Environmental Research & Technology, Vol. 2 (2), pp. 63-72, 2019

Turkish JournalPark ACADEMIC

Environmental Research & Technology

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RESEARCH ARTICLE

Removal of indigo dye by photocatalysis process using Taguchi experimental design

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ABSTRACT

The major concern of the present research is degradation of hazardous and stable Indigo dye used in industrial denim dying process. For this purpose, a heterogeneous photocatalysis process was carried out to treat aqueous solution of Indigo dye using pure titanium dioxide (TiO_2) in a batch reactor system under ultraviolet A (UVA) light for 210 min. In the study, individual and synergistic effects of factors such as TiO_2 dosage, pH, and initial dye concentration were scrutinized. Moreover, Taguchi statistical method was performed to optimize influential parameters. The results obtained from the study that TiO_2 concentration had the most effective factor on the Indigo dye degradation. The optimal conditions for dye removal were A (pH) at level 2 (4), B (initial dye concentration) at level 1 (10 mg L^{-1}) and C (TiO_2 concentration) at level 4 (1.5 g L^{-1}). The results presented that the theoretically predicted value for degradation efficiency (100%) was confirmed by the experimental value (100%).

Keywords: Indigo dye, optimization, photocatalytic degradation, Taguchi method, water treatment

1. INTRODUCTION

The textile manufacturing and clothing sector has strategic importance in terms of exports, investments, employment, the value added in the manufacturing sector for the Turkish economy. According to the European Statistical Office (Eurostat), Turkey's clothing exports to the European Union ranked third with around EUR 9.1 billion (9%) after China, Bangladesh in 2017 [1].

Jeans which are sold two billion every year all around the world are the most worn clothing among people. However, one jean alone requires 10.000 L of water, 0.5 kg of chemicals, pesticides, dyes, strong detergents and road and fuel cost due to transportation thus, they cause to enormous disaster [2]. Dyes are major responsible of the water pollution that are generally non-biodegradable and hardly degradable substances due to their synthetic origin and complex aromatic structures [3].

The denim dyeing industry generally use indigo blue is a kind of organic structural dye that has toxic properties in aquatic systems [4]. Indigo ($C_{16}H_{10}N_2O_2$) is belonging to the vat-indigoids class of dyes that is produced naturally by plants or manufactured synthetically in large quantities (20 million kg annually) [5, 6]. Indigo blue is practically insoluble in water (2 ppm) and has no affinity for cellulose fibers in such a state. Thus, it needs to be reduced to its soluble form (leuco from) by a powerful reducing agent such as sodium dithionite ($Na_2S_2O_4$) before dying. This agent helps to convert Indigo dye into a water soluble form. So, the dye can develop a chemical affinity with the cellulose fiber [7, 8]. Moreover, indigo dyes create dye rich effluents that resulted with various environmental problems [9]. These dyes are generally disposed in natural streams that are easily accessed by people for drinking, washing or personal cleaning activities. Hence, this type of water pollution poses threats to human health. Also the disposal of synthetic dyes into the water system damages photochemical activities of aquatic ecosystem by preventing light penetration solubility of gases [10, 11]. Indigo dye is very stable molecule that is difficult to remove using traditional biological treatment methods [12]. Thus, it is necessary to treat colored wastewater before discharging it to the environment and water resources [13].

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Received 6 September 2018; Received in revised form 5 February 2019; Accepted 8 February 2019
Available Online 29 April 2019
Doi: https://doi.org/10.35208/ert.457739

Degradation and decolorization of indigo dye and indigo rich wastewater can be treated by physicochemical methods like adsorption/biosorption [6, 14], ozonation [15], coagulation/flocculation [16, 17], Fenton/Foto-Fenton [18], photocatalysis [5, 19-21], electrochemical treatment methods [12], membrane bioreactors [8], biological process [6, 9]. However, cost of regeneration, secondary pollutants, limited versatility, interference by other wastewater constituents, necessities for reagents, and generation of large quantity of sludge are fundamental disadvantages of these conventional techniques coupled with the increment costs due to handling, treatment and disposal [22, 23]. Nowadays, effective, simple and low cost technologies are tried to find as a solution by researchers to eliminate indigo dye from wastewater.

