IJEPEM

Int. J. of Environmental Pollution & Environmental Modelling, Vol. 2(4): 186-195 (2019)
(Original Paper)

The Sonocatalytic Degradation of 2,4-Dichlorophenoxyacetic acid (2,4-D) Herbicide Using Taguchi Experimental Design

Emre Dikmen[1], Gamze Doğdu Okçu[2*], Arda Yalçuk[2]

[1] Department of Environmental Engineering, Bolu Abant Izzet Baysal University, 14030, Golkoy Campus, Bolu
[2] Department of Environmental Engineering, Bolu Abant Izzet Baysal University, 14030, Golkoy Campus, Bolu

E-Mail: *emredikmen@ibu.edu.tr, gamzedogdu@ibu.edu.tr, ayalcuk@gmail.com*

Abstract: In recent times, the most commonly used herbicide for cleaning weeds in agricultural areas has been based on 2,4-Dichlorophenoxyacetic acid (2,4-D), and increases in its production is particularly alarming for the whole ecological system, especially in terms of human health, and it needs to be removed from sources of water. To achieve this, discrete 2,4-D removal by a sonocatalytic method (sonolysis with a TiO_2 catalyst) has been investigated. In this study, the individual and synergic effects of a TiO_2 dose, the pH, the time and initial 2,4-D concentration factors were investigated. In addition, a Taguchi statistical method was applied to optimize the effective parameters. As a result of the study, it was observed that pH was the most effective parameter for 2,4-D degradation. According to the results obtained from the Taguchi statistical method, the optimum conditions for 2,4-D removal are A (pH) with a value of 2 at level 1, B (TiO_2 concentration) with a value of 0.5 g/L at level 2, C (initial 2,4-D concentration) with a value of 75 mg/L at level 4 and D (time) with a value of 60 minutes at level 1. The results presented by the theoretically predicted value for 100% degradation efficiency were confirmed by the experimental values.
Keywords: 2,4-Dichlorophenoxyacetic acid (2,4-D), Degradation rate, Optimization, Sonocatalysis, Taguchi method

INTRODUCTION

Nowadays pollution of surface and groundwater resources with pesticides is one of the most important environmental problems [1]. Pesticides are generally used to increase yield in agricultural activities [2]. In many countries, intensive agricultural activities due to the use of harmful pesticides and/or herbicides pollute surface water (rain water surface flow), soil (crops) and air (spray applications) [3]. Pesticide wastes caused by production facilities, storage areas, agricultural lands and surface runoff cause contamination of the aquatic environment, while the waters contaminated with this pollution cause effects on the nervous system (vegetative syndrome), respiratory system (bronchial asthma) and skin (eczema etc.) [4]. Therefore, it is vital to treat the wastewater at its source before being released into the natural environment [4]. Chlorophenoxyacids are a subgroup of herbicides and are used extensively worldwide for the control of grain crops, grasslands and weeds in grass [5]. The chlorophenoxyacetic group includes 2,4-Dichlorophenoxyacetic acid (2,4-D) and has a high toxicity for living organisms. It was the first commercial herbicide introduced to the market for control of broad-leaved weeds in the 1940s; due to its low cost, selectivity, efficacy and wide range of weed control, it remains one of the most widely used herbicides worldwide [6]. Because of the toxic properties of this herbicide and the difficulties of biodegradation, conventional treatment processes are insufficient [7, 8].

For this reason, the advanced oxidation processes (AOP), which have been widely used in the treatment of stable pollutants in recent years, are the innovative technologies for the disintegration and mineralization of pollutants (conversion of organic pollutants to CO_2, H_2O and mineral acids) [9,10]. AOPs include processes such as fenton, photofenton, sonolysis, photocatalysis and ozonation [11-14]. Like other advanced oxidation processes, sonolysis is also an environmentally friendly treatment method for the breakdown of organic compounds. During this process, micro-bubbles are generated, enlarged and eventually precipitated by using ultrasonic sound waves to produce acoustic cavitations. Sonolysis leads to the separation of water molecules into H• and •OH radicals (Eq. 1) [9,15].

