O 35. INVESTIGATION OF PARAMETERS AFFECTING THE ADSORPTION PROPERTY OF PHOTOCATALYST IN THE REMOVAL OF ENDOSULFAN USING PHOTOCATALYSIS PROCESS

Mehmet Turkyilmaz[1*], Sezen Kucukcongar[1]

1Konya Technical University, Department of Environmental Engineering, Konya, Turkey

E-mail*: aaaaaa mturkyilmaz@ktun.edu.tr, skucukcongar@ktun.edu.tr*

ABSTRACT: The adsorption of organic pollutants is a prerequisite for a higher and efficient photodegradation process. Higher adsorption by the photocatalyst facilitates the degradation of the pollutants. Adsorption improves interfacial interactions between organic pollutant molecules and photocatalyst to increase the photosensitivity capability. In this study, the removal of endosulfan by the adsorption process of Ag/TiO2/Fe3O4 photocatalyst was investigated. In order to determine the effects of endosulfan concentration, pH and catalyst amount parameters on the removal efficiency, the experimental design and optimization of the adsorption process using the Taguchi method and analysis of variance were performed. As a result of the highest S/N ratios obtained on the basis of parameters, 4 mg/L endosulfan concentration, pH 4 and 0.3 g/L catalyst amount were determined as optimum, and 85.02% removal efficiency was achieved. When the parameter effects on the removal efficiency are evaluated, the most effective parameters are the endosulfan concentration, pH and catalyst amount, respectively. The fcritical value showed that the endosulfan concentration was statistically effective on the removal. The error caused by uncontrollable factors remained below 50%, showing that the errors were not significant. When the %P values were examined, it was determined that there was a significant difference between the levels of endosulfan concentration and pH factors.

Keywords: Endosulfan, Adsorption, Ag/TiO2/Fe3O4, Experimental design, Taguchi Method

1. INTRODUCTION

Persistent organic pollutants (POPs) are compounds that are resistant to photolytic, chemical and biological degradation in aquatic environments, can be detected in environmental matrices for many years due to their high half-life, can bio-accumulate due to their high lipophilicity, have high toxicity even at low concentrations, and as a result, they have long-range transport(Marican & Durán-Lara, 2018). Endosulfan is one of the most recent persistent organic chemical substances to be restricted under the Stockholm Convention, so its presence in environmental matrices is estimated to be high levels (UNEP/FAO/RC/CRC, 2010). Conventional treatment methods (such as coagulation- flocculation, activated sludge process, filtration and oxidation with chemicals such as chlorine, adsorption, membrane treatment) may not be effective in removing POPs from waters (Kumari, Bahadur, & Dumée, 2020). For this reason, various advanced water treatment technologies called advanced oxidation processes (AOP) are applied in the removal of POPs as they provide faster degradation kinetics as well as high removal efficiency. In recent years, greener technologies have been used more widely, therefore, it is preferred to use methods that reduce new waste generation after treatment, minimize the formation of by-products, and have lower energy and investment/operation costs. Heterogeneous photocatalytic processes, which can be used in existing reactors, are more environmentally friendly, green processes that can be applied using the addition of photocatalyst and a light source, provide the mineralization of organic materials without creating a new waste, and can operate with low energy consumption. In advanced oxidation processes, factors such as turbidity of water, solution pH, reaction time, amount/volume of degradable organic compound can significantly affect the decomposition activity of hydroxyl radical (•OH) (Badmus, Tijani, Massima, & Petrik, 2018).

In the photodegradation process, besides the band gap and the light source, the adsorption capacity of organic pollutants on the photocatalyst surface is also important. Higher adsorption by the photocatalyst facilitates the degradation of the pollutants. Adsorption improves interfacial interactions between organic pollutant molecules and photocatalyst to increase the photosensitivity capability (Tachikawa, Fujitsuka, & Majima, 2007). There are studies that conclude that the adsorption of organic pollutants is a prerequisite for a higher and efficient photodegradation process. Guo et al. (2016) showed that for Rhodamine B and methyl orange dyes, the photodegradation ability of fluorinated TiO_2 (f-TiO_2) is related to the adsorption on f-TiO_2. Adsorption of organic pollutants by the photocatalyst is very important for their efficient degradation, as adsorption or interfacial interaction facilitates electron injection. As a result, complete degradation of organic pollutants makes the photocatalytic degradation process a more advantageous approach compared to adsorption. However, to achieve an excellent photodegradation rate, efficient adsorption of organic pollutants is also required (Gusain, Gupta, Joshi, & Khatri, 2019). Ismael et al. (2020) reported that there are two steps in the photocatalysis of pesticides, which are (i) adsorption onto the nanocomposite surface followed by (ii) photodegradation in the presence of UV radiation.

