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Using Experimental Design to Optimize the Photo-degradation of P-Nitro Toluene by Nano-TiO_2 in Synthetic Wastewater

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ABSTRACT

In this project, the degradation of synthetic wastewater comprising p-nitro toluene (PNT) is investigated using UV/TiO_2 process. PNT as a pollutant has a very harmful effect on the environment and human hormones. TiO_2 is one of the best metal oxides it has photo catalyst role. The full factorial design (FFD) of experiment is employed to investigate the effect of working variables including pH, initial dosage of PNT and catalyst concentration. The Analysis of variance (ANOVA) presented a high determination coefficient value (R^2 = 0.9876, R^2_{pred} = 0.8585, R^2_{adj} = 0.9596) for degradation of PNT and acceptable prediction of second-order regression model. The graphical counter plots were used to control the optimum conditions. The operative variables are optimized at [TiO_2] = 0.2g/L , pH value of 4, and [PNT] = 50mg/L. These findings suggest that the percentages of degradation and mineralization of PNT at the forecasted optimum conditions after 120 min of reaction were 64 and 55%, respectively.

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1. INTRODUCTION

The industrial wastewater produced by some chemical plants contains nitro toluene and other aromatic pollutants. Considerable contents of aromatic components with a wide range of non-biodegradable chemicals are lost during a process and cause environmental pollution. Toluene and its derivatives are widely used in industries. One of these derivatives is PNT which is produced as a side product in the production process of trinitrotoluene (TNT). In recent years, million tons of nitro-aromatic has been used for military and industry applications. The phenol compounds are harmful for the nature and resistant contaminant in synthetic wastewater that acts as a basis of many damages in the human body and environment [1]. The remediation of nitro phenols compound polluted wastewaters through traditional methods is very complicated and costly, as well as producing secondary pollution and is a time consuming reaction. In addition, phenol compounds are chemically resistant due to their solubility and constancy in aqueous media [2]. Thus, it is vital to employ new approaches for the treatment of the polluted wastewater by these compounds without above-mentioned issues.

Advanced oxidation processes (AOPs) technology are active and ecologically friendly approaches for the degradation of organic contaminants. AOPs are resilient to the conservative treatment systems into modest byproducts and lastly mineralize them into small molecules such as water and carbon dioxide [3]. AOPs produce hydroxyl radicals which are oversensitive and general oxidants. They have high electrochemical oxidation potential for the degradation of chemical compounds [4].

The heterogeneous photocatalysis methods based on the absorbing the light by metals oxides have been developed for the environmental remediation. Because they are inexpensive, require mild conditions such as ambient temperature and pressure, and are environmentally sturdy and recyclable. To synthesis of these heterogeneous catalysts, different semiconductors metal oxides (TiO_2, WO_3, CeO_2, Fe_2O_3, ZrO_2 and etc.)

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and sulfides (CdS, ZnS, etc.) have been employed [5, 6] and they are used for degradation of chemical substances. Among of them, titanium dioxide (TiO_2) due to its unique properties such as photo stabe, available, non-toxic nature, low operating temperature, low energy intake, high photo catalytic activity and water insolvability under dissimilar environmental conditions has been found to be the most influential ones. On the other hand, it prevents the formation of unwanted by-products [7–10].

In recent years, many studies have been conducted on nitro toluene and its derivatives degradation. Results of such studies showed that AOP affects the degradation of TNT. Among which, the photo catalyst and Fenton oxidation are highly desirable [11, 12]. Ludwichk et al. [13] have reported borosilicate-glass-TiO_2 as a catalyst demonstrated the reduction of 32 and 100% of COD and nitro aromatic compounds in the photo catalyst method.

In another study, it was indicated that the Fe-N-S-dopeTiO_2 showed a higher degradation of TNT comparing to pure TiO_2 due to alteration of crystal microstructure, specific surface area as well as the photo catalytic activity [14]. Modified titanium dioxide impregnated zeolite by silver, was implemented for mineralization of PNT in aqueous medium. The results showed that TiO_2/AgY_2 catalyst resulted up to 60% degradation of PNT in 4 hours and converted PNT into CO_2, NO_3^- $NH_4^+$and H_2O [15].

