photocatalytic process [17,18]. However, recent articles show that the advantage of sonophotocatalytic process of oxidation has a good result, due to the combined effect between sonolysis and photocatalysis.

Few studies have been made on the degradation of hazardous organic compounds by combining ultrasonic irradiation with UV light irradiation in the presence of TiO_2. Bejarano-Perez and Suarez-Herrera [18] studied the photocatalytic and sonophotocatalytic oxidation process of Congo red and methyl orange using titanium dioxide as catalyst. The author observed that in the presence of ultrasound the photocatalytic oxidation rate of Congo red and methyl orange increased remarkably. Kubo et al. [19] investigated phenol degradation using ultrasonication in the presence of TiO_2 and dissolved oxygen. The author reported that the higher amount of TiO_2 and dissolved oxygen concentration increased the rate of phenol removal. Ertugay and Acar [20] studied sono, photo, and sonophotacatalytic degradation of direct blue 71 using ZnO catalyst. The author observed that the ultrasonic degradation of dye was enhanced by the addition of catalyst and reported that acidic pH was favored for the sonocatalytic degradation and sonophotocatalytic oxidation process. Pandit et al. [21] studied the degradation of 2,4,6 trichlorophenol by ultrasonic irradiation in the presence of TiO_2 catalyst. The author reported that the degradation rate increased with increasing TiO_2 concentration. The reported studies are not focused on the statistical design to minimize the experimental runs and optimize the process variables using the factorial method. The aim of the present investigation is to decolorize the reactive red dye using sonocatalysis, photocatalysis, and sonocatalysis followed by photocatalytic process in the presence of TiO_2 catalyst. The operating parameters have been optimized using the factorial design and the adsorption model has been proposed for the color removal of the dye.

2. Materials and methods

2.1. Experimental

The experimental setup of sonocatalysis and photocatalysis for the decolorization of reactive red dye is shown in Fig. 1(a) and (b). The act of applying sound energy frequencies (>20 kHz) is usually used for a process known as ultrasonication. In the laboratory, an ultrasonic bath or ultrasonic probe are usually used for sonication, commonly known as sonicator. Color removal, in the present study, was conducted in a bath-type sonicator. It consists of jacketed stainless–steel reactor equipped with in-built piezoelectric transducer placed at the bottom and an external generator is used. The ultrasonic bath (Model: CB 2150, Cyber Bath) is filled with distilled water up to an optimum level. The bath type operated at the frequency of 40 kHz with the ultrasonic output power of 200 W. The setup consists of a sonication tray in which the reaction bottles are placed and a water inlet and outlet pipes for regular loading and discharge of cool water are processed. The setup is connected to AC power supply. After a definite time interval, the samples are collected from the conical flask and analyzed.

To study the effect of the photocatalytic process, the samples were kept for UV irradiation. In the photocatalytic process, the photocatalytic activity depends on the ability of the catalyst to create electron–hole pairs that generate free hydroxyl radicals ($^{\cdot}OH$), which are able to undergo secondary reactions. The experimental setup consists of an 8 W UV lamp having 365 nm wave length used as a source for UV light. The catalyst is added to each conical flask and kept in UV chamber for irradiation. For the sonocatalysis and photocatalytic experiment, the operating parameters such as initial dye concentration (50–100 mg L^{-1}), TiO_2 concentration (1–5 g L^{-1}), reaction time (30–180 min), and initial pH (2–12) have been varied to measure the percentage color removal of the dye. The samples were collected at regular intervals of time for analysis.

To study the sonocatalysis followed by photocatalytic effect of color removal, first the dye solution was subjected to sonication and then exposed to UV irradiation. The operating parameters were varied and the samples were also withdrawn at definite time intervals and analyzed for the color removal using UV–vis spectrophotometer (Shimadzu, Kyoto, Japan).

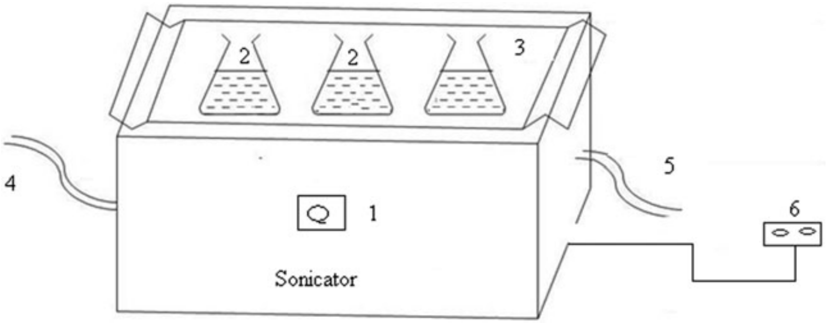

Fig. 1(a) 1. ON/OFF switch, 2. Dye solution, 3. Sonication tray, 4. Water inlet, 5. Water outlet, 6. Power supply.