In this study, the effects of different initial ambient conditions on the adsorption efficiency of the photocatalyst were investigated in the removal of endosulfan by the photocatalysis process. TiO_2, which was synthesized together with Fe_3O_4 and doped with silver as a noble metal, was used as a photocatalyst in order to provide magnetic properties to the nanomaterial, to increase the removal efficiency and to ensure high efficiency under different radiations (UV-A, UV-C and visible light). Initial solution pH, photocatalyst amount and initial endosulfan concentration were selected as different ambient conditions, and Taguchi experimental design and analysis of variance (ANOVA) methods were applied to determine their effects on the adsorption of endosulfan.

2. MATERIAL AND METHOD

2.1. Material

Nano-sized titanium (IV) oxide (Degussa P25, 50 m^2/g, 75% anatase and 25% rutile), silver nitrate ($AgNO_3$) and, ammonium hydroxide (NH_4OH, 30% v/v aqueous solution) were obtained from Sigma Aldrich; ferrous sulfate heptahydrate ($FeSO_4.7H_20$) and ferric chloride ($FeCl_3$) were obtained from Merck KgaA for the synthesis of photocatalyst. α+β-endosulfan (99.5%) in chromatographic purity for the preparation of standard and stock solutions of endosulfan isomers is purchased from Sigma Aldrich company, acetone used as solvent, high purity n-hexane (C_6H_{14}) used in the extraction of endosulfan isomers and metabolites and, acetonitrile (C_2H_3N) used as carrier phase was obtained from Merck KGaA.

2.2. Method

For photocatalyst synthesis, photochemical deposition method was used for doping TiO_2 with silver, and heteroagglomeration method was used for combining it with Fe_3O_4 . Information on the application of the methods is explained in detail in our previously published study (Turkyilmaz & Kucukcongar, 2022). X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDX - EDS) analyzes were used to examine the structure and surface morphology of the synthesized photocatalyst. It was carried out on devices in the Research and Application Center.

The vortex assisted liquid-liquid micro-extraction (VALLME) method was used for the extraction of endosulfan isomers from the aquatic environment. In the method in which n-hexane is used as the extraction solvent, optimum conditions were applied at maximum vortex speed, 10 mL sample volume, 3 min vortex time and 200 µL solvent volume. Phase separation was carried out by centrifugation at 3000 rpm for 2 minutes, after the extraction. Detailed information about the optimization of the method is given in our previous study (Türkyılmaz & Küçükçongar, 2021). Detection of endosulfan isomers was performed with the Shimadzu Prominence-i 2030-3d HPLC liquid chromatography system. Compounds were monitored using a two-channel UV/VIS/PDA dual absorbance detector separated on a GL Science C18 (250 mm x 3.1 mm i.d.) reversed phase column. The column temperature was used at ambient temperature and the injection was carried out with an autosampler. The mobile phase was formed from acetonitrile:water mixture adjusted to 70:30 by volume at a flow rate of 1 mL/min. The injection volume was determined as 20 µL and endosulfan and its metabolites were detected at 214 nm.

In the batch photocatalysis experiments, photocatalyst was added to the synthetic solution prepared under the initial conditions suitable for the orthogonal array (Table 1) determined according to the Taguchi experimental design method, and first of all, it was ensured that the catalyst reached the adsorption equilibrium by shaking in the dark environment. Afterwards, photocatalysis experiments were carried out using suitable light sources. In this study, it was aimed to examine the effect of different environmental conditions on the efficiency of the adsorption process just before the photocatalysis process. For this purpose, three different levels were determined for three different variables in experimental studies. In the experiments, 3 different levels were applied as 4, 7 and 10 values for the initial pH, 0.1, 0.3 and, 0.5 g/L for the photocatalyst amount and, 2, 3 and, 4 mg/L for the endosulfan concentration. After 30 minutes of adsorption for each experimental condition, the photocatalyst was separated with an external magnet and the endosulfan concentration remaining in the solution was analyzed, and the percentage of removal by adsorption was calculated. According to the results of the experiment, the optimization was made with the Taguchi experimental design method with the "larger is better"; preference and the effects of the parameters were determined using the analysis of variance.