In this study, FFD was employed as a statistical method to investigate the main effects and their interaction on each other at three levels in the photocatalytic degradation of PNT [16]. The capability of general FFD in the modeling of multifaceted processing systems comparing other old-style approaches for modeling a multi mutable method is more practical [17].

In this effort, the influence of three different variables including pH, initial concentration of PNT and catalyst dosage was studied on the mineralization of PNT through UV/TiO_2 process. The significant variables and interaction properties between them were considered by FFD manner.

2. EXPERIMENTAL

2. 1. Materials The diluted synthetic wastewater containing 25, 50, 75 (mg/L) of PNT was prepared. Sulfuric acid and sodium hydroxide were supplied by the Merck Company (Darmstadt, Germany). Nano Titanium dioxide was Degussa P-25 and it was in Anatase form (about 99.9% Anatase). It had an APS of 20 nm and BET surface area of 200 m^2/g.

2. 2. General Procedure The tests were done in a 1.4 L cylindrical reactor (Pyrex glass) and a mercury lamp, Philips 15 W (UV-C), was the light source, which was positioned vertically in the middle of reactor. Figure 1 shows the schematic diagram of the cylindrical glass reactor.

A solution containing certain amount of PNT and the catalyst was prepared and permitted to circulating in the reactor in the absence of UV light for 30 minutes to achieve equilibrium. After homogenization, the radiation of solution was started and simultaneously, 0.5 L/min of oxygen was injected from the bottom of the reservoir.

At certain reaction intervals about 5 mL of samples were taken, centrifuged and filtered. Then it was analyzed by a UV–vis spectrophotometer (Agilent, 5453, American) at 286 nm.

The mineralization and degradation of the considered wastewater was estimated by chemical oxygen demand (COD). The COD was measured by HACH's COD technique [18]. The degradation percent of COD and PNT were determined by the following equations:

$$Degaradation\ of\ COD = \left(\frac{[COD]_0 - [COD]}{[COD]_0}\right) \times 100 \quad (1)$$

$$Degaradation\ of\ PNT = \left(\frac{[\mathrm{PNT}]_0 - [\mathrm{PNT}]}{[\mathrm{PNT}]_0}\right) \times 100 \quad (2)$$

where $[PNT]_0$ and $[COD]_0$ are the concentrations of PNT and initial COD of the reaction, respectively. [PNT] and [COD] are the concentrations with respect to time, t.

2. 3. Experimental Design The FFD technique was employed with three self-governing factors comprising the concentration of PNT (C_{PNT}), initial dosage of TiO_2 (C_{cat}), and pH. The experimental design

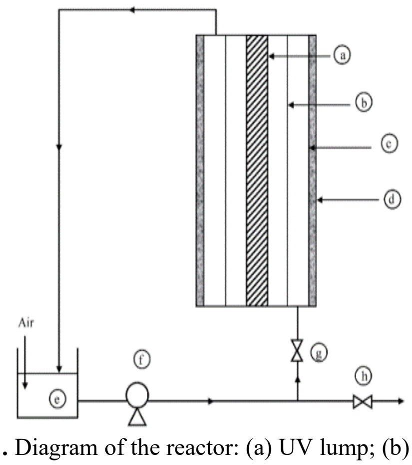

Figure 1. Diagram of the reactor: (a) UV lump; (b) Internal wall; (c) External wall; d) Aluminum foil; (e) Tank; (f) Circulating fluid pump; (g,h) Valve

manner was used and the degradation percentage of PNT was designated as response to get the optimum conditions. The input variables and their levels in the test are summarized in Table 1.

The overall full factorial is a complete design of experiment that all levels of each variable in the examination are joint with all levels of every other variables.

In this work, 3^3 experiments were performed to examine the main effects and interaction between initial dosage of PNT (mg/L), initial dosage of TiO_2 (g/L) and pH. The data were collected and then, the F-test study of variance with a 95% assurance interval was used to evaluate the statistical influence of the important variables and their connections.

