Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22681

123 (2018) 188–195
August

A Box–Behnken design (BBD) optimization of the photocatalytic degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) using TiO_2/H_2O_2

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Received 13 October 2017; Accepted 28 June 2018

ABSTRACT

2,4-Dichlorophenoxyacetic acid (2,4-D), a chlorinated phenoxy-alkanoic herbicide, is used extensively in agriculture. This work investigates TiO_2/H_2O_2 mediated UV photocatalytic degradation of 2,4-D in a laboratory-scale photoreactor. Three levels of Box–Behnken design technique, combined with response surface methodology (RSM), were used to design the experiments. Two kinds of multivariate experimental design (pH, TiO_2, and 2,4-D concentration) and (pH, TiO_2, and H_2O_2 concentrations) were employed to establish two quadratic models (Model 1 and Model 2), showing the functional relationship between degradation rate of 2,4-D and three independent experimental parameters. Model 1 predicted optimum values for pH, TiO_2, and 2,4-D concentrations to be 5.7, 1.20 g L^{-1}, and 32 mg L^{-1}, respectively. Model 2 predicted optimum values for pH, TiO_2, and initial H_2O_2 concentrations to be 4.94, 1.34 g L^{-1}, and 161 mg L^{-1}. Degradation rate of 2,4-D approached 78.10% for Model 1 and 83.63% for Model 2. For both models, similar results were obtained through optimizing variables by RSM and using single factorial batch reactor operation. Regression analysis showed good agreement between experimental results and predictive values for Models 1 and 2, with R^2 values of 0.9958 and 0.9976, respectively.

Keywords: 2,4-dichlorophenoxyacetic acid (2,4-D); TiO_2/H_2O_2 photocatalysis; Box–Behnken design (BBD); Response surface methodology (RSM)

1. Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the most frequently used phenoxyacetic acid herbicides for controlling broadleaf weeds due to its high efficiency [1]. In many regions of the world, and especially in Turkey, 2,4-D is the most commonly used chlorinated phenoxy-alkanoic herbicide for a variety of agricultural activities – especially in potato, grain, and corn productions [2]. 2,4-D is considered moderately toxic by the World Health Organization. It is known to affect the nervous system of humans and animals and to act as a potential carcinogen, as an endocrine disrupter and as a mutagen. Since this compound exhibits high water solubility, mobility, and lifetime, its continuous use may cause soil percolation, and surface and groundwater contamination [3]. The permissible amount of 2,4-D in drinking water is 0.1 and 70 μg L^{-1}, according to the Turkish standard [4] and US standard [5,6], respectively. Being toxic and having the bio-refractory characteristics of the chlorophenoxy herbicides, advanced treatment methods are being developed to treat water contaminated with 2,4-D.

In recent years, by producing hydroxyl radicals ($OH^{\bullet}$) through chemical, photochemical, photocatalytic, and electrochemical reactions, advanced oxidation processes have become a promising technology to eliminate pesticides from water systems [7,8]. Photocatalysis was observed to proceed via two different pathways: (1) generation of $OH^{\bullet}$ from the holes present at valence band, and (2) direct oxidation of compound from valence holes [9]. Heterogeneous photocatalytic oxidation process relies on subsequently generating

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superoxide radicals (O_2^-) and hydroxyl radicals ($OH^•$), which are primary oxidizing species in photocatalytic oxidation processes [10–12].

Some examples for parametric optimization of photocatalytic degradation of organic pollutants in aqueous solutions, such as diuron, acrylonitrile, and chlorpyrifos, using the response surface methodology (RSM) have been previously reported [13–15]. However, these are mainly single-factor studies, based on change of a time-variable and they do not consider the effect of other variables in determining optimum conditions for photocatalysis. Since these studies neglect the combined effects of factors, accuracy of estimations is compromised in case a working parameter is changed [16]. The proposed multivariate method enables accurate estimation of response values and allows the optimal region for the studied process to be found in a shorter time and with lower chemical consumption. To the best of our knowledge, nor photocatalytic degradation of commercial grade 2,4-D herbicide, neither its parametric optimization via Box–Behnken Design (BBD) has been studied before. In this study, for the first time, P25 TiO_2/H_2O_2/UVA facilitated 2,4-D photocatalytic degradation was investigated and further optimized using the RSM with BBD. RSM and BBD were used to optimize and analyze the effect of four operational parameters: TiO_2 photocatalyst dose, the initial 2,4-D, pH, and H_2O_2 concentrations.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals were used without further purification. Titanium (IV) oxide nanopowder (AEROXIDE® P25 ≥ 99.5%, 21 nm, 35–65 $m^2 g^{-1}$ (BET)) was used as the photocatalyst (Sigma Aldrich, Germany) due to its high performance in photocatalytic degradation reactions. Commercial grade Amin EXT 500 SL (equivalent to 500 g L^{-1} of 2,4-D) 2,4-D amine salt ($C_{10}H_{13}Cl_2NO_3$, MW: 266.12 g mol^{-1}) was from Agrofarm Company, Turkey. NaOH and H_2SO_4 (essay 97%) were obtained from Merck, Germany. All solutions and reaction mixtures were prepared with purified water (Merck Millipore, Germany, spec. resistivity: 18.2 MΩ cm).

