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Investigation of UV/H_2O_2 process for removal of ortho-toluidine from industrial wastewater by response surface methodology based on the central composite design

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ABSTRACT

In this project, degradation and mineralization of ortho-toluidine (OT) were investigated by UV/H_2O_2 process in a batch recirculating photo reactor. The full factorial design and response surface methodology were applied for evaluating the effects of experimental variables such as amount of H_2O_2, initial concentration of pollutant and pH on the removal of the OT and chemical oxygen demand (COD). Analysis of variance (ANOVA) showed a high determination coefficient value ($R^2 = 0.9291$, $R^2_{adj} = 0.9122$ for removal of OT and $R^2 = 0.9751$, $R^2_{adj} = 0.9677$ for removal of COD) and satisfactory prediction second-order regression model. The results showed a good agreement with the experimental values. The graphical counter plots and response surface were employed to determine the optimum conditions. Based on the optimum results, maximum efficiency for removal of the OT was achieved in initial pH of 10, dosage of H_2O_2 at 30 mM and initial concentration of the OT at 40 mg l^{-1}. According to the kinetic study, the pseudo-first-order rate constant ($k = 4.95 \times 10^{-2}$ min^{-1}) was obtained for the removal of the OT. The degradation and mineralization of the OT were estimated by HPLC and COD tests, respectively.

Keywords: Response surface methodology; Degradation; Ortho-toluidine (OT); Batch recirculating photo reactor; Analysis of variance (ANOVA); Counter plots

1. Introduction

The wastewater created from the petrochemical plant includes ortho-toluidine (OT) and other aromatic compounds. Certain amounts of aromatic components are wasted during a process which contains a wide range of non-biodegradable contaminants that bring about environmental pollution. OT can also be metabolized in vivo into many compounds, some of that is active internal poison [1,2].

Advanced oxidation processes (AOPs) based on the UV/H_2O_2 system have shown high efficiency in the degradation of several organic compounds [3]. The UV/H_2O_2 process has additional advantages such as no sludge production and high removal of COD [4]. The oxidation products are usually low molecular weight of oxygenated compounds that are easily biodegradable or reduce to carbon dioxide and water. In the UV/H_2O_2 process, the photolysis of hydrogen peroxide generates effective oxidizing species, hydroxyl radicals ($OH^{\bullet}$). The oxidation potential of hydroxyl radical is 2.8 eV, which can completely demolish the pollutants presented in the wastewater or change them to simple harmless compounds.

Factorial design is a statistical technique that is applied in planning experiments which several factors are controlled and their influences on each other are inspected at two or more levels [5]. The general full factorial design is suitable which is dealing with multiple levels of several factors [6]. The capability of general full factorial design in the modeling of complex systems makes it a more practical method than other traditional techniques for modeling a multi variable system, which usually defines one factor at a time [7].

The literature review indicates that significant works have been carried out on OT [8–10], but no study on degradation of OT with UV/H_2O_2 alone has been reported up to this time.

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In this work, degradation and mineralization of OT as an industrial pollutant was studied by UV/H_2O_2 process. Systematic investigations that reveal the behavior of the process, important variable and interaction effects between them have been studied. The degradation and mineralization efficiency of the OT were the optimization responses and the correlation between the response and significant factors including pH, initial OT concentration, reaction time and hydrogen peroxide dosage was determined to obtain best responses with minimum usage of oxidants.

2. Experimental

2.1. Reagents and apparatus

OT (C_7H_9N, 99.5%), hydrogen peroxide (30%v/v), NaOH and H_2SO_4 (0.1 M) were reagent grade from Merck company of Germany. Distillates water was used throughout this study.

A pH meter, PT-10P Sartorius Instrument from Germany Company was used to adjust initial pH of the solution. Water bathe, BW20G model from Korean Company, was used for regulating and fixing temperature at 25°C in all tests. The progress in the degradation of the OT was estimated by a high performance liquid chromatography (Knauer, Germany) equipped with Spectrophotometer (PLATINblue, Germany). A reverse phase column filled with 3 μm Separon C_{18} was 150 mm in length and 4.6 mm in diameter. The isocratic method with a solvent mixture of 40% deionized water and 60% acetonitrile with a flow rate of 1 ml min^{-1} was used.

Spectrophotometer (DR 5000, Hach, Jenway, USA) at 600 nm was used to estimate the absorbance of COD samples.