Corresponding E-mail: gamzedogdu@ibu.edu.tr, +90 3742101000(4905)

$$H2O \rightarrow))) \bullet OH + \bullet H \quad \text{(Equation 1)}$$

$$\bullet OH + \bullet OH \rightarrow H2O2 \quad \text{(Equation 2)}$$

$$\bullet H + \bullet H \rightarrow H2 \quad \text{(Equation 3)}$$

•OH radicals are one of the strongest oxidants that can attack and break down almost all organic pollutants and eventually convert them into H_2O and CO_2 [16]. Sonolysis on its own requires long treatment times, consequently its need for electrical energy increases. Sonocatalysis is one of the most promising methods to shorten the treatment time and reduce the need for energy [17].

Semiconductors such as TiO_2, ZnO, etc. are used as catalysts in the sonocatalysis process for the treatment of pollutants. The advantages of catalysts are their large surface areas, low cost and low degrees of toxicity [18]. The reason for choosing TiO_2 as a catalyst in this study is that it shows high stability in reactions, high yield, low cost, is non-toxic and easy to apply [19]. Because of all these advantages, catalysts break down organic contaminants to low concentrations and provide high pollutant removal efficiency.

The Taguchi method is an approach used to design experiments [20]. The orthogonal sequences used in this method reduce the total number of experiments and significantly reduce the cost [20]. Taguchi analysis can also determine the general trend of feature factors using control factors. Taguchi analysis shows the contribution of individual factors and can be used to estimate the optimal experimental design [21]. Taguchi experimental design and analysis includes the following 5 stages: (A) defining variables (quality characteristics), (B) determining control factors affecting the quality characteristics, (C) selecting levels for control factors, (D) choosing an orthogonal array by number of factors and levels (E) conducting the designed experiments and analyzing the results. After the Taguchi process, variance analysis (ANOVA) can then be applied to determine the percentage of the contribution of individual control factors [22].

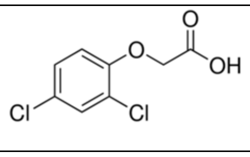
The aim of this study was to observe the degradation of 2,4-Dichlorophenoxyacetic acid (2,4-D) herbicide by using the sonocatalysis (Ultrasonic sound + TiO_2 catalyst) process. The Taguchi method was used for statistical optimization. The variable values examined in the Taguchi method are pH, TiO_2 concentration, time and initial concentration. Following the experiments conducted using the Taguchi method, the results of the ANOVA tests were examined and a regression model was established by a “Stepwise" method”.

MATERIALS AND METHODS

Chemicals

In the experiments, TiO_2 (Sigma-Aldrich Inc., St. Louis, MO; Art. No. 14021) was used as the catalyst. The commercial Amin EXT 500 SL 2,4-D amine salt $C_{10}H_{13}C_{12}N0_3$, MW: 266.12 $gmol^{-1}$ (equivalent to 500 gL 2,4-D), which is the pesticide being removed by the treatment, was obtained from the Agrofarm® Company. The chemical properties of 2,4-D are given in the Table 1. Other chemicals such as NaOH and H_2SO_4 (97%) used to adjust the pH were obtained from Merck (Darmstadt, Germany). All chemicals were used as received without additional treatment. Purified water was used in all solutions and reaction mixtures (Specific Resistance: 18.2 MΩ cm^{-1}; Merck Millipore, Burlington, MA).