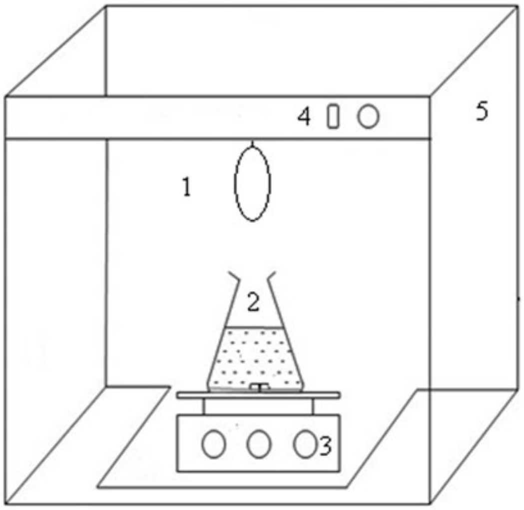

Fig. 1(b) 1. UV lamp, 2. Dye solution, 3. Magnetic stirrer, 4. Switch control, 5. Rectangular insulated box.

3. Factorial design

The factorial design is used to develop a statistical model for a process with the minimum number of experimental runs and to determine the optimal values of the process variables. The level of each variable and the number of variables selected for the present study are shown in Table 1. Four variables have been selected for the present experiment such as reactor system (X_1), reaction time (X_2), catalyst dosage (X_3), and pH (X_4). The reactor system has been selected as sonocatalysis or sonocatalysis followed by photocatalysis (sonocatalysis–photocatalysis). The remaining variables have been selected as two levels (−1, +1) for the factorial experiment. There are 16 experimental runs (2^4) designed and shown in Table 2. The response of the process is measured as color removal of the dye.

The behavior of the system is explained by the following quadratic equation.

$$\begin{aligned} Y = {} & k_0 + k_1X_1 + k_2X_2 + k_3X_3 + k_4X_4 + k_5X_1X_2 + k_6X_1X_3 \\ & + k_7X_1X_4 + k_8X_2X_3 + k_9X_2X_4 + k_{10}X_3X_4 \\ & + k_{11}X_1X_2X_3 + k_{12}X_1X_2X_4 + k_{13}X_1X_3X_4 \\ & + k_{14}X_2X_3X_4 + k_{15}X_1X_2X_3X_4 \end{aligned} \quad (1)$$

where k_0k_1, k_2, k_3, k_4, etc. represent the regression coefficients. The results of factorial design experiments have been analyzed using MINTAB 14 (PA, USA) software tool [22, 23].

4. Result and discussion

4.1. Sonocatalysis process

The experiments were performed on color removal of the dye using sonocatalysis. For this experiment,

Table 1
The range of independent variables used for reactive red dye color removal

			Range of actual and coded variables	
Factor	Variables	Unit	−1	+1
X_1	Reactor system	–	Sonocatalysis process	Sonocatalysis–photocatalytic process
X_2	Time	min	30	180
X_3	Catalyst concentration	$g\,L^{-1}$	1	4
X_4	pH		2	12

Table 2
Factorial design of experiments for reactive red dye color removal

Factors					
Exp. Run	Reactor system	Time (min)	Catalyst (g L^{-1})	pH	Color removal (%)
1	Sonocatalysis	30	1	2	6.85
2	Sonocatalysis–photocatalysis	30	1	2	41.02
3	Sonocatalysis	180	1	2	23.45
4	Sonocatalysis–photocatalysis	180	1	2	90.25
5	Sonocatalysis	30	4	2	16.23
6	Sonocatalysis–photocatalysis	30	4	2	95.55
7	Sonocatalysis	180	4	2	42.12
8	Sonocatalysis–photocatalysis	180	4	2	98.23
9	Sonocatalysis	30	1	12	14.25
10	Sonocatalysis–photocatalysis	30	1	12	28.66
11	Sonocatalysis	180	1	12	30.45
12	Sonocatalysis–photocatalysis	180	1	12	38.98
13	Sonocatalysis	30	4	12	16.38
14	Sonocatalysis–photocatalysis	30	4	12	39.78
15	Sonocatalysis	180	4	12	36.78
16	Sonocatalysis–photocatalysis	180	4	12	40.08

Note: Sonocatalysis–Photocatalysis is sonocatalysis followed by photocatalysis process.