2.2. Experimental procedure and analysis

Photocatalytic experiments were performed in a 4.6 L (operating volume: 1 L) cylindrical, (14 cm D × 30 cm L) batch photoreactor (Fig. 1) maintained at 22°C ± 1°C. The photoreactor was comprised of three parts: (1) an external Pyrex glass; (2) a Pyrex glass thimble, where the head part is fitted to outside container to form a gastight seal and running water is passed through the thimble to cool the reaction solution, and (3) an empty quartz chamber, in which a Philips PL-L UVA 36 W lamp (315–380 nm; 110 μW cm^{-2}) was placed. Reactor was also equipped with a control system, a water level sensor system and a water-inlet and outlet. A gas inlet opening supplied air from a diffuser system with 3.5 L min^{-1} capacity during experiments. Reactor was wrapped in aluminum foil to prevent UV ray penetration.

For irradiation experiments, 2,4-D solutions were prepared daily and upon addition of TiO_2, reactor was stirred and air bubbled constantly for at least 30 min in the dark to allow the system to reach equilibrium in case of adsorption. This time was chosen so that under stirring in the dark no more herbicide molecules could be adsorbed by the photocatalyst. For comparison, irradiation experiments without TiO_2 were also performed. The pH of reaction mixture was adjusted by adding 1 N of NaOH and 1 N of H_2SO_4. Photocatalysis efficiency was determined by withdrawing aliquots at specific

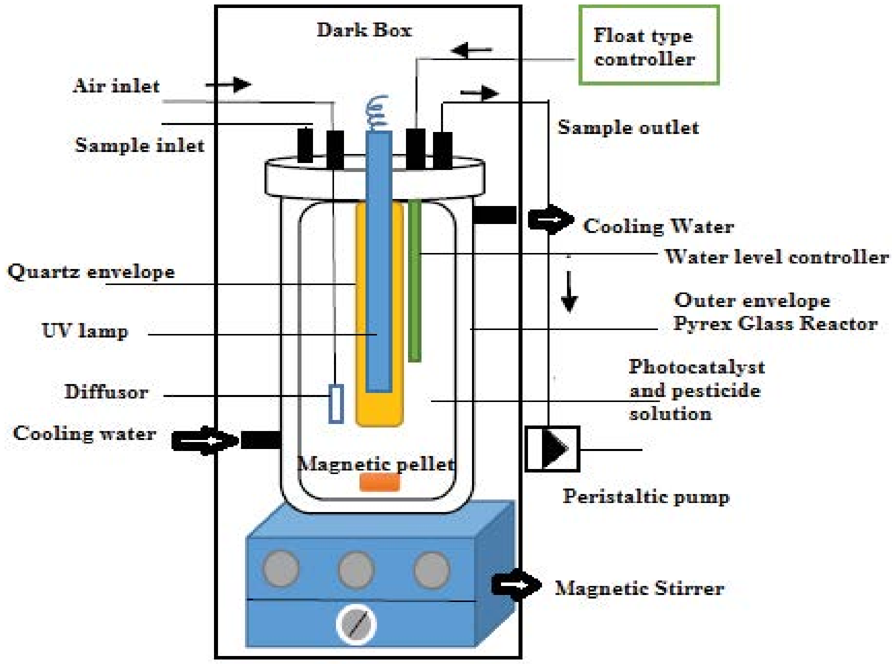

Fig. 1. Experimental setup of photocatalytic reactor.

time intervals, where starting time was defined as the beginning of irradiation. Samples were filtered through 0.45 μm filters (Millipore, Germany) to remove TiO_2 from solution.