Table 1. Chemical structure of 2,4-D

Name	Molecular structure	Chemical Structure
2,4-Dichlorophenoxyacetic Acid	$C_8H_6Cl_2O_3$	

Experimental procedure and analysis

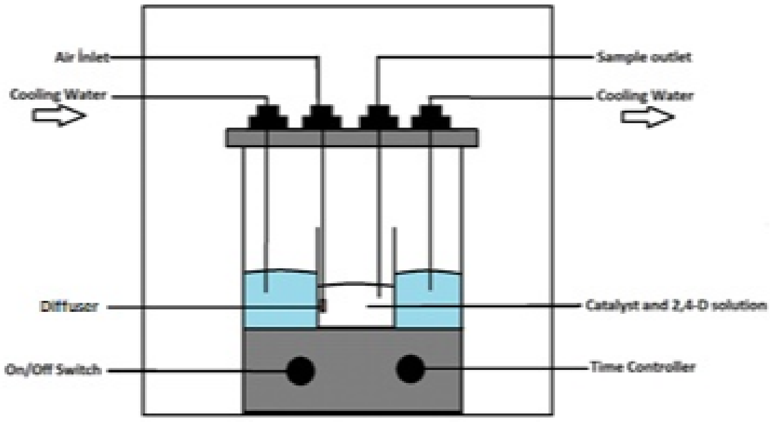


Figure 1. Schematic diagram of the sonocatalytic reactor

In the sonocatalytic experiments, an ultrasonic sound bath (Bandelin DT 106) was used. The device has a cylindrical structure with a total volume of 5.6 L (an operating volume of 1 L), with an operating frequency of 35 kHz (220V). In the study, the reactor was run in batch mode, and the reactor temperature was kept constant at 35 ± 1°C with a continuous water bath and cold water pump. During the experiments, air was supplied to the system with the help of a diffuser with a capacity of 3.5 L/min. For the experiments, the preferred concentrations of 2,4-D solution were prepared daily in amber-glass volumetric flasks from a 1000 mg/L stock solution. The pH of the reaction mixture was adjusted by the addition of 1 N of NaOH and 1 N of H_2SO_4. The samples were centrifuged at 5000 rpm for 15 minutes to remove TiO_2 from the solution, followed by filtration through a 0.45 mm syringe filter. Optimization of the conditions for sonocatalysis was obtained by measuring the optical density (OD) of the samples at 283 nm, the maximum wavelength of 2,4-D**,** using a spectrophotometer (Shimadzu, PharmaSpec UV-1700). A calibration plot based on Beer-Lambert's law was established by relating the absorbance to the concentration. This was also confirmed by a spectrum reading from a spectrophotometer. The percentage of degradation of 2,4-D was calculated using Eq. 4:

$$\text{Degredation percentage of } 2{,}4-\text{D} = \frac{\text{Ci}-\text{Cf}}{\text{Cf}} \qquad \text{(Equation 4)}$$

Ci = Initial 2,4-D concentration
Cf = Final 2,4-D concentration

Experimental design

The Taguchi design was developed by Genichi Taguchi to study multiple factors with various factor levels based on an orthogonal sequence [23]. The Taguchi method uses systematic orthogonal arrays (OA) to design experiments. The OA is a method where the columns for the independent variables are "orthogonal" to one another [24]. This design recommends three steps to achieve an optimal design (concept design, parameter design and tolerance design [25]. The main purpose of the Taguchi method is to find the best combination of design parameters.

Table 2. Process parameters and levels

Parameters	Symbol	Level 1	Level 2	Level 3	Level 4	Level 5
pH	A	2	4	6	8	10
TiO_2 concentration (g/L)	B	0	0.5	1	1.5	2
2,4-D concentration (mg/L)	C	10	25	50	75	100
Time	D	60	120	150	180	210

In this study, a Taguchi experimental design technique was applied to optimize the 4 parameters (pH, initial 2,4-D concentration, treatment time and initial TiO_2 concentration) to be used for the treatment of 2,4-D. In order to find the optimum conditions, 25 parameters (a total of 50 with the control set) were tested and the optimum values for removing 2,4-D were obtained. Minitab software (version 17-trial edition) was used for the Taguchi experimental design and the signal-to-noise ratio (S / N) was recorded at all levels for various factors. The desired value for the output was termed as the signal (S) while noise (N) represented the value that was not needed for the output characteristic. The S/N ratio i.e. the ratio of the signal to the noise was used to quantify how a specific quality characteristic deviated from the desired value [26]. Depending on the characteristics in published literature there are several categories of S/N ratios used: low best (LB), nominal best (NB) and high best (HB) [27]. In this study, HB characterization was adopted to determine the 2,4-D treatment efficiency.