3. RESULTS AND DISCUSSION

3.1. Photocatalyst Characterization

In this study, it was aimed to determine the contribution of the synthesized Ag/TiO_2/Fe_3O_4 catalyst to the removal by adsorption and the effects of the selected control parameters on the adsorption, before the endosulfan removal by the photocatalysis process.

For this purpose, Ag/TiO_2 catalyst was first produced by bonding Ag to TiO_2 by photochemical deposition method. Then, Ag/TiO_2/Fe_3O_4 catalyst was synthesized by connecting Fe_3O_4 to Ag/TiO_2 by heteroagglomeration method. XRD, SEM-EDX, TEM-EDS analyzes were performed to examine the structural properties of the prepared catalysts. The crystal structures and compositions of the catalysts were characterized by the XRD diffraction model. The results confirmed that the synthesized catalysts contained Ag, Ti, O and Fe components and were free of impurities. The surface morphologies of the catalysts were determined by SEM analysis. Ag, Ti, O and Fe mass ratios were determined in EDX spectrum analyzes. The results showed that the main elements Fe, O, Ag and Ti were present without unexpected elements being observed, and this Ag supported magnetic TiO_2 was successfully prepared and confirmed the purity of the synthesized catalyst. TEM-EDS analyzes confirmed that the main elements in the synthesized Ag/TiO_2 and magnetic Ag/TiO_2/Fe_3O_4 catalyst are Ti, O, Fe and Ag. It revealed that the nanocomposite is pure without any scattered impurities. It was also confirmed by mapping that the expected elements were well distributed throughout the catalyst sample (Turkyilmaz & Kucukcongar, 2023).

3.2. Adsorption experiments

Adsorption experiments were carried out in accordance with the order of initial conditions determined according to the Taguchi experimental design method. The effects of catalyst amount, initial endosulfan concentration and pH parameters on removal efficiency were investigated. After the experiments were completed, the photocatalyst was separated from the samples with the help of an external magnet. Endosulfan was extracted with VALLME and HPLC readings were made. Taguchi optimization and analysis of variance of the results obtained in the experiments were made using Minitab 19 program and the results are given below.

In order to determine the time required for the adsorption to reach equilibrium, agitation was carried out in the dark. Equilibrium data for 6 different times between 10-60 min were obtained for 2.5 mg/L initial endosulfan concentration, 0.05 g catalyst amount and pH 7. The adsorption capacity reached its maximum in the first 30 minutes and then decreased and stabilized in the next period. Therefore, the reaction time was applied as 30 min for the effect and optimization of the control parameters in the adsorption experiments to be carried out in the Taguchi experimental design. Similarly, Ismael et al. (2020) reported that the adsorption equilibrium was reached in 20 minutes for the removal of chlorinated pesticides from wastewater, with the TiO_2/GO/$CuFe_2O_4$ nanocomposite photocatalyst.

The S/N ratios obtained from the Taguchi experimental design program of the endosulfan removal efficiencies obtained in the experiments on the basis of parameters suitable for the "Larger is better " design and the estimated S/N ratios of the program are given in Tables 1 and 2. When we evaluate the effect orders and levels of the parameters on the removal efficiency from the tables, it is seen that the most effective parameter according to the estimated S/N ratio is the initial endosulfan concentration (4 mg/L at the third level), pH (first level, 4) and the amount of catalyst (second level, 0.3 g/L). Since these results are included in the experiment design table (experiment 12), there is no need for a further confirmation experiment. Since these results are included in the experiment design table (experiment 12), there is no need for a further confirmation experiment. In addition, since the highest removal efficiency was obtained at these levels with 85.02%, it can be stated that the test result and the analysis result of the experimental design program are compatible.