2. 4. Data Analysis Based on data collected from experimental design, experimental data was fitted by the following equation:

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

Where ε is the residual term, b_0 is a constant, b_{ij} is the linear interaction effect between the input variables, x_i and x_j (i=1, 2 and 3; j=1, 2 and 3) are self-governing variables, b_i is the slope of the variable and b_{ii} is the second order of input variable (x_i). ANOVA was employed to inspect the importance of each term in the above equation [19]. MINITAB 17 with Response Surface Methodology (RSM) was used to control the coefficients of Equation (3). The experimental and forecasted response standards for the degradation of PNT are showed in Table 2. Reaction time was set at 120 min for all experiments.

3. RESULTS AND DISCUSSION

3. 1. Statistical Analysis ANOVA was employed to analyze the important role of the three basic factors and their interactions on the degradation percentage of PNT. The amounts of mean square, sum of squares of each factor, P-value and F-value are presented in Table3. The significance of data is determined by the value of P. According to statistics, P-value close to zero are more considerable. The P-value should be less than or equal 0.05 (≤0.05), so that the 95% confidence level is statistically significant. The purpose of this section was to obtain maximum degradation of PNT in favorable conditions. Many researchers investigated the steps of the FFD [20].

The exactness of predicted model is confirmed as exposed in Figure 2, which associates the experimental values versus predicted amount of degradation by the model. The results presented a good agreement between the predicted and experimental values. Taking a look at the predicted degradation by the model equation shows it has adaption with the experimental data.

3. 2. ANOVA Tests for The Degradation of PNT in UV/TiO_2 Process In this reading, the influence of three independent variables on the degradation of

TABLE 1. The range and levels of the factors

variables	Symbol	Range and levels		
		-1	0	+1
Initial dosage of PNT (mg/L)	C_{PNT}	25	50	75
Initial dosage of TiO_2 (g/L)	C_{cat}	0.1	0.2	0.3
pH	pH	4	7	10

TABLE 2. The 3-factor full factorial design medium and the response function (degradation of PNT (%) for 120 min)

Run number	Initial dosage of PNT (mg/L)	Initial dosage of TiO_2 (g/L)	Initial pH	Degradation of PNT (%)	
				Exp.	Pred.
1	50	0.3	10	57.42	57.11
2	50	0.2	4	64.00	63.82
3	50	0.1	10	56.83	56.75
4	50	0.3	7	58.33	58.47
5	50	0.2	10	58.20	58.59
6	25	0.2	10	32.53	35.38
7	50	0.1	4	59.42	59.43
8	50	0.1	7	57.52	57.59
9	75	0.2	4	54.48	56.03
10	25	0.3	10	29.01	27.60
11	25	0.2	4	48.20	46.83
12	75	0.1	4	48.51	47.85
13	75	0.1	10	35.96	37.48
14	75	0.3	4	49.83	48.93
15	25	0.1	4	35.64	36.28
16	75	0.2	10	46.36	43.12
17	25	0.1	10	28.82	27.38
18	25	0.2	7	38.09	36.62
19	75	0.2	7	49.17	50.86
20	25	0.1	7	29.13	29.93
21	25	0.3	7	30.01	30.68
22	25	0.3	4	36.19	36.92
23	50	0.3	4	60.04	60.21
24	75	0.1	7	47.40	46.53
25	75	0.3	7	48.54	47.72
26	75	0.3	10	36.43	38.15
27	50	0.2	7	58.33	58.12

PNT and COD was explored using the RSM and FFD, to achieve the optimum situations. Quadratic polynomial equation as a mathematical relative can employed between the degradation of PNT and COD and three significant variables. The statistical possessions of the designated model are offered in Table 2 to designate the degradation efficacy of PNT as a function of the considered variables.

To test the importance of the regression coefficient, the information listed for the proposed model such as the ANOVA and the coefficients are presented in Table 3. It can be seen that more than 95% of the data (R^2 = 98.76%, adjusted R^2 = 95.96%) is well predicted by the model. Therefore, the terms noted in the proposed model made remarkable predictions. However, adding more terms to the model increase sits predictions accuracy. The high value of F-value (35.34) approves the significance of the proposed model. The P-values

TABLE 3. ANOVA tests for quadratic models in the degradation of PNT by UV/TiO_2 process