Optimization of photocatalysis conditions was initially done using a spectrophotometer (Shimadzu UV-1601-PC) and measuring the optical density (OD) of samples at its λ_{max} of 283 nm, which is the given maximum absorption wavelength for 2,4-D molecules for 15 min irradiation. This was also confirmed by a spectrum reading from the spectrophotometer. Percentage of 2,4-D degradation was calculated using Eq. (1):

$$\text{Percentage of degradation of } 2,4-\text{D} = \frac{C_i - C_f}{C_i} \tag{1}$$

where C_i and C_f are the initial and final 2,4-D concentrations in the reaction mixture, respectively.

2.3. Experimental design and statistical analysis

RSM is a design technique that is used for optimization of process variables in multivariable systems by using experimental statistical methods. Even in very complex systems the relative importance of influencing factors is analyzed by combining mathematics and statistics. Therefore, once optimal conditions are determined by response surface method, not only study period is significantly shortened but also costs associated with the study are decreased [17]. Many RSM studies have been conducted to model experiments for analysis of photocatalytic processes [17–22]. The reason for choosing the Box–Behnken experimental design is to allow this method to efficiently evaluate multiple variables in each study test. Among all statistical experimental design methods, a BBD is a practical method for optimization studies because it requires fewer study sets than other design methods – such as 15 datasets for a 3-factor experimental design. Furthermore, the BBD method allows calculation of the response function at intermediate levels, which are not experimentally studied [23,24]. So, in this study, a statistical multivariate approach using two types of three-level, three-factorial BBD in combination with RSM was adopted to observe the photocatalytic process parameters affecting degradation efficiency of 2,4-D. While three parameters were set as independent variables, degradation efficiency of 2,4-D herbicide was the dependent response variable. Independent variable levels and ranges were presented in Table 1. Two optimization studies were conducted on the effect of pH, TiO_2, and H_2O_2 concentrations as the independent variables on the dependent 2,4-D degradation efficiency response variable. The factor levels were coded as −1 (low), 0 (central point or middle), and 1 (high). Independent variable value ranges were determined based on previous experimental studies and in order to maximize the 2,4-D removal. All analytical tests were carried out in triplicate. Second-order polynomials were used to represent experimental data to obtain the best-fit regression equations and to provide good predictions throughout the area of interest [14].

RSM was used for three variables in these experiments with a BBD [25]. BBD was adopted to evaluate the combined effect of the three independent variables from 15 sets of experiments of which 3 are repetitions at the center point. The 2,4-D herbicide removal-yield dependent changed as a result of 15-min experiments. Degradation efficiency of 2,4-D herbicide resulting from 15-min experiments was the dependent variable. A second-order polynomial, Eq. (2), was used with nonlinear regression to fit experimental data and to identify relevant model terms. Considering all linear terms, square terms and linear-by-linear interaction terms, quadratic response model could be described as:

Table 1
Experimental design levels of chosen parameters for two models

Model 1	Ranges and levels		
Independent variables	Low (−1)	Medium (0)	High (+1)
pH (x_1)	3	5	7
TiO_2 (x_2, g L^{-1})	0.5	1	1.5
2,4-D (x_3, mg L^{-1})	10	30	50
Model 2	**Ranges and levels**		
Independent variables	Low (−1)	Medium (0)	High (+1)
pH (x_1)	3	5	7
TiO_2 (x_2, g L^{-1})	0.5	1	1.5
H_2O_2 (x_3, mg L^{-1})	50	150	250

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i x_i + \sum_{j=2}^{k}\sum_{i=1}^{j-1}\beta_{ij}x_i x_j + \sum_{i=1}^{k}\beta_{ii}x_i^2 + e_i \tag{2}$$

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{33}x_3^2 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 \tag{3}$$

Y (%) represented the response variable (degradation efficiency of 2,4-D). β_0 was the interception coefficient, β_{11}, β_{22}, and β_{33} were quadratic terms, β_{12}, β_{13}, and β_{23} were interaction coefficients [25]. Since we ran two models x_1, x_2, and x_3 represented pH, TiO_2, and initial 2,4-D concentrations for Model 1 and represented pH, TiO_2, and initial H_2O_2 concentrations for Model 2. This equation only changed within studied intervals. Regression analysis and optimization processes were performed using Minitab 17.0 Statistical Software. Adequacy of designed models was assessed using "goodness of fit" and analysis of variance (ANOVA) techniques. The p value of <0.05 for any factor in ANOVA test indicated a significant effect for corresponding variable on response. RSM was used to generate 3D surface plots from validated models. These surface plots were used to locate the optimum points for process parameters to deliver maximum degradation of the 2,4-D.