2.1.1. Photo reactors

In this project, experiments were performed in two teflonic cylindrical recirculating photo reactors. Each of them has 1 l of volume and connected to each other in series. The system was equipped with a sampling system (Fig. 1). The light source was two mercury lamps, Philips 15 W (UV-C), which was immersed vertically in the center of reactors. The reactors were equipped with a water-flow exchanger, using an external circulating flow of a thermostat for regulating temperature about 25°C. The solution in reservoir pumped with the flow rate of 1.3 l min^{-1} and entered from below to the reactor. After radiation the solution was recycled to the reservoir from the top of the second reactor. The volume of solution in the loop was 2.5 l.

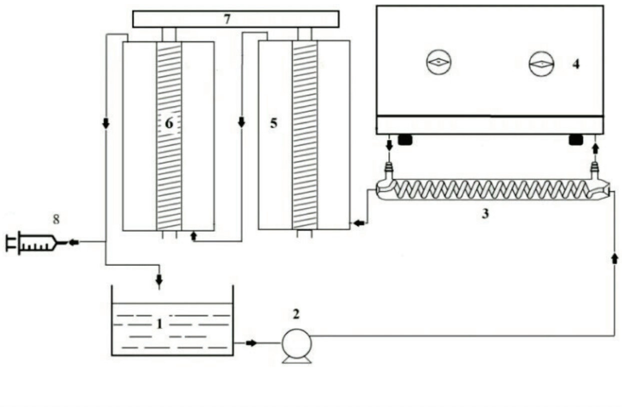

Fig. 1. Experimental setup of the process.
Note: (1) Reservoir, (2) Circulation pump, (3) Heat exchanger, (4) Thermo bath, (5) Reactor, (6) UV Lamp, (7) Electric supply, (8) Sampling port.

2.2. General procedure

Exactly 2,500 ml of solution containing OT was used during each experiment. After pumping the solution and passing through the tube of an exchanger for regulating temperature by thermo bath, it was entered from the bottom of the reactor.

The desired concentration of OT and H_2O_2 were fed into the loop. After recirculating for 5 min, UV lamps were switched on to initiate the reaction at different intervals proposed by experimental design. The samples were taken and determined with UV/Vis spectrophotometer and validated by HPLC.

Chemical oxygen demand (COD) was measured based on standard methods [11]. The suitable efficiencies were calculated with respect to its initial value and the removal percent for the OT and COD was obtained as in Eqs. (1) and (2):

$$\text{Removal of OT}\left(\%\right)=\left(\frac{[\text{OT}]_0\text{-}[\text{OT}]}{[\text{OT}]_0}\right)\times 100 \tag{1}$$

$$\text{Removal of COD}\left(\%\right)=\left(\frac{[\text{COD}]_0\text{-}[\text{COD}]}{[\text{COD}]_0}\right)\times 100 \tag{2}$$

where $[OT]_0$ and $[COD]_0$ are the concentration of the OT and amount of COD at the start of the reaction and [OT] and [COD] are the concentration of the OT and amount of COD at time *t*, respectively.

MnO_2 powder was used for removing the residual hydrogen peroxide and its interaction with COD test. Samples were filtered to separate MnO_2 powders [12].

2.3. Experimental design

The percentage of the degradation and mineralization of the OT were chosen as a response to investigate the optimum conditions in UV/H_2O_2 process. The process depends on various parameters involving the concentration of H_2O_2, pH and initial concentration of OT. The input variables and their levels in the experiment were demonstrated in Table 2. In this work, the experimental design method was used to optimize the removal of pollutant. Also, three important factors were

Table 1
Experimental ranges and levels of the independent test variables

Variables	Ranges and level		
	Level 1	Level 2	Level 3
Initial concentration of OT (X_1)	40	60	80
Initial pH(X_2)	4	7	10
Initial dosage of H_2O_2 (X_3)	15	30	45

selected for assessment the effect of operational parameters on removal efficiencies of the OT and COD. In this work, degradation was optimized by application of the central composite design (CCD) for three independent variables including concentration of OT (X_1), initial pH (X_2), and dosage of H_2O_2 (X_3). The experimental design included 27 experiments.

The natural values of these factors for the removal of the OT are presented in Table 1. All tests were done randomly to minimize experimental errors. Two responses, removal efficiencies of the OT and COD were obtained from experiments mentioned in Table 2.

2.4. Data analysis

Based on the experimental design, the following model was fitted to the response variable (Y) in the form of a polynomial equation (Eq. (3)):

$$Y = b_0 + \sum b_i x_i + \sum\sum b_{ij} x_i x_j + \sum\sum b_{ii} x_i^2 + \varepsilon \tag{3}$$

where b_0 is a constant, ε is the residual term, x_i (i = 1, 2 and 3), b_{ij} is the linear interaction effect between the input variables, x_i and x_j (i = 1, 2 and 3; j = 1, 2 and 3), b_i is the slope of the variable, b_{ii} is the second order of input variable (x_i). The ANOVA was used to inspect the importance of each term in the polynomial equation [13]. MINITAB 17 was used to conclude the coefficients of Eq. (3) by RSM.