Advanced Oxidation Processes (AOPs) generally based on the production of hydroxyl radicals (•OH) can be considered as a promising alternative for the treatment of stable, non-biodegradable pollutants [24, 25]. Among the existing AOPs, heterogeneous photocatalysis is an effective technique that comprises a semiconductor catalyst such as TiO_2, ZnO, CdS which works with ultraviolet light (UV) to degrade pollutants [26]. Titanium dioxide (TiO_2) has been widely used catalyst due to its biological and chemical stability, relatively high photocatalytic activity, non-toxic nature, low-cost and long span [27].

The multivariate optimization methods have various benefits compared to traditional one-at-a-time method because they help us to get a greater set of data with fewer experimental runs [13]. The main principles of Taguchi methods are to obtain information about main effects and synergistic effects of design parameters from minimum number of experiments [28]. In this study, all of the operational parameters were optimized by using Taguchi design to achieve the maximum removal of Indigo dye from the aqueous solution. This technique has been used in the literature by other researchers for optimization of the experimental factors in advanced oxidation processes [29-31]. To the best of our knowledge, the optimization of process parameters for the dye degradation by Taguchi method is very scarce and there is no report in the literature on the optimization of photocatalytic degradation of commercial grade indigo dye in aqueous heterogeneous suspension by TiO_2/ultraviolet A (UVA) with Taguchi experimental design. For this reason, an orthogonal array experiment design L_{25} comprising of each experimental variable with different levels was applied. Moreover, for the determination of optimal photocatalysis conditions (pH, initial dye concentration and TiO_2 concentration) for maximum degradation of Indigo dye, Taguchi's signal-to-noise ratio (S/N) and the analysis of variance (ANOVA) was used. Also, a confirmation test with the optimal levels of process parameters was done in order to demonstrate the performance of Taguchi's optimization method [31].

2. MATERIALS AND METHOD

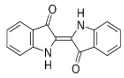
2.1. Chemicals and reagents

A TiO_2 photocatalyst (Sigma-Aldrich Inc., St. Louis, MO, USA; Product Code: 14021) was used as received. Other chemicals were of analytical grade and used without purification. Commercial synthetic Indigo dye (Molecular formula: $C_{16}H_{10}N_2O_2$) dissolved in water (40%) containing some impurities in solution which was supplied from Realkom Denim Textile Factory (Düzce, Turkey) to simulate realistic operating conditions. Table 1 shows the chemical structure of the original Indigo dye. Other chemicals such as NaOH and H_2SO_4 (assay 97%) used for adjusting pH were obtained from Merck (Darmstadt, Germany). All chemicals were used as received without further treatment. All solutions and reaction mixtures were prepared using purified water (spec. resistivity: 18.2 MΩ cm; Merck Millipore, Burlington, MA, USA).

2.2. Experimental setup and procedure

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 25±1ºC by circulating the coolant (water) through inlets of the inner cylinder. The photoreactor was constructed from three parts: i) an external Pyrex glass; ii) a Pyrex glass thimble, where the head part is fitted to the outside container to form a gastight seal and running water is passed through the thimble to cool the reaction solution and iii) an empty quartz chamber, in which a Philips PL-L UVA 36 W lamp (315 to 380 nm; 110 µW cm^{-2}) was placed. The reactor was also equipped with a control system, a water level sensor system and a water-inlet and outlet. A gas inlet opening supplies air from a diffuser system of 3.5 L min^{-1} capacity during experiments. The reactor was wrapped in aluminum foil to prevent UV ray penetration. For irradiation experiments, the desired concentrations of Indigo solution were prepared from 1000 mg L^{-1} of stock solution daily in amber-glass vessels, and the system was stirred and had air bubbled through – in order to increase the oxygen transfer to the solution – following the addition of TiO_2 for at least 30 minutes 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 dye molecules could be adsorbed by the photocatalyst. For comparison, irradiation experiments without adding TiO_2 were also performed.

Table 1. Chemical structure of Indigo

Name	Molecular structure	Chemical structure	Molecular weight (g mol^{-1})	λmax (nm)
Indigo, Indigotin	$C_{16}H_{10}N_2O_2$		262.26	610

The pH of the reaction mixture was adjusted by adding 1 N of NaOH and 1 N of H_2SO_4. The extent of substance conversion under radiation was determined by withdrawing aliquots after specific reaction time intervals, where the starting time was defined as the beginning of irradiation. Samples were centrifuged in a stoppered tube for 15 minutes at 5000 rpm to remove the TiO_2 from the solution.