3. Results and discussion

3.1. Model fitting and statistical analysis

BBD is generally used for process optimization and it is very suitable for compatibility with quadratic surfaces [26]. Results from 2,4-D degradation efficiency experiments under various conditions are given in Table 2. As expected increasing TiO_2 concentration when other variables were

Table 2
Experimental values and predicted response

Run	Experimental conditions			% 2,4-D degradation		Experimental conditions			% 2,4-D degradation	
	x_1 pH	x_2 TiO_2 (g L^{-1})	x_3 2,4-D (mg L^{-1})	Experimental	Predicative	x_1 pH	x_2 TiO_2 (g L^{-1})	x_3 H_2O_2 (mg L^{-1})	Experimental	Predicative
1	3	0.5	30	25.974	25.281	3	0.5	150	37.703	51.250
2	7	0.5	30	50.433	51.126	7	0.5	150	35.268	67.875
3	3	1.5	30	54.113	53.420	3	1.5	150	55.492	43.625
4	7	1.5	30	66.450	67.143	7	1.5	150	48.458	52.750
5	3	1	10	27.273	27.413	3	1	50	42.167	36.313
6	7	1	10	48.052	46.807	7	1	50	24.614	45.188
7	3	1	50	35.325	36.569	3	1	250	32.900	90.812
8	7	1	50	56.883	56.742	7	1	250	43.791	107.687
9	5	0.5	10	23.377	23.929	5	0.5	50	56.169	40.438
10	5	1.5	10	48.701	49.253	5	1.5	50	67.127	26.063
11	5	0.5	50	37.273	36.721	5	0.5	250	60.227	95.937
12	5	1.5	50	56.104	55.552	5	1.5	250	75.568	87.562
13	5	1	30	73.593	73.882	5	1	150	84.091	69.667
14	5	1	30	74.026	73.882	5	1	150	84.375	69.667
15	5	1	30	74.026	73.882	5	1	150	83.631	69.667

kept constant (pH and initial 2,4-D concentrations for Model 1, pH and H_2O_2 concentrations for Model 2) increased 2,4-D degradation efficiency. The best degradation efficiency was measured in experiments and was predicted by Model 1 for pH 5 and values. Once H_2O_2 was included in experimental study the best degradation efficiency was observed for pH 5, 1 g L^{-1} TiO_2 concentration and 150 mg L^{-1} H_2O_2 concentration values. On the other hand, the best prediction by Model 2 was given for pH 5, 0.5 g L^{-1} TiO_2 concentration and 250 mg L^{-1} H_2O_2 concentration values.

The response functions generated for Y_1 (Model 1) and Y_2 (Model 2), the percentage 2,4-D degradation using Eq. (3) are presented in Eqs. (4) and (5):

$$Y_1 = 73.882 + 9.892x_1 + 11.039x_2 + 4.773x_3 - 3.030x_1x_2 + 0.195x_1x_3 - 1.623x_2x_3 - 12.060x_1^2 - 12.579x_2^2 - 19.939x_3^2 \quad (4)$$

$$Y_2 = 84.032 - 2.017x_1 + 7.160x_2 + 2.801x_3 - 1.150x_1x_2 + 7.111x_1x_3 + 1.096x_2x_3 - 34.353x_1^2 - 5.449x_2^2 - 13.811x_3^2 \quad (5)$$

For Eqs. (4) and (5), Y represented the percentage degradation efficiency of 2,4-D herbicide. Positive coefficients of TiO_2 at both response functions implied an improvement in 2,4-D mineralization by residual catalyst loadings. Negative coefficient of initial pH in Eq. (5) indicated that mineralization was faster in an acidic medium with H_2O_2. López-Vásquez et al. [27] reported that free hydroxyl radicals attack the aromatic ring preferably on side chains at an acidic pH, and 2,4-D degraded better in an acidic medium. In Model 1, quadratic terms of TiO_2 concentration-initial 2,4-D concentration and pH-TiO_2 concentration had negative effects on herbicide removal. Likewise Model 2 demonstrated that quadratic term of pH-TiO_2 concentration also worked against the 2,4-D degradation. Consequently, their value-based increase in aqueous solution could lead to less herbicide degradation [28].

According to Eq. (4), there was a synergistic interaction between TiO_2 and the initial pH, and the highest synergistic interaction was obtained between the pH and H_2O_2 concentrations in the presence of H_2O_2. Moreover, interaction between 2,4-D concentration and initial pH was also significant. It was related to the anionic character of 2,4-D and its intermediates being favored by the attack orientation of oxidant species in an acidic medium [27]. López-Vásquez et al. [27] stated that the optimum conditions obtained from a flat plate photoreactor system were: 5.58, 0.56 g L^{-1}, and 30.41 mg L^{-1} for pH, TiO_2, and 2,4-D concentrations, respectively. Also, they mentioned that 66.87% 2,4-D mineralization was achieved, which was similar to the results obtained in this study.