3. Results and discussion

3.1. CCD model

The principal purpose of this section was to determine the optimum condition for maximum removal of OT and COD in UV/H_2O_2 process. The steps of CCD were presented by many authors [14–16]. The two responses, 3-factor CCD matrix and experimental results obtained from the removal runs of the OT and COD are shown in Table 2.

The mathematical relation between the responses and three significant variables can be approximated by a quadratic polynomial equation. The equations for the removal of the OT and COD are shown in Eq. (4):

The second-order polynomial response equation (Eq. (4)) was used to correlate the independent and dependent variables.

Table 2
The 3-factor central composite design matrix and the two responses function (Removal of OT and COD (%) in 100 min of reaction)

Run number	Initial dosage of OT (mg l^{-1})	Initial pH	Initial dosage of H_2O_2 (mM)	Removal of OT (%)		Removal of COD (%)	
				Exp.	Pred.	Exp.	Pred.
1	80	10	30	93.9	81.67	46	43.54
2	80	4	45	76.4	85.5	39.8	42.4
3	60	4	30	88.2	87.36	46	48.87
4	80	4	30	74.8	72.5	34.5	38.1
5	60	4	15	53.7	57.26	24.5	23.3
6	80	7	15	27.1	31.76	10.5	7.56
7	80	7	30	90.3	77.1	44.5	43.95
8	40	10	45	96.3	93.64	43	47.65
9	80	7	45	90.2	90	47	48.2
10	40	4	30	97.6	>100	61	59.62
11	60	4	45	87.6	85	43.5	42.32
12	60	10	45	92	94.2	51.1	47.73
13	40	7	15	96.8	91.9	45	50.68
14	80	10	15	33	36.34	4.3	7.155
15	60	10	15	68.3	66.4	29	28.7
16	40	7	30	97.5	>100	66.3	65.43
17	60	7	30	92.9	91.9	53	54.7
18	40	10	30	99.4	>100	67.9	65
19	80	10	45	88.9	94.62	48.9	47.8
20	60	10	30	92.5	96.5	53.5	54.3
21	80	4	15	21.2	27.2	0	1.75
22	40	7	45	94.2	89.06	45.9	48.06
23	60	7	45	91.3	89.57	51	48.13
24	40	4	15	92.6	87.31	47.3	44.52
25	60	7	15	65.2	61.8	33	29.12
26	40	4	45	88.7	84.5	43.5	42.25
27	40	10	15	98.9	96.46	49	50.27

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{13}x_1x_3 + b_{33}x_{23} \quad (4)$$

$$\text{Removal of OT(Y)} = 124.7 - 2.267X_1 + 1.526X_2 + 2.189X_3 - 0.072X_3^2 + 0.05092X_1X_3 \quad (5)$$

where Y is a response variable for the removal efficiency of OT and COD and b_i, b_{ik} and x_i are regression coefficients for linear effects, regression coefficients for quadratic effects and coded experimental levels of the variables, respectively. According to these results, an empirical relation between the response and independent variables was obtained and expressed by the following second-order polynomial equations:

These results were revealed good agreements between predicted and experimental values for degradation and mineralization efficiencies. The important parameters of the reaction were as follows: direct effect of dosage of the OT (–2.267) > direct effect of concentration of H_2O_2 (2.189) > direct effect of pH (1.526) > second-order effect of dosage of H_2O_2 (–0.072) > interaction between the concentration of H_2O_2 and OT (0.05092). The significance of the coefficients was decided by P-value (Table 3).

The removal efficiencies of the OT and COD are shown in Table 3, and they have been forecasted by Eqs. (5) and (7), respectively.

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{13}x_1x_3 + b_{22}x_{22} + b_{33}x_{23} \quad (6)$$

$$\text{Removal of COD(Y)} = 43.76 - 1.6189X_1 + 6.12X_2 + 2.753X_3 - 0.368X_2^2 - 0.07138X_3^2 + 0.03606X_1X_3 \quad (7)$$

Table 4 presents the statistical properties of selected significant model terms to describe the removal efficiency of COD as a function of the studied variables.