RESULTS AND DISCUSSION

Determination of optimal conditions using the Taguchi Method

In this study, Taguchi's L25 design was used and the test results are presented in Table 3. In the experiments, the range of 2,4-D removal yield was between 0% and 91.45%. The Taguchi design is considered a method with an accurate estimation rate. The controlled variables in these experiments are pH, initial 2,4-D concentration, TiO_2 concentration and time. S/N ratios were determined using these variables and optimum 2,4-D removal results were obtained.

Table 3. Full factorial design with Taguchi L_{25} (5^4) orthogonal array

Exp. no.	Factor A	Factor B	Factor C	Factor D	Response (%)	S/N (dB)	Mean Value
1	1	1	1	1	54.67	21.86	54.67
2	1	2	2	2	91.45	36.58	91.45
3	1	3	3	3	77.10	30.84	77.10
4	1	4	4	4	87.84	35.13	87.84
5	1	5	5	5	42.85	17.14	42.85
6	2	1	2	3	52.41	20.96	52.41
7	2	2	3	4	71.66	28.66	71.66
8	2	3	4	5	71.77	28.70	71.77
9	2	4	5	1	86.26	34.50	86.26
10	2	5	1	2	0	0	0
11	3	1	3	4	22.14	8.85	22.14
12	3	2	4	5	67.42	26.96	67.42
13	3	3	5	1	52.76	21.10	52.76
14	3	4	1	2	0	0	0
15	3	5	2	3	0	0	0
16	4	1	4	5	25.83	10.33	25.83
17	4	2	5	1	50.51	20.20	50.51
18	4	3	1	2	0	0	0
19	4	4	2	3	0	0	0
20	4	5	3	4	0	0	0
21	5	1	5	1	8.03	3.21	8.03
22	5	2	1	2	12	4.8	12
23	5	3	2	3	51.75	20.7	51.75
24	5	4	3	4	23.4	9.6	23.4
25	5	5	4	5	14.75	5.9	14.75

The desired value for the output is referred to as signal (S), while noise is expressed as (N). The S/N ratio, i.e. the ratio of signal to noise, is used to measure how a certain quality property deviates from the desired value [28]. In this study, the aim was to determine the maximum treatment efficiency for 2,4-D herbicide. Therefore, "The larger the feature the better" formula was applied to define the S/N ratios.

$$\frac{S}{N}[dB] = -10log\left[\frac{1}{n}\sum_{i-1}^{n} {}^{1}/_{yi2}\right] \quad \text{(Equation 5)}$$

yi: characteristic property
n: number of experiments

The average S/N ratio for each level of the parameters is summarized as the S/N response shown in Table 4.

Table 4. S/N response table for % removal of 2,4-D

Levels	**Control factors**			
	% removal of 2,4-D			
	A	B	C	D
Level 1	**36.64**	26.78	11.27	**28.87**
Level 2	29.34	**33.64**	21.63	25.92
Level 3	19.59	28.72	25.70	25.91
Level 4	12.46	20.93	**32.78**	16.94
Level 5	23.25	11.20	29.90	23.65
Delta	24.18	22.44	21.51	11.93
Rank	1	2	3	4

*Bold values shows the optimal levels for control factors

The optimum control factors are A1, B2, C4 and D1. Using these optimal control factors: (A) a pH of 2 at level 1, (B) a TiO_2 concentration 0.5 g/L at level 2, (C) an initial concentration of 75 mg/L of 2,4-D at level 4 and (D) a time of 60 minutes at level 1, it is estimated that treatment can be carried out to achieve 100% removal of the herbicide.