3.2. Analysis of variance

The ANOVA for Model 1 and Model 2 was shown in Tables 3 and 4. Using an F-test, the lack-of-fit (variation of data around the fitted model) was evaluated. When ANOVA for empirical quadratic polynomial equation model was investigated, p values were low (<0.0001) for both models. F values of Model 1 (369.99) and Model 2 (636.87), with a p value less than 0.0001, implied that models were statistically significant at 95% confidence level [29].

According to Model 1, p values for coefficients x_1, x_2, x_3, quadratic coefficients x_1x_1, x_2x_2, x_3x_3 and influence coefficients x_1x_2, x_2x_3 were less than 0.05. Similarly, for Model 2, p values for coefficients x_1, x_2, x_3, quadratic coefficients x_1x_1, x_2x_2, x_3x_3 and influence coefficient x_1x_3 were less than the 0.05, emphasizing statistical significance of 2,4-D degradation efficiency. The effect of synergistic interaction between pH and 2,4-D concentration was statistically insignificant ($p > \alpha$, $\alpha = 0.05$) on 2,4-D herbicide removal for Model 1. For Model 2, effects of TiO_2-H_2O_2 concentration and pH-TiO_2 concentration

Table 3
ANOVA test responses for Y_1 (without H_2O_2)

Source	Sum of squares	Degree of freedom	Mean square	*F* Value	*p* Value
Model	4,262.31	9	473.59	369.99	<0.0001[a]
x_1, pH	782.78	1	782.78	611.53	<0.0001
x_2,TiO_2	974.87	1	974.87	761.60	<0.0001
x_3,2,4-D	182.23	1	182.23	142.37	<0.0001
x_1^2	353.97	1	537.01	419.53	<0.0001
x_2^2	453.16	1	584.27	456.45	<0.0001
x_3^2	1,467.88	1	1,467.88	1,146.76	<0.0001
x_1x_2	36.73	1	36.73	28.70	0.0030[a]
x_1x_3	0.15	1	0.15	0.12	0.7450
x_2x_3	10.54	1	10.54	8.24	0.0350[a]
Residual	6.40	5	1.28		
Lack of fit	6.28	3	2.09	33.49	0.0290[a]
Pure error	0.12	2	0.06		
Total	4,268.71	14			
	$R^2 = 0.9985$		R^2(pred) = 0.9764	R^2(adj) = 0.9958	

[a] Statistically significant

synergistic interactions on 2,4-D herbicide removal were statistically insignificant. The quadratic and interactive effects of variables would be lost if experiments were applied using conventional methods [30].

Lack-of-fit *F*-values were 33.49 (*p* value, 2.90%) and 10.79 (*p* value, 8.60%) for Model 1 and Model 2, respectively, and lack-of-fit-*F* values were derived from noise by chance as only a 2.90% and 8.60% ratio. The coefficient of determination (R^2) can be defined as the ratio of the considered variable to the total variation, and a measure of the degree of fit. The significance of a linear model is determined by the coefficient of determination (R^2), the predicted coefficient of determination (R^2_{pred}), and the adjusted coefficient of determination (R^2_{adj}) [31]. When R^2 is close to 1, the model fits the actual experimental data better [32,33]. As shown in Tables 3 and 4, R^2_{pred} and R^2_{adj} were reasonably consistent with each other. Joglekar and May [34] suggested that, for a good fit, R^2 should be at least 0.80. The R^2 values for these response variables were higher than 0.80 (0.9985 and 0.9991 for Model 1 and Model 2, respectively), which indicated that the regression model accurately explained the 2,4-D degradation process by TiO_2/UVA and TiO_2/UVA/H_2O_2 photocatalysis. In addition to these, R^2_{adj} values of Model 1 and Model 2 (Tables 3 and 4) proved that the Box–Behnken experimental design

Table 4
ANOVA test responses for Y_2 (with H_2O_2)