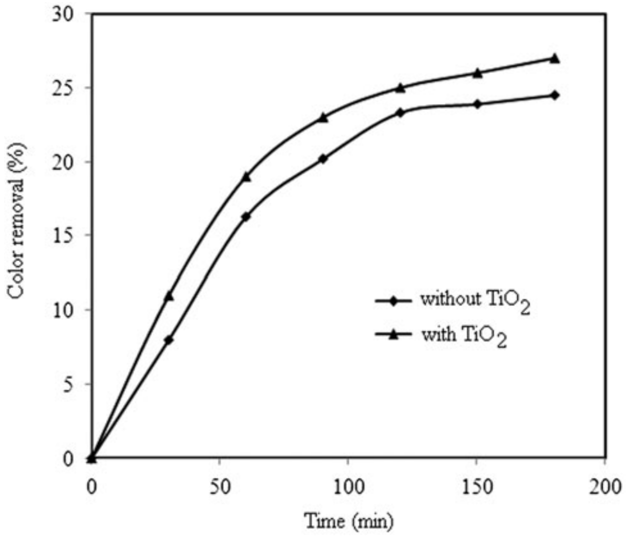

Fig. 2. Effect of sonication time on color removal for the sonocatalysis process: initial dye concentration 50 mg L^{-1}; pH 2.

50 mg L^{-1} of reactive red dye was taken in a conical flask and kept in a sonicator with and without TiO_2 catalyst. The sonication power of 40 kHz with ultrasonication power output of 200 W was fixed and liquid temperature of 25°C was maintained constant with the help of cooling water circulation. The effect of sonication on color removal with and without TiO_2 catalyst is shown in Fig. 2. It is observed from the figure that with and without TiO_2 catalyst the color removal increases with the increase in sonication time. The color removal is high for TiO_2 sonication process. This is due to the fact that the presence of catalyst can enhance the dissociation reaction of H_2O molecules thereby increasing the number of free radicals generated, which results an increase in the rate of color removal of the dye. The dissociation reaction is given as

$$H_2O+))) \rightarrow {}^{\cdot}OH + {}^{\cdot}H \qquad (2)$$

Similar observation has been made for phenol and methyl orange degradation [19,24].

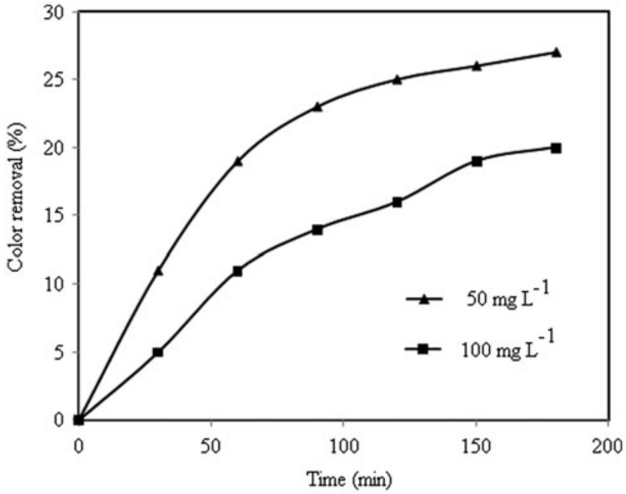

Fig. 3. Effect of concentration on color removal for the sonocatalysis process: catalyst dosage 4 g L^{-1}; pH 2.