Statistical analysis

The analysis of variance (ANOVA) is a method used to determine the difference between group means or process averages of data from independent or dependent groups [29]. Table 5 shows the results of ANOVA for 2,4-D removal as a result of sonocatalysis.

Table 5. ANOVA results resulting from the Taguchi method and regression equations

Factors	**For the Taguchi method**				
	df	**Adj SS**	**Adj MS**	**F-value**	**P-value**
pH (A)	1	19253.4	19253.4	30.94	0.000
TiO_2 concentration (g/L) (B)	2	25002.11	12501.05	24.35	0.000
2,4-D concentration (mg/L) (C)	3	28378.42	9459.47	20.97	0.000
Time (D)	4	31229.54	7807.38	19.36	0.000

The importance of the experimental parameters was determined by using variance analysis. The analysis was evaluated for a 95% confidence level. P values less than 0.05 indicate that the parameters are statistically significant. Because there are more than 2 groups, the ANOVA F values were examined. The most effective factors were selected according to these F values.

The ANOVA values in Table 5 show that the most important factor contributing to 2,4-D removal is pH (A), followed by TiO_2 concentration (B), the initial 2,4-D concentration (C) and time (D), respectively.

Process parameters in the removal of 2,4-D are shown in Figures 2 and 3. As depicted in Figure 2, the pH concentration plays an important role in the sonocatalysis process. In the study, 5 different values of pH between 2 and 10 were tested. The pH value has been frequently observed to be related to sonocatalytic degradation efficiency due to its dependency on charged substrates such as pesticides. The S/N value was found to be larger at a pH value of 2 as shown in Figure 2 and Figure 3. After this point, the S/N ratio decreases at a faster rate, which means the degradation of the herbicide is more efficient at lower pH value. The load on the TiO_2 surface depends on the pH as a result of the amphoteric properties of the surface [30]. The point of zero charge (pH_{zpc}) for TiO_2 is approximately at a pH of 6.5 and the pKa of 2,4-D herbicide is 2.73, hence negatively charged molecules are more readily degraded at acidic pH values when the photocatalytic surface is positively charged [31,32]. Accordingly, the S/N ratio was found to be higher in acidic conditions and the highest S/N ratio was obtained at a pH of 2. Similarly, Cai et al., 2018 [33], treated the 2,4-D using the thermally activated persulfate oxidation method in the pH parameter range of 3 to 12 and observed that the optimum 2,4-D removal was achieved at a pH value of 3.