According to the analysis, it was obtained that $x_1, x_2, x_3, x_3^2, x_2^2$ and x_1x_3 were significant terms and other model terms are not significant (with a probability value larger than 0.05). These results showed good agreements between experimental and predicted values of degradation and mineralization efficiencies. As it can be seen, the important reaction parameters were as follows: direct effect of pH (6.12) > direct effect of H_2O_2 (2.753) > direct effect of OT concentration (–1.6189) > second-order effect of pH (–0.368) > second-order effect of H_2O_2 (–0.07138) > interaction between the concentration of the OT and H_2O_2 (0.03606). The significance of the coefficients is presented in Table 4.

Table 3
ANOVA test for the removal of OT by Central Composite Design

Removal of OT					
Coefficient	Coefficient estimate	Standard error sum	Factor effect	T-value	P-value
b_0	124.7	2.21		41.52	0.000
b_1	–2.267	1.57	–29.58	–9.45	0.000
b_2	1.526	1.57	9.16	2.92	0.008
b_3	2.189	1.57	27.64	8.83	0.000
b_{33}	–0.072	2.71	–32.42	–5.98	0.000
b_{13}	0.05092	1.92	30.55	7.97	0.000

3.2. Analysis of variance (ANOVA)

Tables 3, 4 and 5 show the results of the quadratic response surface model fitting in the form of ANOVA for degradation and mineralization efficiencies, respectively. The ANOVA was demanded to test the importance and the fit of the model [17,18]. Based on the ANOVA, the predicted removal efficiencies by the above equation were in good agreements with the experimental data. The correlation coefficient (R^2) was a quantitative scale for judging the correlation between the experimental data and the predicted values. By discriminating the predicted data and experimental results, it was found that there was a good agreement between the experimental data and the predicted values with $R^2 = 0.9291$.

Adjusted R^2 (R^2_{adj}) shows a measure of goodness of fit, and it is more appropriate for comparing models with different numbers of independent variables as showed in Table 6. It was achieved to be 0.9122 and 0.9677 for the removal OT and COD which were close to the corresponding value of R^2. Results showed a good agreement between the monitored and calculated results in the studied range of experiments [13].

Therefore, in the removal of OT the linear influence of all variables, including coefficients b_1, b_2, b_3, and interaction of the concentration of OT and hydrogen peroxide (b_{13}) and with the quadratic effect of dosage of H_2O_2 (b_{33}) were the most impressive parameters. Also for the removal of COD, the

Table 4
ANOVA test for the removal of COD by central composite design

Removal of COD					
Coefficient	Coefficient estimate	Standard error sum	Factor effect	T-value	P-value
b_0	43.76	1.27		42.95	0.000
b_1	–1.6189	0.698	–21.489	–15.40	0.000
b_2	6.12	0.698	5.844	4.19	0.000
b_3	2.753	0.698	19.011	13.62	0.000
b_{22}	–0.368	1.21	–6.62	–2.74	0.013
b_{33}	0.07138	1.21	–32.12	–13.29	0.000
b_{13}	0.03606	0.855	21.633	12.65	0.000

Table 5
Information obtained from the analysis of variance

Source of variation	Removal of OT		Removal of COD	
	Total	Error	Total	Error
Sum of squares	13055.7	926.1	13055.7	926.1
Degree of freedom	26	21	26	21
Mean square		44.1		44.1

Table 6
R^2, R^2_{adj} and R^2_{pred} for the removal of OT and COD

	R^2	R^2_{adj}	R^2_{pred}
Removal of OT	0.9291	0.9122	0.8804
Removal of COD	0.9751	0.9677	0.9521

quadratic effect of pH (b_{22}) was an efficient parameter. If the experiments were executed by conventional methods the significance of these interactions and quadratic effects between the variables would have been lost.

The T-value and P-values together with the calculated parameters are presented in Tables 3 and 4. The P-values were used as a tool to control the importance of the coefficients, which in turn were necessary for investigating the interactions between variables. The coefficient with the larger extent of T-value and smaller P-value was the more significant.

3.3. Effect of various parameters on the removal efficiency of OT

In this work, three important factors, including the initial concentration of OT, dosage of hydrogen peroxide and pH were chosen as variables in the CCD. The removal efficiency of the OT and COD were selected for response functions. The values of variables, the experimental data and the result are indicated in Table 2 for all 27 experimental runs performed. Results from the CCD experiments were exhibited that the minimum and the maximum removal rate of the OT was 21.2% and 99.4%, respectively. The removal of the OT was only 21.2% (run number 21), in 15 mM of hydrogen peroxide, pH at 4 and 80 mg l^{-1} of the OT. Results showed that raising the pH from 4 to 10 can enhance removal efficiency of OT. The removal of OT in neutral and alkaline conditions was higher than that in acidic condition, due to the fact that in neutral or basic pH conditions, the production of hydroxyl radical increased because more OH$^-$ were created.