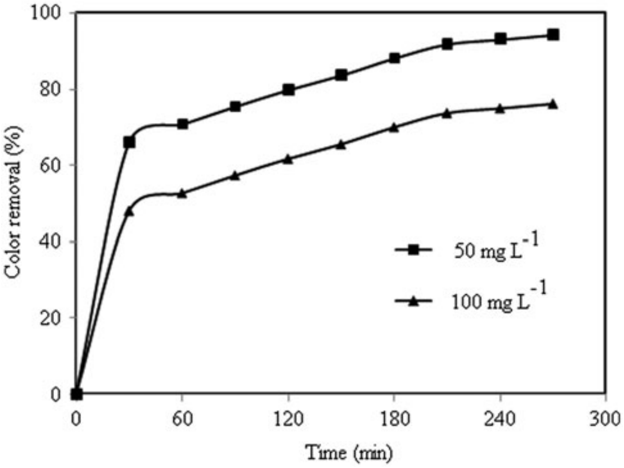

Fig. 4. Effect of concentration on color removal for the photocatalysis process: catalyst dosage 4 g L^{-1}; pH 2.

The effect of the initial dye concentration on color removal is shown in Fig. 3. It is observed from the figure that the percentage color removal decreased with increasing the initial dye concentration. For the initial dye concentration of 50 mg L^{-1}, the percentage color removal of the dye was 24.5% in 180 min, but for 100 mg L^{-1} of initial dye concentration the percentage color removal of the dye decreased to 20%. This is due to the fact that higher dye concentrations would provide interferences which inhibited the degradation rate. This effect is increased due to the formation of more intermediate species during the reaction. The similar effect was reported by Abbasi and Asl [17].

4.2. Photocatalytic process

The effect of UV irradiation on the percentage color removal of the dye for the concentration 50 and 100 mg L^{-1} is shown in Fig. 4. It is observed from the figure that the percentage color removal increases with the increase in UV irradiation time. The color removal is high for the low concentration of the dye. This is due to the reason that at higher concentrations, large amount of dye molecules is adsorbed on the surface of the TiO_2 catalyst. This decreases the hydroxyl radicals generation, resulting in the decrease in the rate of color removal. The effect of pH on color removal for the UV irradiation process is shown in Fig. 5. The pH of the solution is varied from 2 to 12. It is observed from the figure that the percentage color removal is high in the acidic pH. In general, the percentage color removal increases with decreasing pH value which indicates that the number of OH radical generation increases on the surface of the TiO_2 particles in the solution by trapping photons. The percentage removal at high and low pH values changes can be explained by the integrative effects of adsorption and desorption. At low pH values, the surface of TiO_2 particles is positively charged and is easily capable of adsorbing the negatively charged anions. At higher pH values, the surface of TiO_2 particles are negatively charged and there is repulsion due to the negatively charged dye molecules resulting in lower adsorption on the catalyst surface. Similar results were reported by Abbasi and Asl [17] and Wang et al. [24].

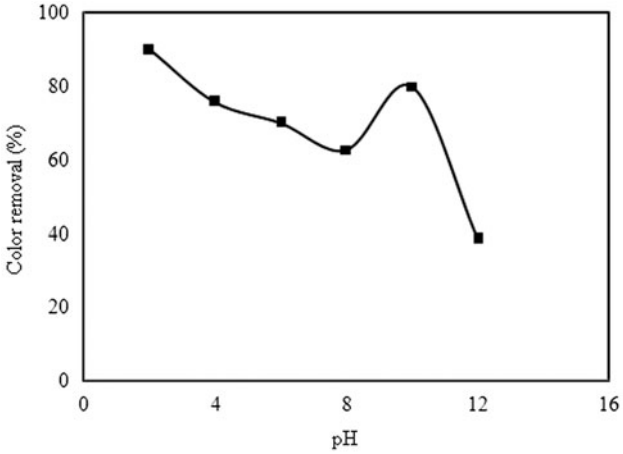

Fig. 5. Effect of pH on color removal for the photocatalysis process: initial dye concentration 50 mg L^{-1}; catalyst dosage 4 g L^{-1}.

4.3. Sonocatalysis followed by photocatalytic process

The effect of sonication on color removal is shown in Fig. 6. The samples were kept first in the sonication and then kept for the UV irradiation for 0.5 and 1 h. It is observed from the figure that sonication followed by UV irradiation improves the color removal. This is due to the fact that the sonication in the presence of TiO_2 catalyst becomes nanocatalyst and kept in the presence of UV irradiation improves the color removal. The effect of the catalyst dosage on the percentage color removal of the dye is shown in Fig. 7. It is observed from the figure that color removal for the sonocatalysis alone shows less color removal of the dye compared to sonocatalysis followed by UV irradiation. It is also observed from the figure that UV alone shows less color removal compared to sonocatalysis followed by UV irradiation. The better results are obtained for 2 h sonocatalysis followed by 1 h UV irradiation. The color removal was almost 98.23% for the catalyst dosage of 4 g L^{-1}.