Optimization of photocatalysis conditions were initially done using a spectrophotometer (Merck Pharo 100, Germany) and measuring the optical density (OD) of samples at its λ_{max} of 610 nm, which is the given maximum absorption wavelength for Indigo molecules for 210 minutes irradiation. 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 the spectrophotometer. The percentage of degradation of Indigo was calculated using Eq 1:

$$\textit{Percentage of degradation of Indigo} = \frac{C_i - C_f}{C_i} \quad (1)$$

where C_i and C_f are the initial and final Indigo concentrations in the reaction mixture, respectively.

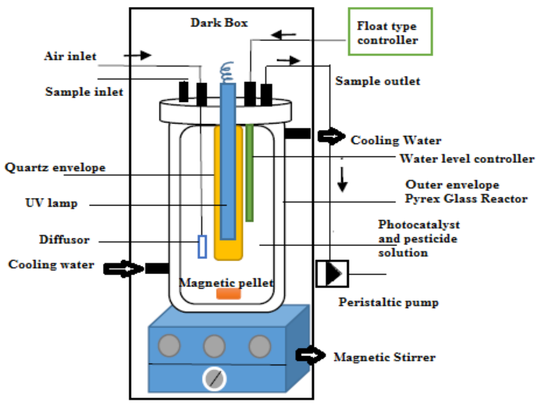


Fig 1. Schematic diagram of photocatalytic reactor

The photocatalytic experiments were performed using aqueous solutions of Indigo dye at different initial pH values (2-10), dye concentrations (10-50 mg L^{-1}) and catalyst dosages (0-2.0 g L^{-1}).

2.3. Taguchi orthogonal array experimental design

The Taguchi method is a powerful design that has been extensively used in engineering analysis. The method reduces the number of tests by using orthogonal arrays and minimizes the effects of the uncontrollable factors [32, 33]. Japanese scientist Dr. Genichi Taguchi developed this statistical experimental design method that enables to examine the parameters affecting an experiment in two groups, that is controllable and uncontrollable. Also, it allows studying multiple parameters at two or more levels [34]. The fundamental aim of the Taguchi method is to find out the best combination of design parameters and reduce the variation for quality [35].

Experiment with one variable or one factor at a time is a traditional approach that is time consuming and labor-intensive [36]. Recently, the systematic orthogonal array (OA) is frequently used to optimize and design experiments in Taguchi method. The OA is a kind of experiment where the columns for the independent variables are "orthogonal" to one another [31]. The analysis of variance (ANOVA) and signal-to-noise ratio (S/N) are generally used to analyze the results of designed experiments. Hence, process parameters can be easily identified that have important contribution on the process [37]. According to previous works about Indigo dye removal using photocatalysis process [9, 18], main operational parameters and their levels were selected and given in Table 2.

In this study, for optimizing the experimental variables of Indigo removal three factors (pH, initial dye concentration and TiO_2 concentration) in five levels were studied with fractional factorial design leading to twenty-five experiments (L_{25} design, Table 3). Three-five level factors are arranged in an L_{25} orthogonal array table. L indicates the Latin square and 25 means replication number of the experiment. The number in table implies the level of factors [38]. Experimental data were analyzed using the Minitab software (version 17-trial edition).

3. RESULTS AND DISCUSSION

3.1. Determination of optimal conditions using Taguchi method

Taguchi method enables to identify the optimal conditions of photocatalysis experiment and it determines the parameters having the most significant effect on the dye removal. The structure of Taguchi's L_{25} design and the results of experiments are given in Table 3. Each run of the matrix indicates one test run. However, the sequence in which these tests were applied was randomized. A range of values from 16% to 100% was obtained from the removal efficiency. This statistical experiment design is considered as a strong predictive model because it allows evaluation by separating the controllable and uncontrollable factors. In this study, there are no uncontrollable variables. Hence, the controllable variables are taken as pH, initial concentration of the Indigo dye, and TiO_2 concentration.