Sources	DF	Adj SS	Adj MS	*F*-value	*P*-value
Model	18	3366.87	187.05	35.34	0.000
linear	6	3225.76	537.63	101.59	0.000
X_{PNT}	2	2749.96	1374.98	259.81	0.000
X_{cat}	2	164.95	82.48	15.58	0.002
X_{pH}	2	310.85	155.43	29.37	0.000
2-Way Interaction	12	141.11	11.76	2.22	0.132
$X_{PNT}X_{cat}$	4	39.25	9.81	1.85	0.212
$X_{PNT}X_{pH}$	4	86.12	21.53	4.07	0.043
$X_{cat}X_{pH}$	4	15.74	3.93	0.74	0.589
Error	8	42.34	5.29		
Total	26	3409.21			
Model Summary	S	R^2	R^2_{adj}	R^2_{pred}	
	2.30047	98.76%	95.96%	85.85%	

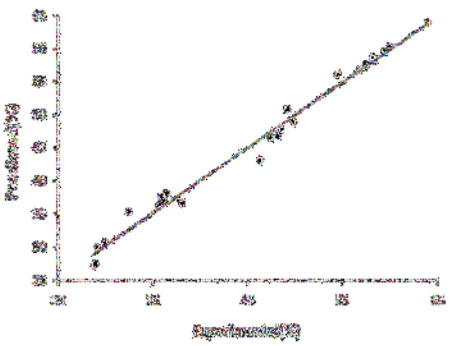

Figure 2. Comparing the experimental and predicted values

less than 0.05 designate the significance of model terms. The amounts larger than 0.10 indicate that the paprameters of the model are not significant. However, the term of the binary interaction between the variables has a *p*-value of higher than 0.05, which implies that the interaction of variables is insignificant [21, 22].

3. 3. Influence of Different Variables on the Degradation of PNT

The results can be achieved as contour plots for the study of the influence of different variables on the response. It can be seen that the desired percentage of degradation is achieved in the middle concentrations of PNT and TiO_2 at low pH.

The response surface plots for degradation of PNT in UV/TiO_2 process are illustrated in Figures 3, 4 and 5. From these contour plots, the simultaneous interaction of the two factors on the responses are shown.

3. 3. 1. Effect of pH in UV/TiO_2 Process

The pH of the solution has a significant influence on the photo catalytic degradation of various pollutants [21, 22]. The results presented that pH is a main factor and in this project at low pH values photo degradation rates were high. The best pH for the degradation was close to the zero point of charge (zpc) of TiO_2. This issue can be explained by the influence of pH on degradation rate which is based on the influence of pH on TiO_2 particles itself.

TiO_2 shows a zpc at pH values between 5.6 and 6.4 [23]. It means, the catalyst surface at acidic media with pH<5.4 is positively charged, while it is negatively charged at pH values above 6.4.

$$TiOH + H^+ \rightarrow TiOH_2^+ \qquad pH < pH_{pzc} \qquad (4)$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \qquad pH > pH_{pzc} \qquad (5)$$

where $TiOH_2^+$, TiO^- and TiOH are the positive, negative and neutral surface hydroxyl groups, respectively [24]. These properties caused changes in

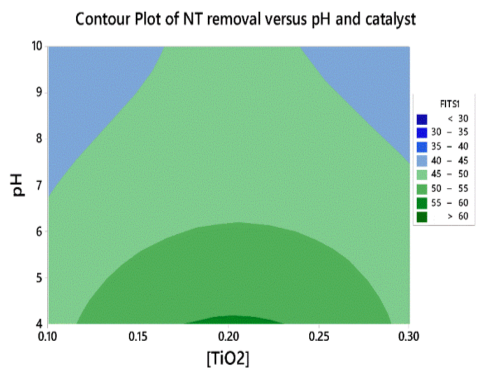

Figure 3. Counter plot for the degradation efficiency of PNT versus: the dosage of TiO_2 and pH

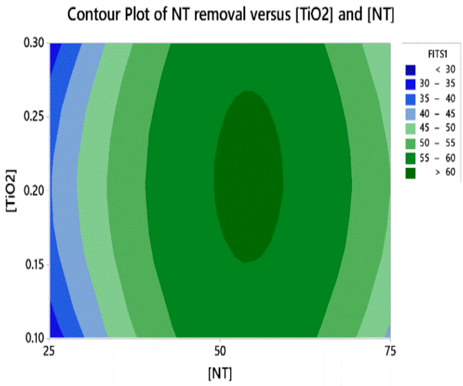

Figure 4. Counter plot for the degradation efficiency of PNT versus: the dosage of TiO_2 and PNT