4.4. Statistical analysis and modeling

Experimental observation of the factorial runs of percentage color removal is shown in Table 2. The analysis was focused on percentage color removal for sonocatalysis; sonocatalysis followed by photocatalysis of the dye has been carried out using MINTAB 14. The maximum color removal of 98.23% was achieved under typical operating conditions. The mathematical relationship between the independent variables and their responses can be related in terms of coded variables as:

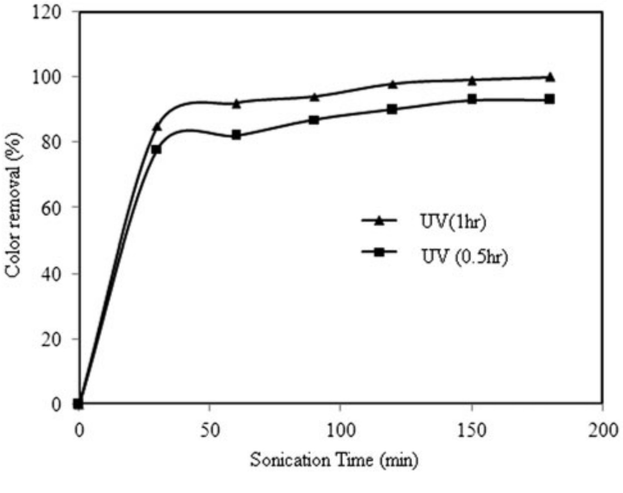

Fig. 6. Effect of sonication on color removal for the photocatalysis process: Initial dye concentration 50 mg L^{-1}; catalyst dosage 4 g L^{-1}; pH 2.

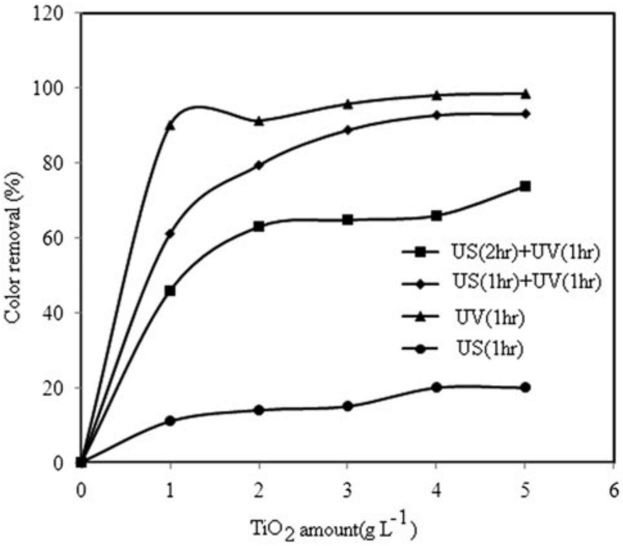

Fig. 7. Effect of catalyst concentration on color removal for the photocatalysis process: initial dye concentration 50 mg L^{-1}; pH 2.

$$\begin{aligned}\text{Color removal } (\%) = {} & 41.19 + 17.88X_1 + 8.85X_2 \\ & + 6.95X_3 - 10.52X_4 - 1.03X_1X_2 \\ & + 2.39X_1X_3 - 11.67X_1X_4 \\ & - 2.69X_2X_3 - 2.95X_2X_4 \\ & - 4.37X_3X_4 - 4.38X_1X_2X_3 \\ & - 2.21X_1X_2X_4 - 1.92X_1X_3X_4 \\ & + 1.96X_2X_3X_4 \end{aligned} \tag{3}$$

The adequacy of the regression model predictions using Eq. (3) are compared with the experimental observations and are shown in Fig. 8. It is observed from the figure that model predictions satisfactorily match the experimental values with the R^2 value of 0.991. The significance of regression coefficients was analyzed using p and t-test and the values for the present experiment are shown in Table 3. Larger magnitude of "t" value and lesser values of 'p' confirm the significance of variables in the model equations. It is observed from the table that the reactor system is a more significant parameter. The present model equations are further checked by regression coefficients R^2 and R^2_{adj}. The values of R^2 (=0.991) and R^2_{adj} (=0.869) close to 1 indicate that the model is highly significant. The significant effect of process variables has been verified using analysis of variance (ANOVA) and the results are presented in Table 4. Larger p value shows that the terms are insignificant. It is observed from the table that single effects are more significant when compared to 2- and 3-way interaction effects of variables. The combined effect of operating variables on