However, an increase in the concentration of OT caused the efficiency of degradation to be decreased. By increasing the concentration of H_2O_2 from 15 to 30 mM, the removal of OT increased, indicating that hydrogen peroxide has an important effect on the degradation of OT. The contour plots (two-dimensional) and three-dimensional (surface plots) were created for the predicted responses to inspect the effect of each variable.

As shown in Fig. 2, the contour plots were developed as a function of initial concentration of the OT and H_2O_2. At low concentrations of OT, its removal efficiency was high and optimum concentration of H_2O_2 was 30 mM, because the lifetime of hydroxyl radicals is very low and they can only react while they are created. Therefore, increase in the dosage of H_2O_2 from 15 to 30 mM leads to the formation of OH radicals and afterwards the removal efficiency of the OT and COD increased. With the extra amount of hydrogen peroxide, higher than 30 mM, radical scavenging had occurred and degradation decreased and this theory has been confirmed by many authors [19]. It was found that there was an optimum concentration of hydrogen peroxide which resulted in the highest degradation rate. The optimum concentration of initial hydrogen peroxide corresponded in a $\frac{[H_2O_2]_0}{[OT]_0}$ molar ratio, was about 80 [20]. The fact of having an optimum concentration of initial hydrogen peroxide that leads to the highest removal rate was also reported by many researchers [21,22].

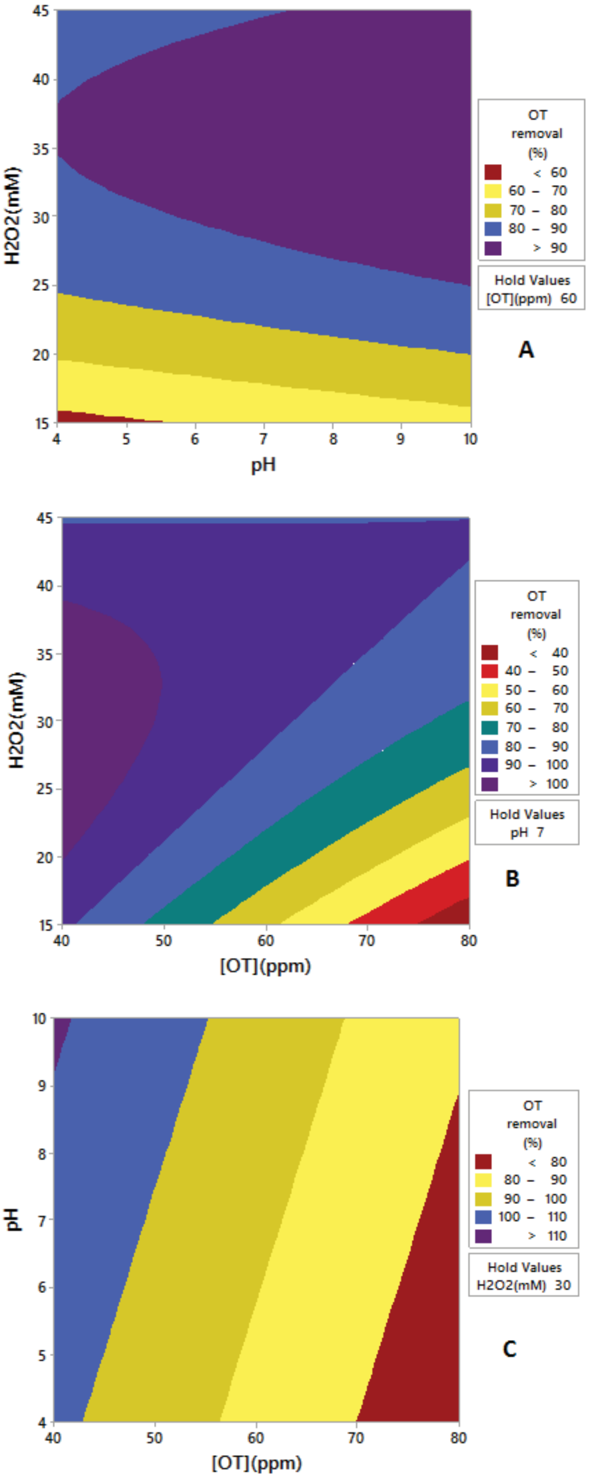

Fig. 2. Contour (2D) plots for the removal of OT vs. independent variables: (A) pH and dosage of H_2O_2, (B) Concentration of OT and H_2O_2, (C) Dosage of OT and pH.

The production of hydroxyl radicals was enhanced by an increase in the initial concentration of hydrogen peroxide.