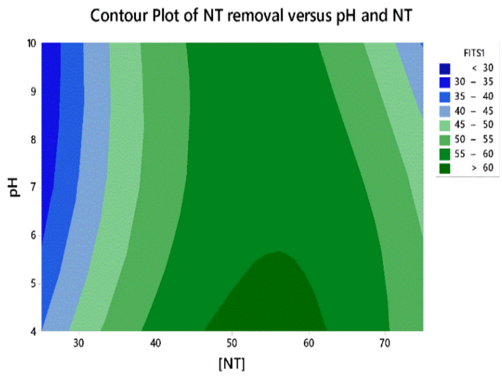

Figure 5. Counter plot for the degradation efficiency of PNT versus: the dosage of PNT and pH

the structure of pollutant at various pH and subsequently adsorption on TiO_2 surface [25]. The effect of pH in the range of 4 to 10 on the photo degradation of PNT was investigated and it can be seen in Figure 3. However, it is observed that more increase in pH will conduct to less degradation. Possible reason is at high pH columbic repulsion between OH^- and the negatively charged surface of TiO_2 particles could avoid the creation of hydroxyl radicals and consequently it decrease the degradation rate.

3. 3. 2. Effect of TiO_2 Concentration in UV/TiO_2 Process Degradation experiments were performed with varying TiO_2 concentration from 0.1 to 0.3 g/L. It is reported that the optimum TiO_2 concentrations were depended not only on the pollutants concentration but also to the photo reactor geometry [26]. The results in Figure 4 show that the degradation is enhanced by increase in TiO_2 concentration until it reaches a plateau, and then it remains flat and slightly decreases. The aggregation of TiO_2 particles at high dosages can cause a decrease in the number of active sites on the surface of the catalyst. On the other hand, more loading the catalyst causes opacity, raising the light scattering and therefore, light penetration in the solution would be decreased [27–28]. Therefore, the optimum amount of TiO_2 photo catalyst was selected as 0.2 g/L.

3. 3. 3. Effect of Initial Concentration of PNT in UV/TiO_2 Process Due to presence of more pollutant molecules at higher concentrations and as a significant factor in water treatment which influence on the photo catalytic degradation rate, different initial PNT concentrations (from 25 to 75mg/L) was inspected. The corresponding results are shown in Figure 5.

As it can be seen in Figure 5, by increasing initial concentration of PNT, as degradation reaction occurred on TiO_2 particles; the photo degradation rate of PNT decreases due to above mentioned reason [29]. The photo degradation reaction occurs between the the PNT molecules in the solution and hydroxyl radicals produced by active OH^- sites on the surface of TiO_2. Because of the competitive adsorption of PNT molecules on the surface of TiO_2 at high initial concentration of pollutant (75 mg/L), the number of available active sites decreases. Therefore, the degradation rate will decrease due to covering of active sites by PNT molecules. On the other hand, when the initial concentration of PNT was low (25 mg/L), even though there was more active sites, but the transfer rate of PNT molecules in the solution was low.

3. 4. Photo Degradability of PNT When the pollutant irradiated with only UV light, fair degradation (6%) was occurred. At the same condition, by the presence of TiO_2 and absence of UV light about 10% of PNT was degraded. That is due to the pollutant absorbed on the surface of the catalyst. However, at 120 min reaction time, about 64% of PNT was converted at optimum condition in the presence of TiO_2 along with UV light.

