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Optimization P-nitrotoluene Removal Efficiency in Aqueous Solution by Photocatalyticozonation Reaction

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Abstract

p-Nitrotoluene (PNT) is a hazardous material suspected of causing hormone disruption. Its degradation in aqueous solutions was studied using photochemical ozonation with ZnO as a catalyst and UV radiation. Various factors, including PNT concentration, ZnO concentration, pH, ozone flow rate, and UV exposure time, were varied in laboratory experiments. Response surface methodology (SRM) and central composite rotatable design (CCRD) were used to optimize the process. The PNT removal efficiency ranged from 47% to 99.5%, with a high correlation (R^2 = 0.9558). Significant factors included UV exposure time, pH, ozone flow rate, ZnO concentration, and initial PNT concentration. The maximum removal efficiency was achieved with 76.701 ppm of initial PNT, 0.16 g/l ZnO, pH 8.235, 3.516 ozone flow rate, and 99.548 minutes of UV exposure.

Keywords: ANOVA, CCRD, Ozonation, P-Nitrotoluene, Photocatalytic, RSM.

الخلاصة:

يعد البارانيتروتولوين (PNT) مادة خطرة يُشتبه في تسببها باضطرابات هرمونية. وقد دُرست عملية تحلله في المحاليل المائية باستخدام الأوزنة الضوئية الكيميائية مع أكسيد الزنك (ZnO) كعامل مساعد والأشعة فوق البنفسجية. تم تغيير عوامل مختلفة في التجارب المختبرية، بما في ذلك تركيز البارانيتروتولوين، وتركيز أوكسيد الزنك، ودرجة الحموضة، ومعدل تدفق الأوزون، وزمن التعرض للأشعة فوق البنفسجية. واستُخدمت منهجية سطح الاستجابة (RSM) والتصميم المركزي المركب القابل للدوران (CCRD) لتحسين العملية. تراوحت كفاءة إزالة البارانيتروتولوين من 47% إلى 99.5%، مع معامل ارتباط عالٍ (R^2 = 0.9558). وشملت العوامل المؤثرة بشكل كبير زمن التعرض للأشعة فوق البنفسجية، ودرجة الحموضة، ومعدل تدفق الأوزون،

تحسين كفاءة إزالة البارانيتروتولوين من المحلول المائي باستخدام تفاعل الأوزنة الضوئية التحفيزية

وتركيز أوكسيد الزنك، والتركيز الأولي للبارانيتروتولوين. وقد تحققت أقصى كفاءة إزالة عند تركيز أولي للبارانيتروتولوين قدره 76.701 جزء في المليون، وتركيز أوكسيد الزنك 0.16 غ/ل، ودرجة حموضة 8.235، ومعدل تدفق أوزون 3.516، وزمن تعرض للأشعة فوق البنفسجية قدره 99.548 دقيقة.

1. Introduction

There are many industrial factories that use nitroaromatic compounds such as explosives, textiles, paper industries, preparation of pesticides, etc. They will pollute water when discharged with factory wastewater without suitable treatment and cause hazards to human health and water resources [1]. In general, these compounds are complex and difficult to deplete by using conventional wastewater treatments via stability and refectory, which are considered difficult to remove from wastewater [2]. P-nitrotoluene (PNT) is a compound from the nitroaromatic family that was intermediate formed during trinitrotoluene TNT production, purification of toluene diisocyanates TDI, etc., and it's reported at high toxicity, which may represent common pollutants that harm human health [3]. For all mentioned previously, PNT must be removed from wastewater; there are many techniques that are used for TNP degradation, such as UV catalytic Fenton oxidation [4], photo catalytic degradation [5], bio transformation [6], and ozonation under sonolysis conditions US/O3 [7]. The most important technique used for PNT degradation is using ozone with the presence of a catalyst, in which ozone produces free radicals (•OH) that may attack the C-N bond, followed by fast opening of phenol ring, to produce acetic acid and finally oxidized rapidly for water and carbon dioxide [8].