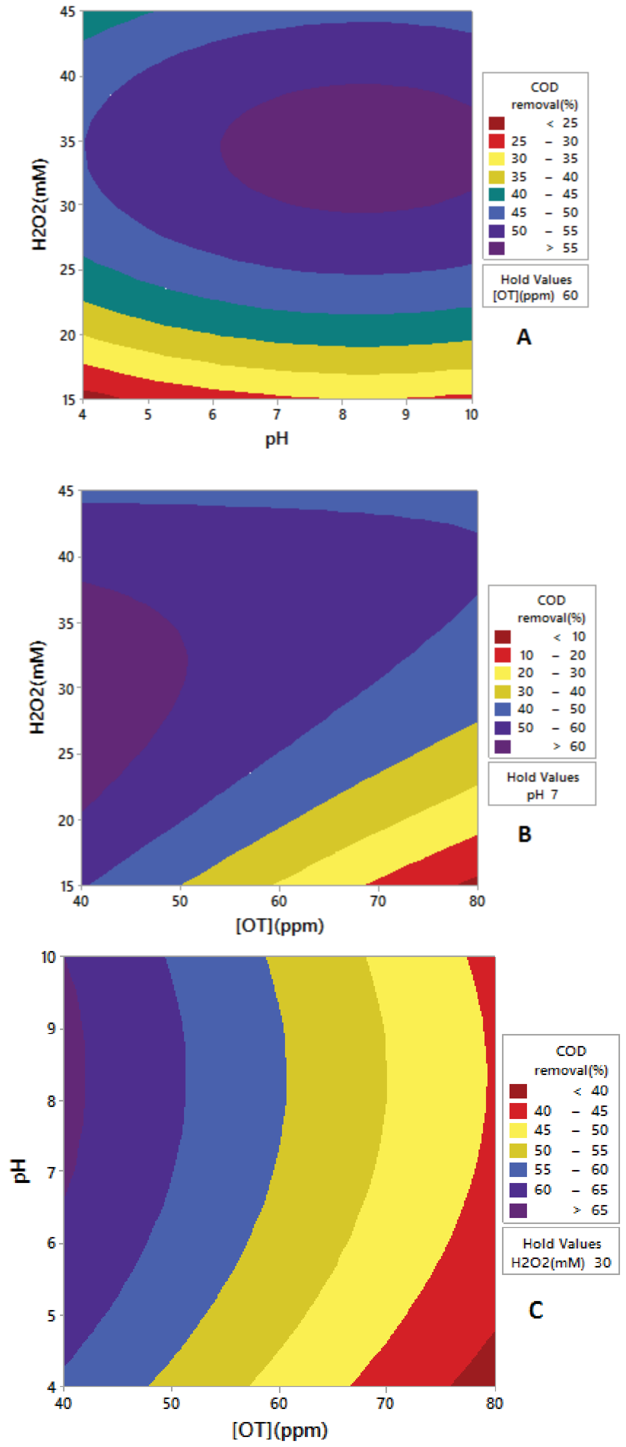

Fig. 3. Contour (2D) plots for the removal of COD vs. independent variables: (A) pH and dosage of H_2O_2, (B) Concentration of OT and H_2O_2, (C) Dosage of OT and pH.

Therefore, the degradation rate of the OT was increased. However, further increase in the concentration of hydrogen peroxide caused the reaction of the produced hydroxyl radicals with the extra H_2O_2 molecules to form hydroperoxyl radicals that were of less oxidizing power due to the following reaction (Eq. (8)):

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (8)$$

In addition, excess amount of H_2O_2 leads to the consuming of active hydroxyl radicals. Therefore, the rate of the latter reactions decreased. This fact was also reported in the literature and mentioned as scavenging effect [23].

High concentration of OT molecules promotes the probability of collision between hydroxyl radicals and pollutant molecules, leading to an increase in the degradation efficiency. But at high concentration of the OT the incident light would be used mainly for OT excitation rather than for the hydroxyl radical production. Moreover, penetrability of solution to UV radiations was reduced and removal rate decreased because photolysis of hydrogen peroxide directly depends on the amount of light absorbed by H_2O_2 molecules [24–26]. By increasing the concentration of the OT, the removal rate decreased at the reaction time (100 min). The reason can be related to the fact that, under the experimental conditions, the ratio of H_2O_2 or hydroxyl radicals to pollutant molecules in the solution decreased with an increase in the dosage of OT, which resulted in more H_2O_2 consumption [27]. In AOPs, with an increase in the concentration of OT, various intermediates, which created upon the degradation of the initial OT, meddle with desirable oxidation. During degradation, the color of the solution was colorless at first, but after the reaction, the color converted to reddish and finally the solution became colorless again.