Table 2. Process parameters and their levels

Parameters	Symbol	Level 1	Level 2	Level 3	Level 4	Level 5
pH	A	2	4	6	8	10
Indigo concentration (mg L^{-1})	B	10	20	30	40	50
TiO_2 concentration (g L^{-1})	C	0	0.5	1	1.5	2

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

Exp. no.	Factor A	Factor B	Factor C	Response (%)	S/N (dB)	Mean value	Predic-tive S/N ratio	Predictive Mean value
1	1	1	1	53.81	34.62	53.81	33.44	55.75
2	1	2	2	58.76	35.38	58.76	37.97	73.63
3	1	3	3	99.56	39.96	99.56	39.47	89.61
4	1	4	4	74.67	37.46	74.67	37.76	79.67
5	1	5	5	80.52	38.12	80.52	36.90	68.66
6	2	1	2	100.00	40.00	100.00	39.74	97.33
7	2	2	3	100.00	40.00	100.00	40.83	104.22
8	2	3	4	100.00	40.00	100.00	40.44	104.51
9	2	4	5	99.90	39.99	99.90	38.16	90.09
10	2	5	1	24.38	27.74	24.38	28.56	28.13
11	3	1	3	100.00	40.00	100.00	39.33	97.28
12	3	2	4	99.34	39.94	99.34	38.52	88.47
13	3	3	5	71.31	37.06	71.31	37.57	84.28
14	3	4	1	16.43	24.32	16.43	26.55	18.91
15	3	5	2	40.92	32.24	40.92	31.59	39.08
16	4	1	4	100.00	40.00	100.00	39.86	95.68
17	4	2	5	81.46	38.22	81.46	38.51	82.39
18	4	3	1	26.27	28.39	26.27	28.81	27.25
19	4	4	2	45.86	33.23	45.86	32.43	44.00
20	4	5	3	48.89	33.78	48.89	34.02	53.17
21	5	1	5	100.00	40.00	100.00	42.25	107.78
22	5	2	1	52.68	34.43	52.68	32.14	43.54
23	5	3	2	79.03	37.96	79.03	37.08	70.52
24	5	4	3	72.09	37.16	72.09	37.26	76.28
25	5	5	4	64.07	36.13	64.07	36.96	69.75

In the Taguchi design, the terms "signal" and "noise" represent the desirable and undesirable values for the output characteristic, respectively. S/N ratio gives the measurement of the quality characteristic deviating from the desired value. The S/N ratio is defined as ratio between desirable results (signal) to undesirable results (noise). Maximum S/N ratio gives the optimum conditions [39]. In the study, the maximum dye removal efficiency is tried to measure, so the performance formula of "bigger characteristics are better" was applied as objective function to define S/N ratios.

$$\frac{S}{N}[dB] = -10\log\left[\frac{1}{n}\sum_{i-1}^{n} 1/y_i^2\right] \quad (2)$$

where y_i is the characteristic property, n is the replication number of the experiment.

Table 4 shows the S/N ratio for removal of the solution containing Indigo dye calculated using Eq 2. The mean S/N ratio for each level of the parameters was summarized as S/N response, which was shown in Table 3.

The optimum condition is A2, B1 and C4. According to S/N ratio, the optimal parameters (conditions) for dye removal are A (pH) at level 2 (4), B (initial dye concentration) at level 1 (10 mg L^{-1}) and C (TiO_2 concentration) at level 4 (1.5 g L^{-1}). Based on the optimum conditions, 100.0% dye removal can be obtained.

Table 4. S/N response table for % dye removal

Levels	Control factors		
	% dye removal		
	A	B	C
Level 1	37,11	**38,92**	29,9
Level 2	**37,55**	37,6	35,76
Level 3	34,71	36,67	38,18
Level 4	34,72	34,43	**38,71**
Level 5	37,14	33,6	38,68
Delta	2,83	5,32	8,81
Rank	3	2	1

Bold values shows the optimal levels of control factors

3.2. Statistical Analysis

ANOVA helps to determine the effects of each parameter on the variance of the results, regarding the total variance of all the parameters [31]. Actually, the main aim of the ANOVA is to extract from the results how much variations each factor causes relative to the total variation observed in the result [28]. Table 5 shows the ANOVA results for Indigo dye removal efficiency in the photodegradation process.
The significance of the experimental parameters was found out by using analysis of variance. The analysis was evaluated for confidence level 95%, that is for significance level of α=0.05. The p values <0.05 represents the significance of the parameters. It points out that there is only a 5% chance that a p value this large could occur due to noise.

Hence, the ANOVA results show that the most significant factor contributing the Indigo dye removal is TiO_2 concentration (C), followed by initial Indigo concentration (B) as shown in Table 5. However, according to F-test, pH (A) is statistically insignificant on the degradation of Indigo dye by photocatalysis process. So, the most effective parameters were selected based on their F values.