Table 1. The endosulfan adsorption efficiencies obtained for the initial conditions determined according to the experimental design method.

Sample No.	pH	Catalyst Amount (g/L)	Endosulfan Conc. (mg/L)	% Removal	S/N	Predicted S/N
1	4	0.1	2	20,38	26,1841	30,1329
2	4	0.1	3	45,95	33,2457	33,6204
3	4	0.1	4	64,19	36,1493	35,2090
4	7	0.3	2	22,72	27,1282	31,0536
5	7	0.3	3	44,01	32,8710	34,5410
6	7	0.3	4	65,20	36,2850	36,1296
7	10	0.5	2	34,54	30,7664	29,4440
8	10	0.5	3	43,12	32,6936	32,9314
9	10	0.5	4	46,52	33,3528	34,5200
10	4	0.3	2	35,80	31,0777	31,4080
11	4	0.3	3	79,18	37,9723	34,8954
12	4	0.3	4	85,02	38,5904	36,4840
13	7	0.5	2	42,90	32,6491	30,9618
14	7	0.5	3	48,99	33,8021	34,4492
15	7	0.5	4	67,22	36,5500	36,0378
16	10	0.1	2	34,08	30,6500	28,2607
17	10	0.1	3	31,62	29,9992	31,7482
18	10	0.1	4	40,70	32,1919	33,3367
19	4	0.5	2	34,66	30,7966	31,3162
20	4	0.5	3	48,80	33,7684	34,8037
21	4	0.5	4	66,66	36,4773	36,3922
22	7	0.1	2	40,89	32,2323	29,7785
23	7	0.1	3	62,94	35,9785	33,2660
24	7	0.1	4	47,73	33,5758	34,8545
25	10	0.3	2	33,14	30,4071	29,5358
26	10	0.3	3	44,40	32,9477	33,0232
27	10	0.3	4	52,50	34,4032	34,6118

Table 2. Response Table for Signal to Noise Ratios in Absorption Experiments (Larger is better)

Level	pH	Catalyst	Endosulfan
1	33,81	32,25	30,21
2	33,45	33,52	33,70
3	31,93	33,43	35,29
Delta	1,87	1,28	5,08
Rank	2	3	1