3.4. Effect of various parameters on the removal efficiency of COD

The removal efficiency of COD in various experimental conditions by CCD is exhibited in Table 2. Experiments were shown that the maximum removal of COD was 67.9% using 30 mM of H_2O_2, 40 mg l^{-1} of OT and pH at 10 (run number 18) and the minimum removal of COD was 0% using 80 mg l^{-1} of OT, 15 mM of H_2O_2 and pH at 4 (run number 21).

The counter(2D) and response surface plots of pH, concentration of OT and hydrogen peroxide on COD removal efficiency were presented in Figs. 3 and 4. It was clear that the dosage of H_2O_2 was the most significant factor influenced on the removal efficiency of COD. Also, pH and initial concentration of the OT were significant factors, too. As mentioned in the removal of the OT, the removal of COD was enhanced as the concentration of hydrogen peroxide increased, since there were more hydroxyl radicals presented in the solution. However, using excess dosages of H_2O_2 has a negative influence on the removal of COD, because it could cause a scavenging effect on the hydroxyl radicals and reduce the removal efficiency. In high concentration of pollutant, low pH and low dosage of hydrogen peroxide (run number 21) removal of COD was zero, since hydroxyl radicals produced was not sufficient and only 21.2% of OT molecules changed to other organic intermediate molecules that had COD. With an increase in pH, more hydroxyl radicals produced from hydroxide ions, so mineralization was enhanced. But at very high pHs, efficiency decreased because more radicals were produced and caused the radical scavenging effect.

pH was decreased during treatment because of producing intermediates that had acidic properties. Therefore the mild alkaline pH was optimized for the removal of COD and efficiencies from the experiments were between 0% and 67.9%. The optimum conditions predicted by the RSM for the removal of COD were the initial concentration of OT at 40 mg l^{-1}, the concentration of H_2O_2 at 30 mM and pH at 8.3. The removal efficiencies, reduced when moving away from these points, meaning that either decrease or increase in any of the optimum tested variables lead to decrease in the response. The results showed that UV/H_2O_2 was the most important process affecting the removal of COD.

3.5. Optimization and confirmation of responses

In this study, the main purpose of the optimization was to obtain the optimum conditions and variables for degradation and mineralization of OT in UV/H_2O_2 process. The requested goal in term of the removal percent of OT and COD was introduced as "OT maximum" and "COD maximum" to gain largest decomposition yield. Degradation and mineralization efficiency at optimum values of the process variables presented in Table 7. Further experimental tests were done in the predicted value conditions and the results were verified the predicted values. The results showed that the maximum treatment percent was obtained when the values of each variable were arranged as the optimum values, which was in good agreement with the value forecasted by the model. It reveals that the method employed to optimize conditions for treatment of OT by UV/H_2O_2 process was successful.