The main effect plot of the process parameters on the dye removal efficiency is clearly illustrated in this Fig 2 and Fig 3. Concentration of TiO_2 as a catalyst has a significant role in the efficiency of photocatalytic process. The effect of different doses of catalyst from 0 to 2.0 g L^{-1} was tested in the study. When the catalyst concentration increases, that is found to be the most significant factor among all; the S/N ratio also increases. As shown in Fig 2 and Fig 3., with increasing catalyst concentration at 1.5 g L^{-1}, the reaction rate increases, because with an increasing amount of catalyst more dye molecules are adsorbed onto the catalyst surface and dye removal in the area of irradiation n increases. Moreover, the catalyst has high accessible surface area at the beginning of the photocatalysis process [27].

Secondly, in order to investigate the effectiveness of photocatalytic oxidation with increasing dye concentration, experiments were conducted for 10 to 50 mg L^{-1} concentrations of Indigo dye. As illustrated in Fig 2, when the dye concentration increases, the S/N ratio decreases sharply. This indicates that degradation is achieved better at lower dye concentrations. Reference [31] reported that when the Carmoisine dye increased from 20 to 30 mg L^{-1}, S/N ratio decreased for Fenton and photo Fenton processes. Furthermore, Reference [24] stated that when the concentration of a kind of textile dye, Bezacryl Yellow (BZY) increased from 10 mg L^{-1} to 117 mg L^{-1} in the presence of TiO_2, the dye removal decreased from 100% to 57%.

Table 5. ANOVA results by Taguchi method and regression equations

Factors	For Taguchi method				
	d.f.	Adj SS	Adj MS	F-value	P-value
pH (A)	1	291.4	291.4	1.22	0.281
Indigo conc (mg L^{-1}) (B)	1	4481	4481	18.83	0.000
TiO2 conc (g L^{-1}) (C)	1	8006.6	8006.6	33.65	0.000
Error	21	4996.7	237.9		
Total	24	17775.8			