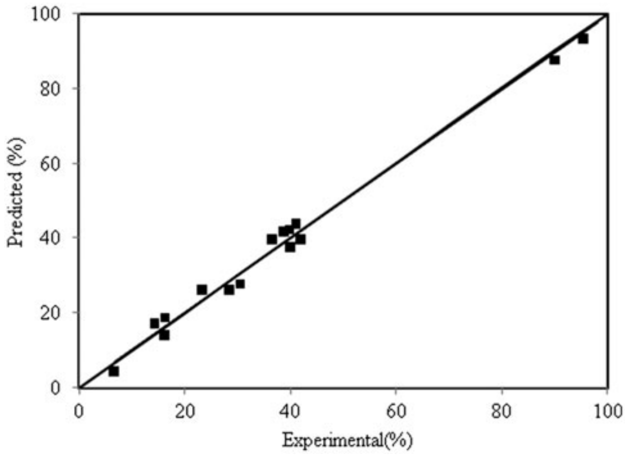

Fig. 8. Comparison of experimental and predicted color removal using factorial design.

Table 3
Estimated regression coefficient and corresponding “*t*” and “*p*” values for percentage color removal of reactive red dye

Term	Effect	Coefficient	*t*	*p*
Constant		41.19	15.84	0.04
X_1	35.75	17.88	6.87	0.092
X_2	17.7	8.85	3.4	0.182
X_3	13.91	6.95	2.67	0.228
X_4	–21.04	–10.52	–4.04	0.154
X_1X_2	–2.07	–1.03	–0.4	0.759
X_1X_3	4.78	2.39	0.92	0.527
X_1X_4	–23.34	–11.67	–4.49	0.14
X_2X_3	–5.39	–2.69	–1.04	0.489
X_2X_4	–5.9	–2.95	–1.13	0.46
X_3X_4	–8.74	–4.37	–1.68	0.342
$X_1X_2X_3$	–8.76	–4.38	–1.68	0.341
$X_1X_2X_4$	–4.43	–2.21	–0.85	0.551
$X_1X_3X_4$	–3.84	–1.92	–0.74	0.595
$X_2X_3X_4$	3.93	1.96	0.76	0.588

color removal is presented in contour plots. The amount of the catalyst dosage and reaction time is shown in Fig. 9. It is observed from the figure that higher catalyst dosage and reaction time increases the percentage color removal. Fig. 10 shows the contour plot of pH and catalyst concentration. It is observed from the figure that for pH 2 the percentage color removal is high for the corresponding catalyst dosage of 4 g L^{-1}. The main effect plot is shown in Fig. 11. It is observed from the figure that sonocatalysis followed a photocatalytic process, 180 min of reaction time, 4 g L^{-1} of catalyst dosage, and pH 2 show the higher percentage removal of color.

4.5. Adsorption kinetics

The percentage color removal of reactive red dye was investigated by sonocatalysis followed by photocatalytic process. In this process, the color removal

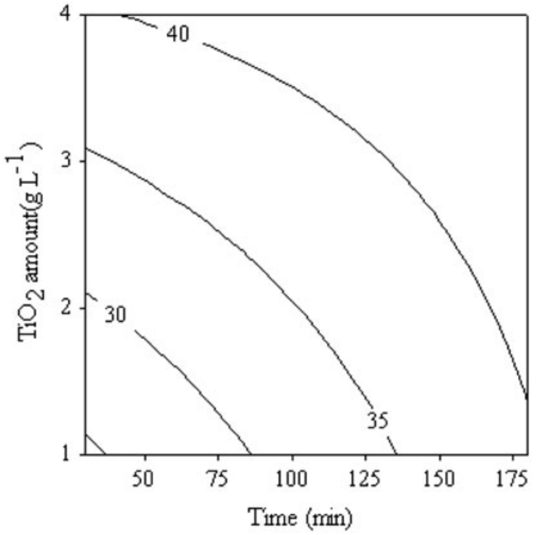

Fig. 9. Contour plot for percentage color removal: sonocatalysis process; pH 2.