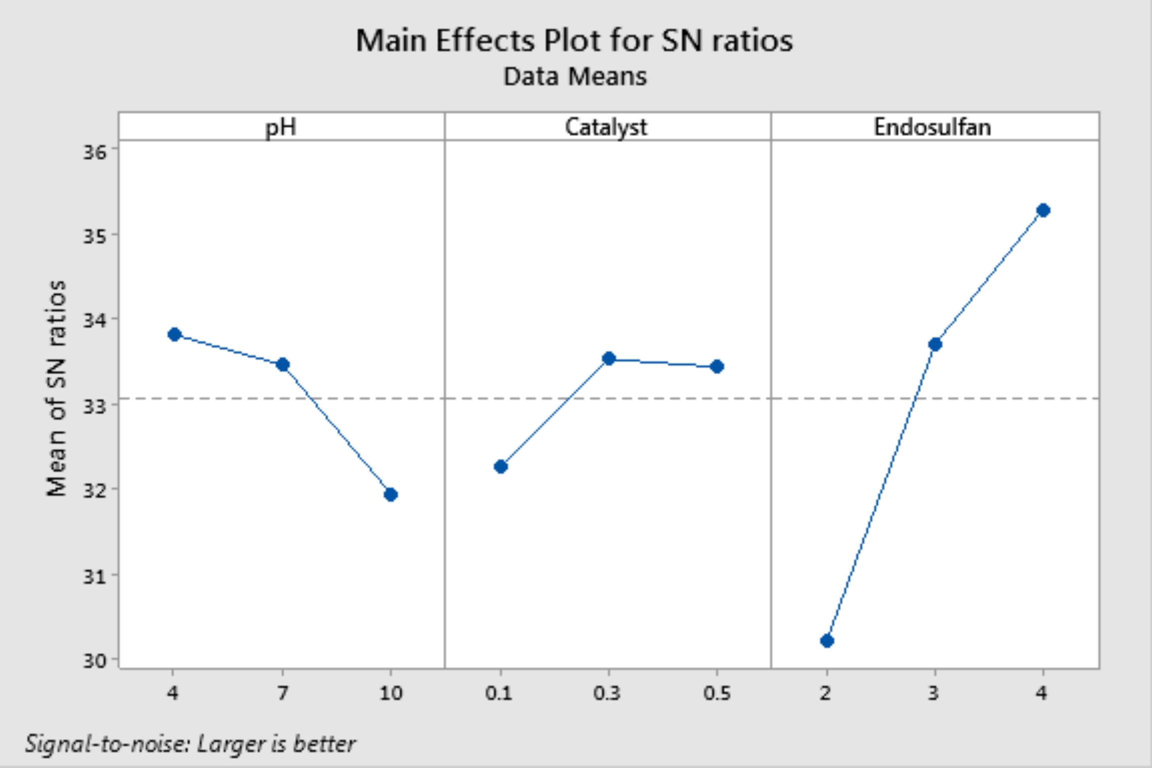

Figure 1. S/N ratios of parameters in adsorption experiments.

When Figure 1 is examined, the following conclusions can be reached;

- Since solution pH is a factor that affects the properties of pesticide molecules, adsorbent surface charge, ionization, functional groups in active sites, as well as the chemical properties of the solution (solubility, etc.), it is an important parameter to examine in the adsorption process. In the acidic state, the surface of the catalyst is positively charged, which is beneficial for the catalyst to absorb negatively charged organic compounds. In an alkaline state, however, there will be significantly less interaction due to the repulsion between the negatively charged catalyst surface and organic compound anions (Huang et al., 2008; Lu, Yang, Fang, Li, & Jiang, 2017). For this reason, as seen in Figure 1, the shift of the pH value from the acid medium to the neutral and basic medium had a reducing effect on the yield, and the pH 4 value was taken as the optimum. It has also been stated that low pH limits the formation of rust on the iron surface and provides more availability of the active sites of the adsorbent for the pollutant (Dong, Zhao, Zhao, & Zhou, 2010; Shih & Tai, 2010). It has been reported that under basic conditions, the formation and deposition of the hydroxide layer on the iron surface increases, resulting in less reactivity of FeO (Shih & Tai, 2010). Rauf, Tahir, Kang, and Chang (2012) reported that with increasing pH value, the amount of alpha and beta endosulfan adsorbed by bentonite decreased. Similarly, S. Memon, Memon, Memon, and Latif (2011) investigated the effect of pH between 2-12 values in their study on endosulfan adsorption with calix(4)eren and reported that the adsorption percentage was highest at acidic pH. In the study on nitrate removal with magnetic nanoparticles, it was reported that nitrate removal was pH dependent, maximum removal was achieved with 90.26% at the original sample pH of 6.9, and nitrate removal efficiency began to decrease above pH 6.9. It has been stated that this decrease in efficiency at high pH is probably due to the repulsion force between the OH- ion that negatively charges the surface of magnetic nanoparticles and the negatively charged nitrate ions (Pourzamani, Mengelīzadeh, Jalil, & Moosavian, 2017).
- The amount of adsorbent is an important parameter that affects the adsorption capacity and pollutant concentration. The increase in the amount of adsorbent effectively increased the S/N ratio at doses of 0.1 to 0.3 g/L. This can be attributed to the increased adsorbent surface area

and the availability of more adsorption sites resulting from the increased adsorbent dose. However, increasing the amount to 0.5 g/L had a slight negative effect on the removal. This negative situation was reported by S. Memon et al. (2011) and Rauf et al. (2012) have also been reported in their study. The result shows that as the adsorbent concentration increases, the adsorption percentage generally increases, but as the amount of adsorbate is fixed, the amount adsorbed per unit mass of the adsorbent decreases due to the unsaturated adsorption sites during the adsorption process (G. Z. Memon, Bhanger, & Akhtar, 2009).

- The initial endosulfan concentration is the most effective parameter on the removal efficiency, and the increase in concentration increased the efficiency. This is likely because when the initial endosulfan concentration is high, the number of pesticide molecules available with which the active site of the adsorbent interacts increases, resulting in higher removal efficiencies. Mishra and Patel (2008) reported that the removal rate of endosulfan was increased by increasing the initial endosulfan concentration from 5 mg/L to 15 mg/L in their study examining the removal of endosulfan from water with Sal Wood charcoal.