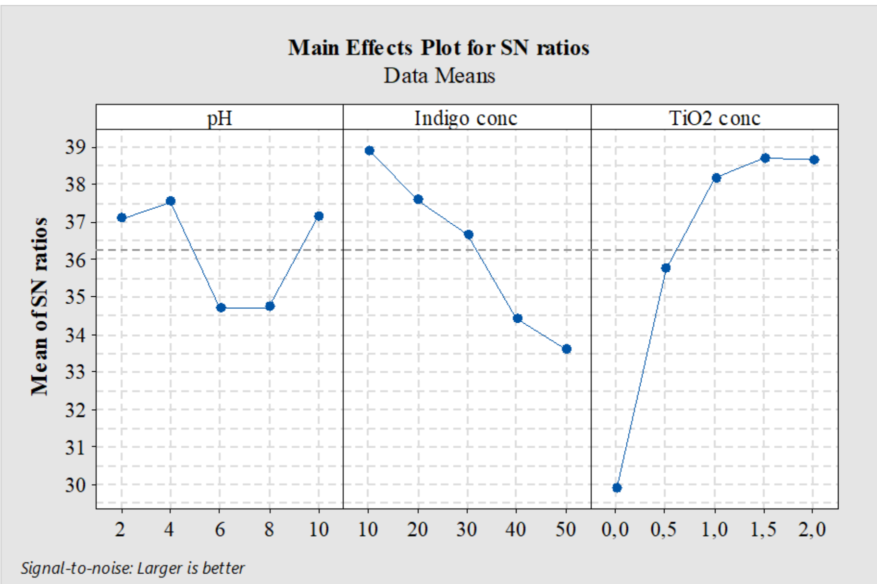


Fig 2. Effects of process parameters on S/N in photocatalysis process

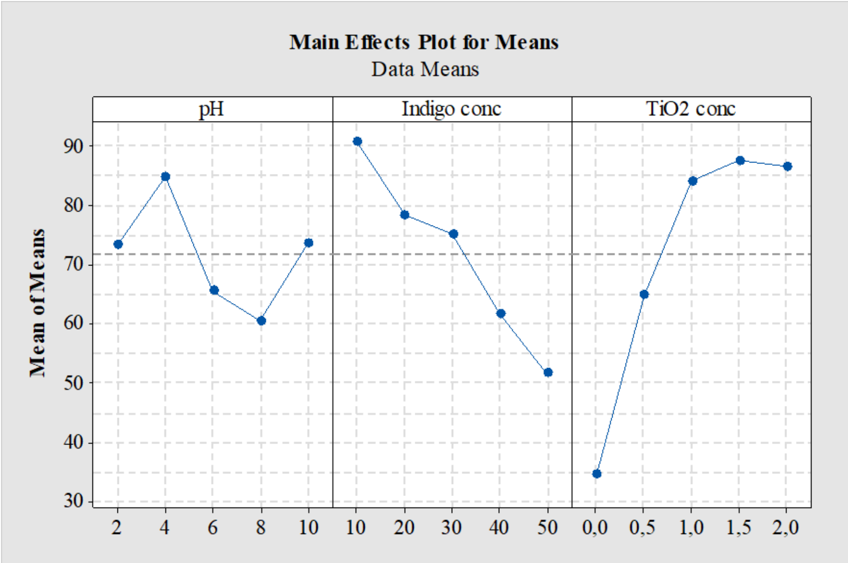


Fig 3. Effect of process parameters on Means in photocatalysis process

pH value has been frequently observed due to dependency of charged substrates such as dyes to the photocatalytic degradation efficiency. S/N value is found to be larger at the pH 4 as shown in Fig. 2. After this point, the S/N ratio decreases with sharper slope, which means the degradation is performed better at lower pH value. The zero point of charge (pH_{zpc}) for TiO2 is approximately pH of 6.50, hence negatively charged molecules are more readily degraded at acidic pH values when the photocatalyst surface is positively charged [30]. Reference [3] reported that as the pH increased from 1.0 to 2.0, the biosorption capacity of Spirulina pacifica reached a maximum value of 86.08% (17.22 mg g^{-1}) for Indigo dye. Although the pH is an extremely important parameter for photocatalysis experiments, it has less significance on the removal of Indigo dye compared to other factors such as catalyst or dye concentration. As illustrated in Fig 3, S/N ratio increases again at pH 10 at lower dye concentration (10 mg L^{-1}) and higher catalyst concentration (2.0 g L^{-1}). It is thought that the molecular characteristic of Indigo dye, the type of degradation process, and other experimental factors affects the degradation parameters and their influence levels.

3.3. The Results of Multivariable Regression Model

The experimental results are given by multivariable linear regression model analysis that is conducted to determine the effects of pH, TiO_2 and initial dye concentration on Indigo removal. SPSS (version 17-trial edition) software was used to set regression model. In order to establish a multiple regression model, linear and "step-by-step" model were used. As a result of regression analysis, 2 different models were set and accuracy of prediction values for each model was presented in Table 6.

Variables for each model are summarized in Table 7. The interaction of TiO_2 and initial dye concentration is statistically significant on the removal of dye removal as shown in Table 7 ($p<\alpha$, $\alpha=0.05$). Second model has the highest R^2 ratio that can express the 70% of the results of variance. Hence, it is decided to use Model 2 for prediction model.

Table 6. The multivariable regression model for Indigo dye removal

Model	R	R2	R2 Change	Adjusted R2	F	P
1	0.671	0.45	0.45	0.427	18.85	0
2	0.838	0.703	0.252	0.675	18.642	0

Table 7. The coefficients of variables in Model 2

Variables	Unstandardized Coefficients		Standardized Coefficients	T	P	Pearson-Corelation	
	B	Std. Error	Beta	t	p	Pearson-Corelation	p
(Constant)	74.691	8.492		8.796	0		
TiO_2 conc. ($g\ L^{-1}$)	25.309	4.385	0.671	5.771	0	0.785	0
Initial dye conc. ($mg\ L^{-1}$)	-0.947	0.219	-0.502	-4.318	0	-0.688	0.007

Table 7 summarizes the data of the coefficients of variables that were used in Model 2. The variables enable to interpret results according to the standardized regression coefficients. When the variables were arrayed in accordance with relative significance order, it was determined that the first interpretive variable was TiO_2, and the second variable was the initial dye concentration. In the regression model, the level variables for pH weren't seen to have any relation to dye removal.

It was determined that the t-test results regarding the significance of the regression coefficients indicated the same order and that $p < 0.05$ was statistically significant. Furthermore, when the t-test values were examined, it appeared that TiO_2 linearly affects the dye degradation, but the concentration has an inverse interaction on the dye removal. This was also determined in the Taguchi experimental design. The prediction model established by using the coefficients of the variables is as follows;

$$Y = 74.691 + 25.309*(TiO_2) - 0{,}947*(\text{Initial dye concentration}) \quad (3)$$

In addition, when the Pearson-correlation coefficients were analyzed, it was observed that the amount of TiO_2 and initial dye concentration had strong effects on the outcome variable and it was statistically significant ($p<\alpha$, $\alpha=0.05$). The coefficient calculated for pH was -0.235 ($p = 0.281$), so that the effect on the result was weak and this correlation was statistically insignificant. Since there wasn't any direct relationship for pH variable, new regression models were established via "curve prediction" model by using only this variable. The summary information on these models is summarized on the Table 8 and Fig 4.