Source	Sum of squares	Degree of freedom	Mean square	*F* Value	*p* Value
Model	5,553.56	9	617.06	636.87	<0.0001[a]
x_1, pH	32.53	1	32.53	33.58	0.0020
x_2,TiO_2	410.10	1	410.10	423.26	<0.0001
x_3,H_2O_2	62.77	1	62.77	64.79	<0.0001
x_1^2	4,060.09	1	4,357.47	4,497.33	<0.0001
x_2^2	71.46	1	109.62	113.14	<0.0001
x_3^2	704.27	1	704.27	726.87	<0.0001
x_1x_2	5.29	1	5.29	5.46	0.0670
x_1x_3	202.25	1	202.25	208.74	<0.0001
x_2x_3	4.80	1	4.80	4.96	0.0770
Residual	4.84	5	0.97		
Lack of fit	4.56	3	1.52	10.79	0.0860[b]
Pure error	0.28	2	0.14		
Total	5,558.40	14			
	$R^2 = 0.9991$		R^2(pred) = 0.9868	R^2(adj) = 0.9976	

[a] Statistically significant.
[b] Statistically insignificant.

choice was correct in the statistical analysis of experimental studies.

A normal probability plot and histograms of the residuals for the degradation efficiency of 2,4-D are shown in Fig. 2(a) without H_2O_2, and with H_2O_2 in Fig. 2(b). The data points on this plot were close to a straight line, supporting the conclusion that the underlying assumptions of the analysis were satisfied [14]. In addition, histogram diagrams pointed out that the residuals were in the proximity of straight diagonal line. Therefore, the developed models were considered to be adequate since residuals for prediction of each response were low [14]. As shown in Table 3, all variables were statistically significant without interaction of pH (x_1) and initial 2,4-D concentration (x_3) ($p < 0.05$). According to Table 4, the interaction between pH (x_1) and TiO_2 (x_2), (x_1x_2), and the interaction between TiO_2 concentration (x_2) and H_2O_2 concentration (x_3), (x_2x_3), were statistically insignificant ($p > 0.05$). TiO_2 concentration and pH had a more significant effect than 2,4-D concentration on the 2,4-D degradation efficiency, according to single terms in the regression model in Table 3. Kaur et al. [9] stated that coefficient of TiO_2 concentration was high, and that improved the degradation effect of TiO_2 parameter. Furthermore, as shown in Table 4, TiO_2 concentration and later H_2O_2 concentration values had a more significant effect than pH on herbicide degradation. In addition, the synergistic effect of pH and H_2O_2 concentration was highly effective in herbicide removal.

3.3. Optimization of multiple responses

For Model 1, negative quadratic factors of catalyst load, initial herbicide concentration and pH in the polynomial expression confirmed that optimal concentrations of all parameters were intermediate values (around 1.20 g L^{-1}, 32 mg L^{-1}, and 5.70, respectively). Hence, very high and very low values for all parameters inhibited herbicide degradation. For Model 2, negative quadratic factors of catalyst load and peroxide concentration in the polynomial expression confirmed that the optimal concentrations of both parameters were intermediate values (around 1.34 g L^{-1} and 161 mg L^{-1}, respectively). In this way, very high and very low values of TiO_2 and H_2O_2 inhibited herbicide degradation [35]. Also, TiO_2 was the most significant term ($F = 761.60$) for a single independent variable in the removal of herbicide in Model 1 and Model 2. However, in Model 1 it was closely followed by pH ($F = 611.53$).

Fig. 3(a) shows the interaction of pH and TiO_2 concentration on the removal efficiency of 2,4-D. Degradation rate of 2,4-D gradually increased when both pH value and TiO_2 concentration increased; however, trend of 2,4-D degradation rate decreased when pH increased beyond the optimum level (pH 5) at varying experimental levels of TiO_2. Herbicide degradation increased with the level of catalyst concentration increasing under a pH of 5. A low amount of catalyst also resulted in a lower herbicide degradation percentage. Minimum herbicide removal was observed at low pH and low catalyst dose. Hence, at higher pH values, the oxidizing radicals were rapidly scavenged and they could not react with herbicide molecules [36]. Fig. 3(b) shows that degradation rate of 2,4-D increased when TiO_2 concentration and initial 2,4-D concentration increased. However, degradation rate trend for 2,4-D decreased at high TiO_2 concentrations and initial 2,4-D concentration. Interaction effects of pH value and 2,4-D initial concentration on the degradation rate of 2,4-D depicted a bell-shaped response surface (Fig. 3(c)). With the pH value and 2,4-D concentration up to optimum points, degradation rate approached the maximum level. Quadratic term of pH and initial 2,4-D concentration had a positive coefficient and their combined increase lead to faster herbicide degradation. As shown in Fig. 3(d), 2,4-D degradation increased at acidic