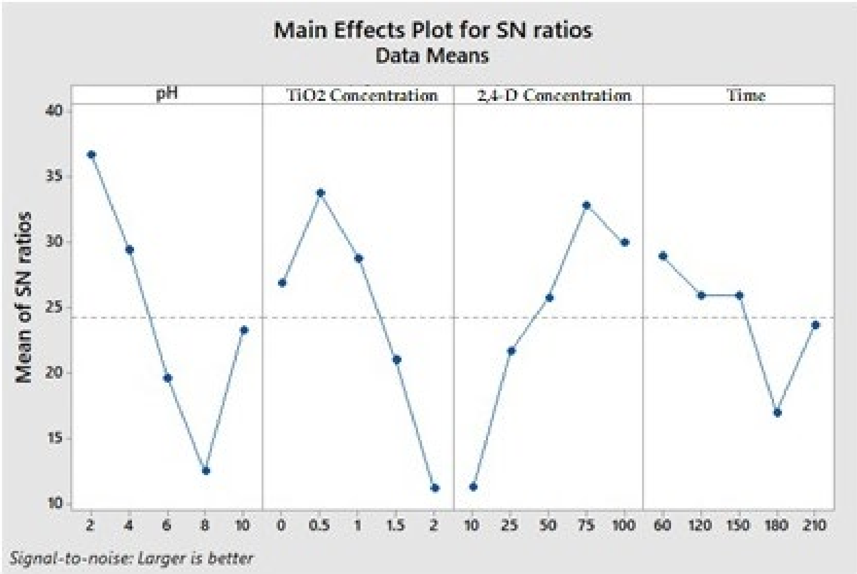


Figure 2. Effects of process parameters on S/N in the sonocatalysis process

Another parameter examined after pH was the TiO_2 concentration. Five different TiO_2 concentration values were tested between 0 g/L and 2 g/L as shown in Figure 2, with the catalyst concentration increasing in 0.5 g/L steps. The degradation of 2,4-D increases with increasing concentration because, with an increasing amount of catalyst, more 2,4 D molecules are adsorbed onto the catalyst surface and herbicide removal in the area of treatment increases. However, it was observed that above a certain concentration (0.5 g/L), the formation of catalyst clusters occurred that lead to active sites on the catalyst surface that are inaccessible [34,35]. The TiO_2 concentration at which the 2,4-D removal is optimal is 0.5 g/L. TiO_2 particles become saturated with the degrading molecules and increasing the catalyst concentration beyond a certain limit – which is 0.5 g/L in this case – does not increase the photodegradation efficiency [36]. Rong[37], in his study in 2016, treated Methyl Orange dye with the sonocatalytic method at an optimum concentration of 1 g/L across a range of TiO_2 catalyst concentrations from 0 g/L to 2 g/L.

Another parameter studied was the 2,4-D initial concentration. The experiment tested the initial concentration of 2,4-D in the range from 10 to 100 mg/L. As seen in Figure 2, the S/N ratio decreased as the concentration increased, and this rate reached a maximum 2,4-D concentration of 75 mg/L. However, when the 2,4-D concentration was increased from 75 mg/L to 100 mg/L, the S/N ratio sharply decreased. Bian et al., 2013[38], treated 2,4-D using TiO_2 by photocatalysis. In this study, the initial concentration was between 20 mg/L and 100 mg/L, and the optimum removal concentration of the target pollutant was found to be 40 mg/L.

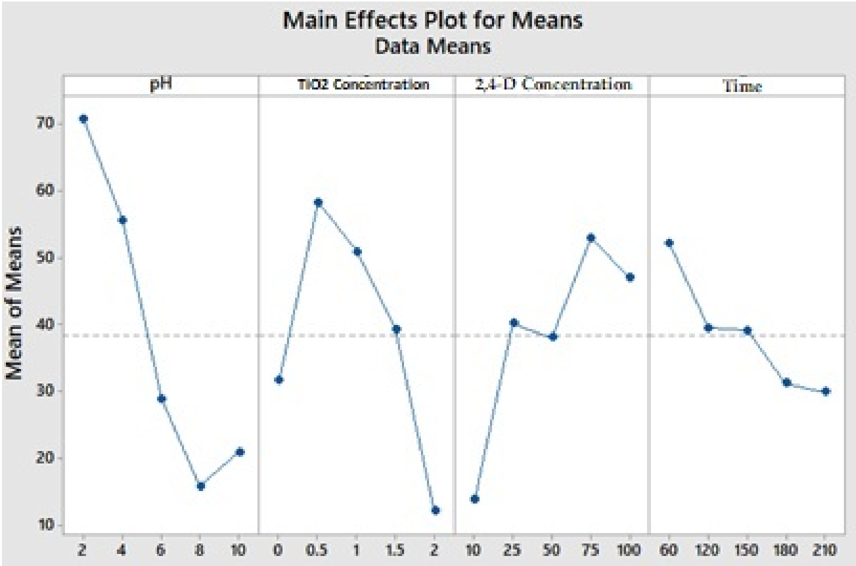


Figure 3. Effect of process parameters on the Means in the sonocatalysis process

The last parameter examined was the treatment time. As shown in Figure 2, the study period was chosen from between 60 to 210 minutes and the highest yield was obtained after 60 minutes. After 60 minutes, the efficiency of 2,4-D removal was sharply reduced, This is similar to the results obtained by Musterman et al.[39] who obtained an optimum duration time of 60 minutes in their sonocatalytic experiments using the TiO_2 catalyst to purify Methyl Orange dye.