After determining the control parameters in terms of endosulfan adsorption efficiencies, ANOVA analyzes of the results obtained from the experimental design procedure were performed (Table 3). Thus, the extent to which the investigated factors affect the total adsorption efficiency and how different levels cause variability were also investigated.

Table 3. Analysis of Variance

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
pH	2	836,0	12,59%	836,0	418,0	3,61	0,0458
Catalyst	2	305,0	4,59%	305,0	152,5	1,32	0,2899
Endosulfan	2	3184,7	47,96%	3184,7	1592,3	13,76	0,0002
Error	20	2314,0	34,85%	2314,0	115,7		
Total	26	6639,7	100,00%				

Evaluation of the ANOVA analysis results is made by considering the F ratio, P% values and contribution percentage data. The F ratio is compared with the Fcritical value determined for a certain confidence interval value from the statistical tables, and if the F ratio is greater than the Fcritical value determined from the table in the predicted confidence interval, it is concluded that the effect of the specified factor is important for the performance examined (Özçelep, 2009). The degrees of freedom of each factor are 2 and the degrees of freedom of error are 20, for endosulfan adsorption removal. In this case, the Fcritical value was determined as 3,634 (F0.05;2.20) for the 95% confidence interval (Land, 1971).

In the experimental design part, since we are working with the criterion of " Larger is better ", the value with the highest F value represents the most important parameter. When the F ratios in Table 3 are compared with the Fcritical value, we can state that the effect of the initial endosulfan concentration is statistically significant. The value given as error in the table means error caused by uncontrollable factors (noise). It is important for the reliability of the results that this value is below 50%; otherwise, the results will not be reliable (Özçelep, 2009). As can be seen in Table 3, the calculated error value of 34.85% remained below the 50% value, indicating that the errors of the experiments were not significant.

The %P values in the analysis of variance are used to quantitatively evaluate the effects of the factors. Significance can be evaluated between groups according to %P values. In cases where this value is less than 0.05, we conclude that there is a significant difference between the groups. When Table 3 is examined, it is seen that there is a significant difference between the initial endosulfan concentration (P=0.0002) and the levels of the pH factor (0.0458) for endosulfan removal. In addition, the contribution of the parameters to the removal is given as % value in the table. The initial endosulfan concentration was the highest contributing factor with 47.96%. It is another factor that has the highest contribution on pH removal with 12.59%.