Table 8. Results for all estimated models for pH and dye removal efficiency

Model	R	R^2	F	t	P
Linear	0.128	0.016	0.383	-0.619	0.542
Logarithmic	0.127	0.016	0,376	-0.613	0.546
Inverse	0.106	0.011	0.263	0.513	0.613
Quadratic	0.15	0.023	0.254	-0.483	0.778
Cubic	0.299	0.09	0.689	1.079	0.569
Compound	0.092	0.008	0.196	27.776 (p=0)	0.662
Power	0.12	0.015	0.339	-0.582	0.566
S	0.129	0.017	0.392	0.626	0.537
Growth	0.092	0.008	0.196	-0.442	0.662
Exponential	0.092	0.008	0.196	-0.442	0.662
Logistic	0.092	0.008	0.196	27.776 (p=0)	0.662

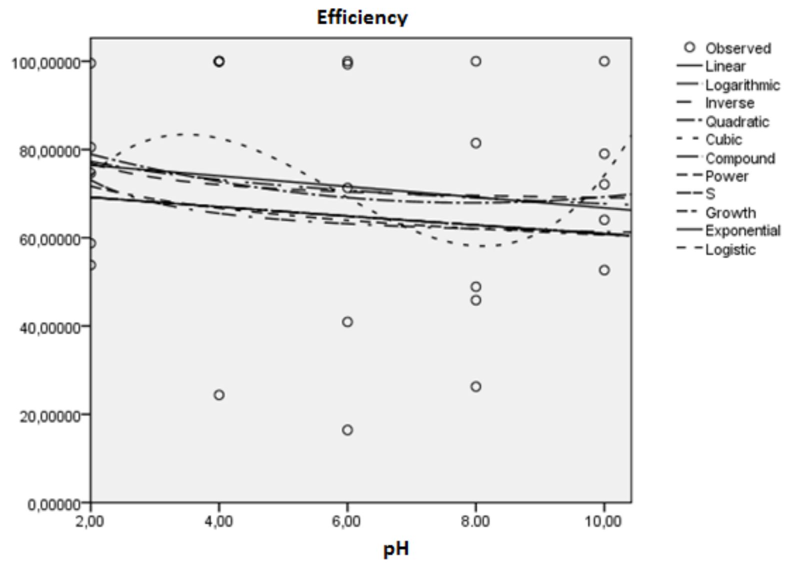


Fig 4. Results for all estimated models for pH and dye removal efficiency

When F, t and p values belongs to all models were investigated, there weren't seen any statistically significant effect of pH on the removal of dye. Two different p values were calculated for compound and logarithmic functions. One of them was calculated for general model, and other one was for predictive coefficient. While these estimated coefficients are significant, they are considered statistically insignificant since they predominantly deviate from actual values together with these coefficients. When the all situations were evaluated, it has been decided that it is more appropriate to predict the efficiency of dye removal by using other variables other than pH.

4. CONCLUSIONS

In this study, the obtained results show that a kind of textile vat dye, Indigo blue can be efficiently degraded by heterogeneous photocatalysis process in aqueous suspension of TiO_2 as photocatalyst under UVA irradiation. Based on the S/N ratio method, the degradation of Indigo dye was found to dependent on the initial dye concentration and TiO_2 concentration. The optimal conditions for dye removal were A (pH) at level 2 (4), B (initial dye concentration) at level 1 (10 mg L^{-1}) and C (TiO_2 concentration) at level 4 (1.5 g L^{-1}). The results indicate that TiO_2 concentration is the most effective compared to the other experimental parameters. Under the above optimum conditions, 100% Indigo dye degradation was achieved within 210 minutes.

ACKNOWLEDGEMENT

The authors are grateful for the support provided by Bolu Abant Izzet Baysal University (BAIBU) Scientific Research Projects Coordination Unit and BAIBU Faculty of Engineering and Architecture, Department of Environmental Engineering, Turkey.

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