Table 4
ANOVA for percentage color removal

Source	Degree of freedom	Sum of squares	Mean squares	*F*	*p*
Main effects	4	8,911.7	2,227.9	20.58	0.164
Two-way interactions	6	2,848.7	474.8	4.39	0.35
Three-way interactions	4	505.8	126.4	1.17	0.593
Residual error	1	108.3	108.3		
Total	15	12,374.5			

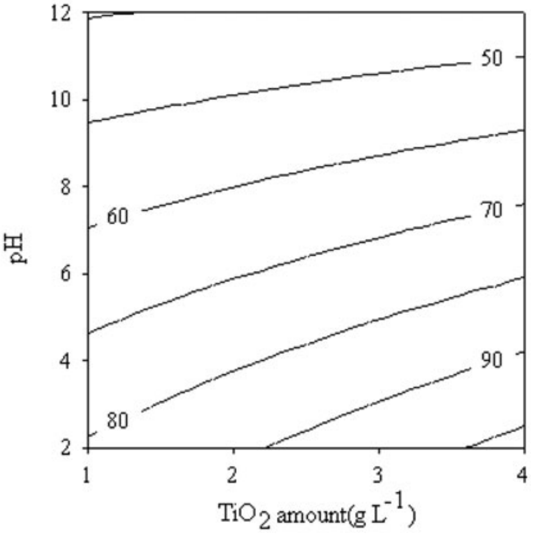

Fig. 10. Contour plot for percentage color removal: sonocatalysis process: time 30 min.

was attempted with the pseudo-first-order and second-order adsorption kinetics.

The pseudo-first-order adsorption kinetic equation can be given as [25,26]

$$\log\,(q_\mathrm{e} - q_t) = \log\;q_\mathrm{e} - \frac{k_1}{2.303}t \qquad (4)$$

where k_1 is the equilibrium rate constant of pseudo-first-order adsorption. The slope and intercept of plot of log $(q_\mathrm{e} - q_t)$ versus t were used to calculate the first-order rate constant $k_{1,}$

where $q_\mathrm{e} = (C_\mathrm{o} - C_\mathrm{e})\ V/m$; $q_\mathrm{t} = (C_\mathrm{o} - C_\mathrm{e})\ V/m$; q_e = amount of catalyst adsorbed per gram of dye at equilibrium, mg L^{-1}; V = volume of dye, L; m = mass of $\mathrm{TiO}_{2,}$ g; C_o = initial concentration, mg L^{-1}; C_e = equilibrium concentration, mg L^{-1}.

Fitting the above equation to the experimental value is shown in Fig. 12. It is observed from the figure that the correlation coefficient is 0.990. It shows lesser fit of the experimental value with the model prediction.

The pseudo-second-order adsorption kinetic equation can be given as [25,26]

$$\frac{t}{q_t} - \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption. The intercept of plot t/q_t versus t was used to calculate the second-order rate constant k_2, where $q = (C_\mathrm{o} - C_\mathrm{e})\ V/m$; $q_\mathrm{t} = (C_\mathrm{o} - C_\mathrm{e})\ V/m$; q_e = amount of catalyst adsorbed per gram of dye at equilibrium, mg L^{-1}; q_t = amount of catalyst adsorbed per g of dye at time t, mg L^{-1}; V = volume of dye, L; m = mass of $\mathrm{TiO}_{2,}$ g; C_o = initial concentration, mg L^{-1}; C_e = equilibrium concentration, mg L^{-1}.