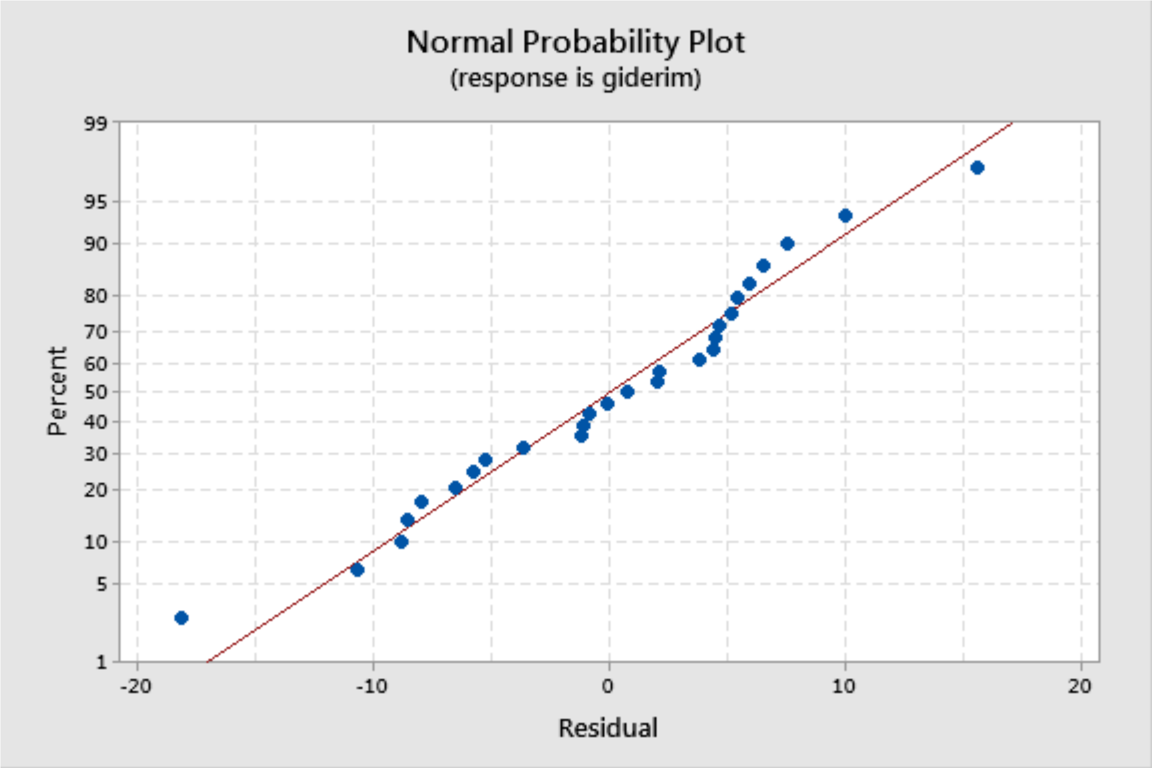

Figure 2. Normal probability plot for total endosulfan removal in adsorption experiments.

The normal probability plot for endosulfan removal by the adsorption process is given in Figure 2. From the figure it can be seen that in the normal probability plot of the linear model, the residuals are reasonably close to the straight line. This means that the errors are normally distributed and that the terms specified in the model are significant.

The R^2 values of the model are given in Table 4. R^2 value; It shows how well the data fit the model. The higher the R^2 value, the more the data fit the model. The R^2 value is 65.15% suitable for the model created according to the experimental results of endosulfan removal.

Table 4. Model Summary of Adsorption Experiments

S	**R-sq**	**R-sq(adj)**	**PRESS**	**R-sq(pred)**	**AICc**	**BIC**
10,75	**65,15%**	**54,69%**	**4217,22**	**36,48%**	**220,80**	**223,16**

4. CONCLUSION

High photocatalytic activity is expected as a result of high adsorption. For this reason, for the endosulfan removal and degradation to metabolites experiments by the photocatalysis process, firstly, the adsorbing process of the catalyst was carried out by shaking in the dark. In the next step of the study, experimental design of the photocatalysis process with Taguchi method and analysis of variance (ANOVA) for endosulfan removal and degradation to metabolites were performed.

After the adsorption process, photocatalysis experiments were applied to the samples under UV-A LED, UV-C and visible LED light sources in accordance with the initial conditions order determined according to the experimental design method. The effects of light intensity, catalyst amount, initial endosulfan concentration, pH and time parameters on removal efficiency were investigated. The highest removal efficiency was obtained as 91.9% , 93.2 and 94.2 % under UV-A LED, UV-C and visible LED light sources, respectively. In addition, when we evaluated the effects of the parameters on the removal efficiency, it was seen that the most effective parameters were the initial endosulfan concentration and pH.

In addition, it was followed whether metabolite formation as a result of endosulfan degradation. For this purpose, the concentrations of the main metabolites endosulfan sulfate, endosulfan lactone and endosulfan ether were monitored. As a result, metabolite formations at high concentrations were not observed while endosulfan was removed, on the contrary, the formations remained below 2% in all experiments on a concentration basis. These results support that the adsorbed endosulfan is effectively degraded by the photocatalysis process.

The repeated use of a photocatalyst is an important issue in the practical application of a catalysis process. The $Ag/TiO_2/Fe_3O_4$ catalyst produced for this purpose was studied 5 times in a row. Similar removal efficiencies of approximately 80% were obtained in four replicates after the first trial. This result shows that the endosulfan adsorbed by $Ag/TiO_2/Fe_3O_4$ catalyst is degraded by the photocatalysis process. The obtained results confirmed that the catalyst must have an effective adsorption capacity for an effective photocatalysis to occur.

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Ethical Approval

This article does not contain any studies with human participants or animals performed by the author

Conflict of Interest

The author declares that he has no conflict of interest

Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Mehmet Turkyilmaz and Sezen Kucukcongar. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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