The results of the multivariable regression model

A multivariate linear regression model analysis was performed to determine the effects of pH, TiO_2 concentration, time and initial 2,4-D concentration on 2,4-D removal. SPSS (17.0 version) software was used to prepare the regression model. A “stepwise” model was used to create multiple regression models and is presented in Table 6.

Table 6. The multivariable regression model for 2,4-D removal

Model	R	R^2	Adjusted R^2
1	0.626	0.392	0.379
2	0.713	0.509	0.488
3	0.760	0.578	0.550
4	0.797	0.636	0.603

Model 1: (Constant), pH_a
Model 2: (Constant), pH, Initial 2,4-D concentration $_b$
Model 3: (Constant), pH, Initial 2,4-D concentration, TiO_2 concentration $_c$
Model 4: (Constant), pH, Initial 2,4-D concentration, TiO_2 concentration, Time $_d$
As shown in Table 6, pH was statistically significant for the 2,4-D concentration, TiO_2 concentration and 2,4-D herbicide removal time parameters ($p < 0.05$). Model 4 had the highest R^2 ratio with 64%. For this reason, it was decided to use Model 4 as the estimation model.

Table 7. The coefficients of variables in Model 4

Variables	**Non-standardized Coefficients**		**Standardized Coefficients**	**T**	**P**
	B	Std. Error	Beta	t	p
Constant	96.174	11.904		8.079	0.000
pH	−6.938	0.997	0.626	6.959	0.000
Initial 2,4-D conc. (mg/L)	0.328	0.086	0.342	3.802	0.000
TiO_2 conc. (g/L)	−11.621	3.988	0.262	2.914	0.006
Time	−0.146	0.055	0.241	2.678	0.010

Table 7 summarizes the data of the coefficients of the variables used in Model 4. It is seen that t-test results for regression are in the same order as the Taguchi method and all factors were found to be statistically significant, since all of them below $p < 0.05$. When T values are considered, it is seen that the one with the highest estimated power is pH with $t = -6.959$. The pH is followed by the initial concentration, TiO_2 concentration and time, respectively. When we look at the coefficients, the pH, TiO_2 and time variables have an antagonistic effect in terms of removal. Accordingly, as the pH, TiO_2 and duration parameters increased, the 2,4-D removal efficiency decreased, and this was confirmed by the Taguchi model. The estimation model generated using the coefficients of the variables are as follows:

$$Y = 96.174 - 6.938 * (pH) + 0.328 * (\text{Initial 2,4-D concentration}) - 11.621*(TiO_2 \text{ concentration}) - 0.146*(\text{Time})$$

CONCLUSIONS

The results obtained in this study proved that 2,4-D, one type of herbicide, can be successfully removed by sonocatalysis. According to the ANOVA results, the treatment of 2,4-D was found to be dependent on pH, TiO_2 concentration, initial 2,4-D concentration and time. The optimum conditions for the treatment of 2,4-D, according to the Taguchi method, are A (pH) with a value of 2 at level 1, B (TiO_2 concentration) with a value of 0.5 g/L at level 2, C (initial 2,4-D concentration) with a value of 75 mg/L at level 4 and D (time) with a value of 60 minutes at level 1. According to the "stepwise" regression study, model 4 with the highest R2 value was chosen. It shows that pH is more effective than the other experimental parameters. In the experiments, it is seen that the estimated rate from the Taguchi method (100%) is proven.

ACKNOWLEDGMENTS

This study is supported by Bolu Abant Izzet Baysal University Scientific Research Projects Coordination Unit. Project Number: 2018.09.02.1346.

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