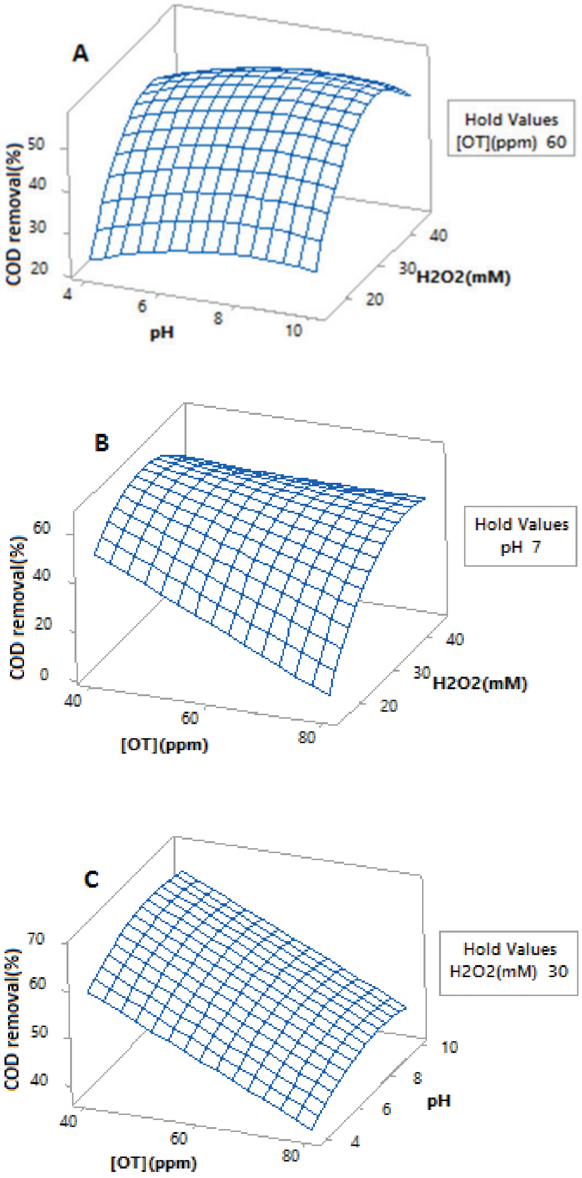

Fig. 4. Response surface (3D) plots for the removal of COD vs. independent variables: (A) pH and dosage of H_2O_2, (B) Concentration of OT and H_2O_2, (C) pH and dosage of OT.

3.6. Kinetics of reaction

From the experimental results, it was obvious that the numbers of hydroxyl radicals were higher than OT, so hydroxyl radicals can be supposed to be approximately fixed. Therefore, the kinetic constant of reaction was obtained by fitting the experimental data using pseudo-first-order kinetic equation [28–30]. However, when the experimental data were plotted they were similar to a first-order reaction with respect to the OT degradation. The rate constant of this model was estimated in optimum conditions. The modeling of experimental results was executed by the Curve Expert program to find the best curve for experimental data, and it was shown that the function with minimum error and the highest correlation coefficient was the best curve.

As shown in Fig. 5, the term ln $[OT]_0$/ $[OT]_t$ vs. reaction time was plotted and after linear regression analysis, the apparent first-order rate constants ($k = 4.95 \times 10^{-2}$ min^{-1}) and half-life of degradation reaction ($t_{1/2}$ = 14 min) were determined (Eq. (9)).

$$\left[\ln\frac{[OT]_0}{[OT]_t}\right] = k_{ap}t \tag{9}$$

where $[OT]_0$ and $[OT]t$, were the concentration of OT at times 0 and t and k_{ap} was a pseudo-first-order rate constant, also t is the time of the reaction in minutes.

Table 7
Degradation and mineralization efficiency at optimum values of the process variables

Variables	Optimum values for removal of OT	Optimum values for removal of COD
Initial OT concentration (mg l^{-1})	40	40
Initial pH	10	8.3
Initial concentration of H_2O_2 (mM)	30	30
Removal of OT (%)	Pred.(100), Exp.(99.4)	
Removal of COD (%)		Pred.(66.1), Exp.(68.9)

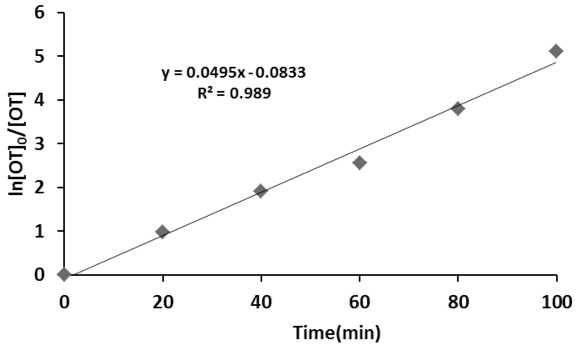

Fig. 5. The curve of Ln ([OT]$_0$/[OT]) vs. reaction time in optimum conditions: H_2O_2 concentration = 30 mM, [OT]$_0$= 40 mg l^{-1} and pH = 10.

4. Conclusions

In this work, the full factorial design of experiment and response surface method were used and showed that OT can be completely degraded by UV/H_2O_2 process. The influence of the main process variables on OT and COD removal was estimated by RSM. In the project, the useful indications were obtained by RSM on the optimum set of used operating conditions. Effect of experimental parameters on the degradation efficiency was accepted by the response surface and contour plots of the model predicted.

The pH and concentration of the OT were the most important factors for removal efficiency of COD and OT, respectively. The optimum conditions for the maximum removal of OT were pH of 10, initial concentration of OT at 40 mg l^{-1} and initial dosage of H_2O_2 at 30 mM.

The optimal conditions for the removal of COD were an initial concentration of OT at 40 mg l^{-1}, the initial dosage of H_2O_2 at 30 mM and pH of 8.3.

Therefore, the removal percent of the OT and COD in optimal condition were 99.4% (experimental), 100% (prediction) and 66.1% (prediction) and 68.9% (experimental), respectively. By ANOVA, a relatively high determination coefficient (R^2 = 0.9291, R^2_{adj} = 0.9122) was achieved and showed a satisfactory agreement between the prediction model and the experimental values, indicating the trustworthiness of the methodology used.

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