Ultra violet UV radiation is used for the enhancement of ozone decomposition to produce free radicals, leading to an increased ozonation reaction rate [9]. When paired with UV radiation, ozonation free radicals may hasten the breakdown of less reactive contaminants [10]. Ozone was reactive in acidic media, but as the solution became more basic, the ozone rate decomposition increased [11]. This may have come from two factors: in a high pH solution, more free radicals were created, and second, the rate of (•OH) was slow at a pH range of 2.8- 4.5 [12]. The presence of ozone at a high value provided a high gas-liquid interface, which increased free radical formation as well as increased PNT degradation [13].

In this study, was performed PNT degradation by UV/ozonation in the presence of ZnO as a catalyst under varied conditions, including initial PNT concentration, ZnO concentration, pH, Ozone flow rate, and UV exposure time, which was arranged by using RSM combined with CCRD to determine the optimum conditions lead to high PNT removal efficiency and explain mathematical relation between PNT removal efficiency with studied (controllable) variables.

Response Surface Methodology (RSM) is a statistical and mathematical tool that models and optimizes processes where multiple variables influence a response [14]. It helps in the identification of the ideal operating conditions by analyzing interactions between factors and reducing the number of experimental trials needed. RSM is widely utilized in chemical and environmental engineering to enhance efficiency and lower operational costs by providing predictive models for process optimization [15].

In recent studies, RSM has been effectively applied to optimize photocatalytic degradation processes. For instance, Li et al. [16] used RSM to enhance the removal of pharmaceutical contaminants from wastewater using TiO_2-based photocatalysts, achieving over 90% degradation efficiency under optimized conditions.

1.1. Aim of the study

1. Optimize the photocatalytic degradation of PNT using ZnO as a catalyst under ozonation and UV irradiation.
2. Apply Response Surface Methodology (RSM) to evaluate the impact of key operational parameters on removal efficiency.
3. Analyze the effects of pH, ZnO concentration, ozone flow rate, UV exposure time, and initial PNT concentration.
4. Determine optimal conditions to achieve maximum pollutant degradation.
5. Minimize energy consumption and operational costs for a more efficient and sustainable wastewater treatment process.

2. Material and Methods

2.1. Chemicals and equipment

The instruments used in this research work were:

A. UV-VIS Spectrophotometer model Agilent 8453.

B. pH meter device model Metrohm 823.

C. Magnetic stirrer model MS-HP.

D. Laboratory built-in photoreactor.

E. Ozone generator, as shown in Figure (1).

Fig. (1): Ozone generator

This device is an ozone generator used for sterilization and purification of water or air by producing ozone gas (O_3), which has a strong ability to kill bacteria, viruses, and fungi and eliminate laboratories and clinics to ensure a clean and safe environment.

The chemicals used in this study include p-nitrotoluene (PNT) (≥99%, Sigma-Aldrich), zinc oxide nanoparticles (ZnO, 10-30 nm) (≥99.9%, Merck), hydrochloric acid (HCl) (37%, Sigma-Aldrich), sodium hydroxide (NaOH) (≥98%, Sigma-Aldrich), and distilled water (DW) (laboratory-grade, ultrapure). The laboratory equipment used is a pH meter type Metrohm model 823, ultrasonic homogenizer, and ozone generation type Ozo+.

A Continuous Stirred Tank Reactor (CSTR) was used in the experiments, ensuring stable operation through continuous reactant inflow and product discharge. The CSTR is widely used in industries such as chemical manufacturing, biotechnology, and pharmaceuticals. It operates with continuous reactant input and product output, ensuring a steady-state condition with uniform mixing [17]. CSTRs offer precise temperature and pressure control but may suffer from efficiency losses due to long residence times and dilution effects [18].

2.2. Method

The ozonation of the PNT photocatalytic reaction was investigated by applying five different factors (initial PNT concentration, ZnO concentration, pH solution, ozone flow rate, and UV time). Simulated wastewater was prepared by dissolving the required weight of PNT in 100 ml DW with an ultrasonic homogenizer. The pH solution was adjusted according to the desired value of hydrochloric acid and sodium hydroxide. The required amount of catalyst zinc oxide was added to the PNT solution. Ozone generation was operated, and UV lamps were used to start up the run. The PNT concentrations before and after the reaction were measured using the UV spectrum to calculate the PNT removal efficiency for each run.