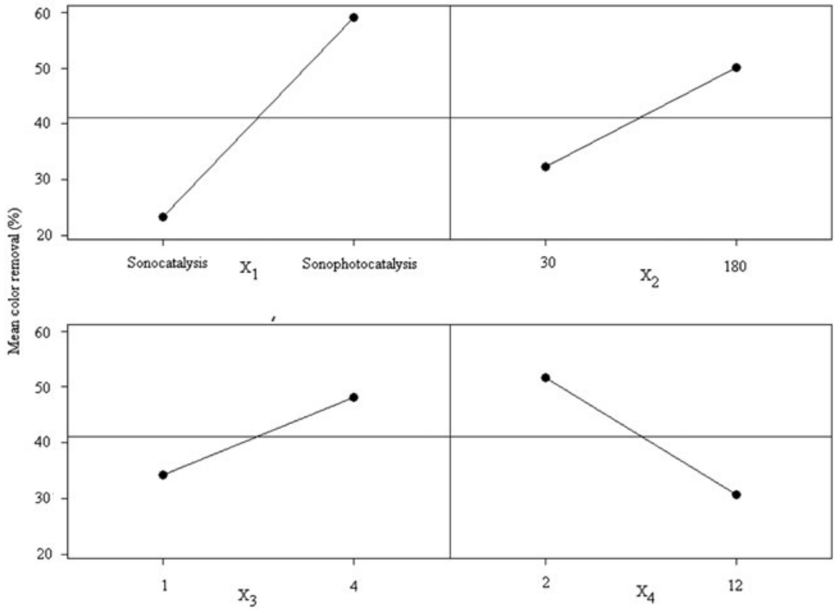

Fig. 11. Mean color removal for sonocatalysis–photocatalytic process.

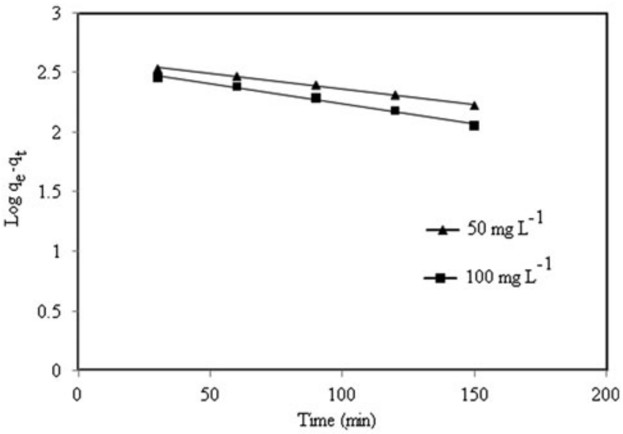

Fig. 12. Adsorption kinetics of pseudo-first-order for color removal of sonocatalysis followed by photocatalytic process: catalyst dosage 4 g L^{-1}; pH 2.

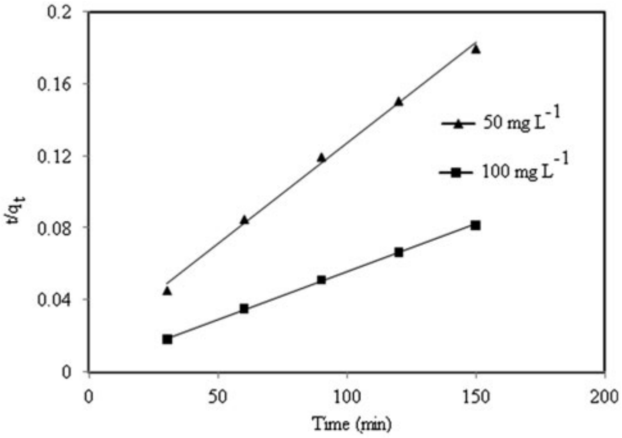

Fig. 13. Adsorption kinetics of pseudo-second-order for color removal of sonocatalysis followed by photocatalytic process: catalyst dosage 4 g L^{-1}; pH 2.

Fitting the above equation to the experimental value is shown in Fig. 13. It is observed from the figure that the correlation coefficient is 0.999. It can be ascertained that higher R^2 is obtained for the pseudo-second-order kinetics. Hence, the sonocatalysis followed by photocatalytic process follows the pseudo-second-order adsorption kinetic.

5. Conclusion

The decolorization of reactive red dye by sonocatalysis, photocatalysis, and sonocatalysis followed by photocatalysis was investigated. Sonocatalysis and photocatalysis shows 27% color removal for 3 h and 73.82% color removal for 3 h UV exposure, respectively. Whereas 2 h sonocatalysis followed by 1 h photocatalysis shows 98.23% color removal for the reactive dye. It has been concluded that the photocatalytic oxidation of reactive red color removal was enhanced by sonication. The operating parameters such as reactor system, catalyst concentration, pH, and reaction time has been studied for the percentage color removal of the dye and these parameters has been optimized using factorial design. The sonocatalysis followed by photocatalytic color removal was observed as pseudo-second-order absorption kinetics with the correlation coefficient of 0.999. From the study of sonocatalysis, photocatalytic process can be used for the wastewater treatment, and sonocatalysis followed by photocatalysis process reduce the treatment time.

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