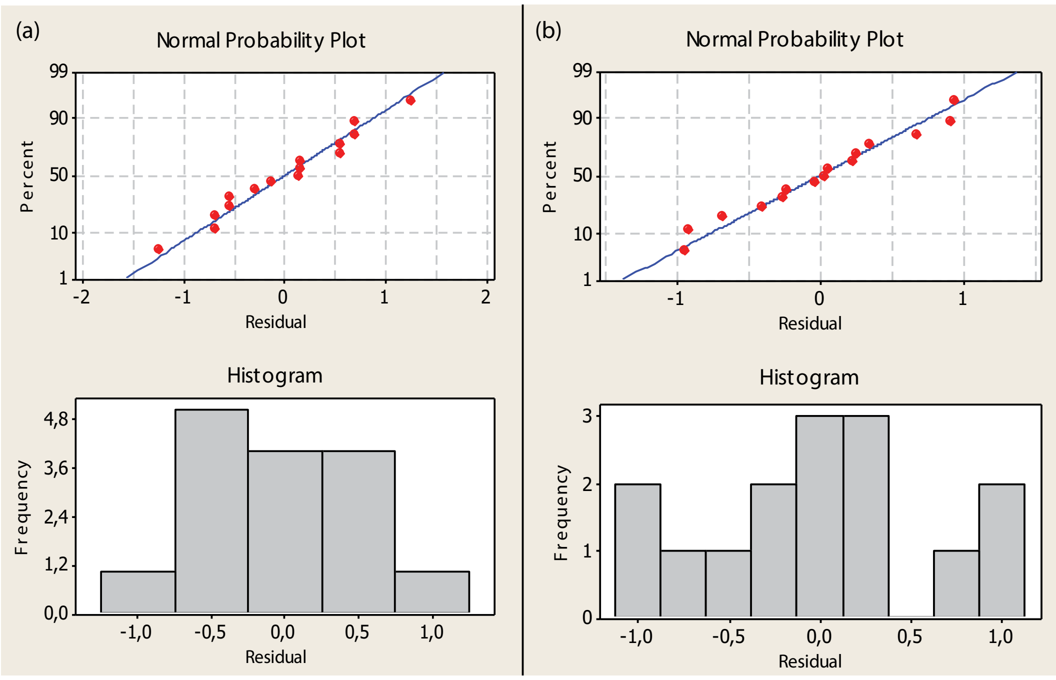

Fig. 2. Normal probability plot for percentage degradation and histograms of residuals (a) in absence of H_2O_2 (b) in presence of H_2O_2.