The hydroxyl radical was non-selective oxidant and an extremely strong that resulted in the degradation of pollutants [30, 31]. This happened only by accompanying the catalyst and UV irradiation .The mechanism of degradation of PNT by TiO_2in the presence of UV light is shown in the following equations:

$$TiO_2 + h\nu < 387\ nm \rightarrow e^-_{CB} + h^+_{vb} \tag{6}$$

$$h^+_{vb} + H_2O_{(ads)} \rightarrow OH^\bullet_{ads} + H^+ \tag{7}$$

$$h^+_{vb} + OH^-_{ads} \rightarrow OH^\bullet_{ads} \tag{8}$$

$$OH^\bullet_{ads} + PNT_{(ads)} \rightarrow intermediate(s) + OH^\bullet_{ads} \rightarrow CO_2 + H_2O \tag{9}$$

3. 5. Response Optimization The main goal of this study was to optimize the variables that are effective in the degradation of PNT in the UV/TiO_2 process. The main purpose was introduced with the maximum percentage of degradation PNT. The optimum values for maximum degradation are presented in Table 4. Predicted experiments by this approach based on design of experiments were performed to evaluate this method. The results illustrated that maximum response obtained from the optimal values have a good agreement with the predicted value of the model. In general, it can be concluded that the optimization method used in this study was successful. At the predicted optimum conditions, the tests were performed and 64% of PNT was degraded.

TABLE 4. Degradation efficiency at optimum values of the process variables.

Variables	Optimum values for degradation of PNT (%)
Initial dosage of PNT (mg/L)	50
Initial dosage of TiO_2(g/L)	0.2
Initial pH	4
Degradation of PNT (%)	Pred.(63.82), Exp.(64.00)

4. CONCLUSIONS

In this study, the FFD approach used to design the experiments and it was performed to remove PNT in synthetic wastewater by UV/TiO_2 process.

This experimental design was used to investigate the effect of operating variables such as initial concentration of PNT, pH and catalyst concentration. The optimum conditions predicted by the model were [TiO_2] = 0.2g/L, pH value of 4, and [PNT] =50mg/L. The ANOVA table shows the second-order regression model. Also, in this model, a high determination coefficient value (R^2 = 0.9876, R^2_{pred} = 0.8585, R^2_{adj} = 0.9596 for the destruction of PNT) was obtained. In this work, the effect of each factor and their interactions on the degradation of PNT, the counter plots were employed. UV/TiO_2 process using batch recirculation photo reactor involving UV light and oxygen could efficiently be used to degrade the PNT. However, using UV light or TiO_2 individually, has negligible effects on the PNT degradation.

FFD design of experiments obviously showed that this approach could successfully employed to predict optimum condition and develop an empirical equation to gain high degradation rates, which is essential for photo catalytic processes.

Initial concentration of pollutant, pH, catalyst dosage and irradiation time clearly affect on the PNT degradation.

The effect of modification of TiO_2 on the degradation intensity of PNT and light intensity would be investigated in future works.

5. ACKNOWLEDGMENTS

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Using Experimental Design to Optimize the Photo-degradation of P-Nitro Toluene by Nano-TiO_2 in Synthetic Wastewater

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چکیده

در این تحقیق، تخریب پارا نیترو تولوئن (PNT) در محلول آبی با استفاده از فرآیند UV / TiO_2 مورد بررسی قرار گرفت. پارا نیتروتولوئن اثرات بسیار مضر بر محیط زیست و هورمون های انسانی به عنوان یک آلاینده دارد. فرآیند UV/TiO_2 یکی از روش های موثر در فرآیند های اکسایش پیشرفته می باشد. همچنین دی اکسید تیتانیوم (TiO_2) یکی از بهترین نیمه هادی ها است که می تواند نقش فوتو کاتالیزوری را به خوبی در این فرآیند ها ایفا کند. طراحی آزمایش با روش فاکتوریل کامل (FFD) به منظور بررسی و بهینه سازی متغیرهای عملیاتی از جمله pH، غلظت اولیه پارا نیتروتولوئن و غلظت کاتالیزور استفاده شده است. تجزیه و تحلیل واریانس (ANOVA) برای تخریب پارا نیترو تولوئن انجام شد و مدل رگرسیون مرتبه دو با دقت مطلوبی ($R^2 = 0.9876$, $R^2_{pred} = 0.8585$, $R^2_{adj} = 0.9596$) ارائه شد. برای تعیین شرایط بهینه، از شکل های گرافیکی استفاده گردید و متغیرهای عملیاتی در $[TiO_2] = 0.2$g/L، pH=4 و [PNT] =50 mg/L بهینه شده است. نتایج نشان داد که در شرایط بهینه پس از 120 دقیقه واکنش، تخریب پارانیتروتولوئن 64% و COD=55% می باشد.

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