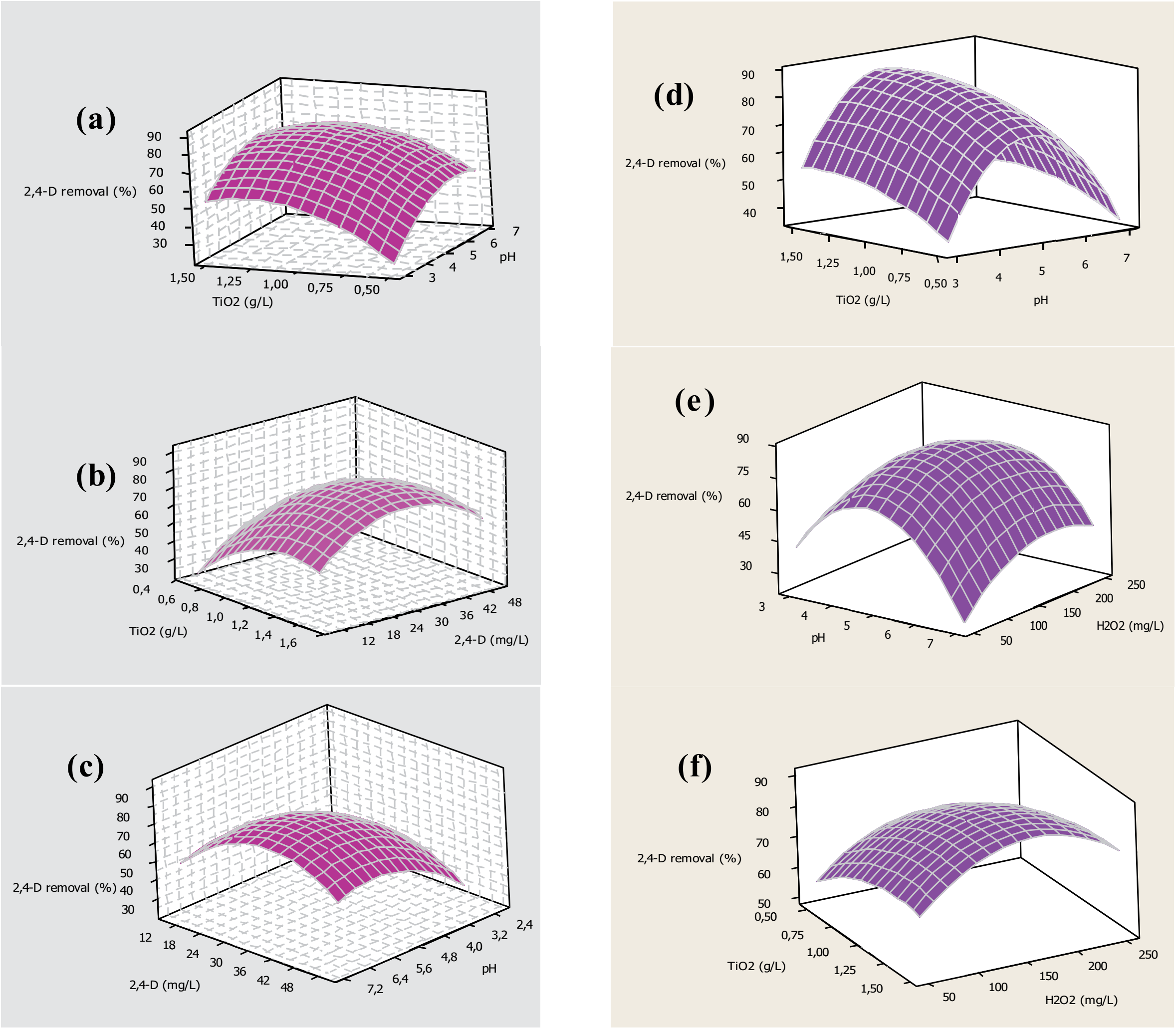

Fig. 3. Effect of pH, TiO_2 concentration, initial 2,4-D concentration and H_2O_2 concentration, on degradation efficiency of 2,4-D (a) initial 2,4-D concentration is constant at 30 mg L^{-1}; (b) pH is constant at 5; (c) TiO_2 concentration is constant at 1 g L^{-1}. Effect of pH, TiO_2 concentration, and H_2O_2 concentration on degradation efficiency of 2,4-D (d) H_2O_2 concentration is constant at 150 mg L^{-1}; (e) TiO_2 concentration is constant at 1 g L^{-1}; (f) pH is constant at 5.

region when TiO_2 concentration increased. In Figs. 3(d)–(e), according to pH-TiO_2 and pH-H_2O_2 surface plots, 2,4-D herbicide degradation increased with increasing pH and then the degradation decreased. At pH values lower than optimal, oxidation of organic contaminants was reduced due to less hydroxyl radical production. H^+ ion production could decrease and this lead to less hydroxyl formation under optimum pH conditions [15]. Removal of 2,4-D herbicide increased to a maximum point and then it began to decrease (Figs. 3(e)–(f). As expected, increase in H_2O_2 concentration removed radicals in aqueous solution, leading to a decrease in herbicide degradation.

4. Conclusions

This study showed the efficiency of photocatalytic degradation of 2,4-D when a P25 TiO_2 catalyst and an H_2O_2 oxidizing agent was employed. The study clearly showed that BBD was an appropriate method to successfully optimize operating conditions for the photocatalytic degradation of 2,4-D. The multivariate experimental designs were employed to establish two quadratic models showing the functional relationship between degradation efficiency of 2,4-D and four independent variables. For Model 1, the combined effect of a pH value of 5.70, a TiO_2 concentration of 1.20 g L^{-1}, and an initial 2,4-D concentration of 32 mg L^{-1} yielded the highest degradation efficiency of 78.10%. whereas for Model 2, the optimum condition yielding the highest degradation efficiency of 86.63% was a pH of 4.94, a 1.34 g L^{-1} concentration of TiO_2 and a 161 mg L^{-1} concentration of H_2O_2. For both models, optimum values obtained from the BBD process were in agreement with the single factor batch photocatalysis process results (pH of 5, 1.5 g L^{-1} concentration of TiO_2, an initial 2,4-D concentration of 25 mg L^{-1}, and a 150 mg L^{-1} concentration of H_2O_2).

Acknowledgments

This study was financially supported by AIBU Scientific Research Project Number: 2016.09.02.1032. The authors would like to thank TUBITAK for the Ph.D. Dissertation Grant given to Gamze Dogdu Okcu within the 2211/A National Doctoral Scholarship Program.

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