2.3. Design of Experiments DOE

The classical experimentation approach is done by studying the effect of one variable while holding other variables over certain values and repeating that with other studied variables. These methods determine quantitative relations between responses and studied variables, but these are incapable of detecting the interaction of variables [19]. Generally, the use of DOE is to obtain a mathematical expression between studied (controllable) variables and absorbed (actual) results for response with interaction effects between each variable; on the other hand, the use of experimental design will reduce the total number of iterations needed to account for all levels of the variables under study. The using of DOE here is to determine the mathematical relationship between studied variables (initial PNT concentration, ZnO concentration, pH, Ozone flow rate, and UV time) on PNT removal efficiency Y based on RSM in conjunction with CCRD and by the aim of design expert software version 11 (Stat-Ease, In Silicon Valley, CA, USA). As mentioned above, the study included five factors: initial PNT concentration (X1), ZnO concentration (X2), pH (X3), Ozone flow rate (X4), and UV time (X5), which are shown with their levels in Table (1).

According to RSM, DOE is required to determine the number of runs, which requires covering the studied variables range as well as giving reliable measurements for response (dependent variable) [20]. Accordingly, the number of experiments was 50 runs, as shown in Table (2). The following is the procedure for fitting the experimental results to a polynomial of second order:

$$PNT\ removal(\%) = \frac{Initial\ PNT\ Conc. - Final\ PNT\ Conc.}{Initial\ PNT\ Conc.} \times 100 \qquad (1)$$

Where Y is the response variable (PNT removal efficiency); X_i and X_j are independent (studied) variables; $b0$ coefficient of intercept; bi and bii are 1st and 2nd order quadratic equation coefficients, respectively, while bij is the coefficient of the model resulting from the interaction between variables i and j and ε is standard error.

Table (1): Studied variables range and levels

Variable	Symbols	Levels				
		-α = 2.378	-1	0	1	α = 2.378
Initial PNT concentration (ppm)	X1	25	46.73	62.5	78.26	100
ZnO concentration (g/L)	X2	0.1	0.128	0.15	0.171	0.2
pH (-)	X3	4	5.73	7	8.26	10
Ozone flow rate (g/hr.)	X4	0	1.44	2.5	3.55	5
UV time (min)	X5	30	56.07	75	93.92	120

Table (2): Experimental design and actual value for removal efficiency Y (response)

Run	Variables in coded levels					Y
	Initial PNT concentration (X1)	ZnO concentration (X2)	pH (X3)	Ozone flow rate (X4)	UV time (X5)	
1	0	0	0	0	0	86
2	1	1	1	-1	1	80
3	1	1	-1	1	1	97.5
4	0	0	0	0	-2.38	64.5
5	1	1	-1	-1	-1	47
6	1	1	-1	-1	1	58.18
7	0	0	0	0	0	81.17
8	-1	1	-1	1	-1	73
9	0	0	0	0	2.38	90
10	-1	-1	1	1	1	75.65
11	-1	-1	-1	1	1	81.87
12	1	1	1	1	1	99.5
13	0	-2.38	0	0	0	90
14	0	0	0	0	0	80.5
15	0	0	-2.38	0	0	80.20
16	-1	-1	1	-1	1	85
17	-1	-1	-1	1	-1	70.71
18	1	1	1	-1	-1	70
19	-1	1	1	1	-1	80.5
20	-1	-1	-1	-1	-1	86
21	-1	1	-1	1	1	88.27
22	-1	-1	1	-1	-1	83.38
23	-1	1	-1	-1	-1	64
24	-1	1	-1	-1	1	87.05
25	0	0	0	0	0	84.46
26	1	1	-1	1	-1	76.59
27	1	-1	1	-1	1	88.89
28	0	0	0	0	0	84.39
29	1	-1	1	1	-1	92
30	1	-1	1	-1	-1	82.55
31	-1	1	1	-1	-1	76
32	1	1	1	1	-1	90.83
33	0	0	2.38	0	0	96.65
34	0	0	0	-2.38	0	0.0005
35	1	-1	-1	-1	-1	76.07
36	1	-1	-1	-1	1	82.98
37	1	-1	-1	1	-1	83.54
38	0	0	0	0	0	80
39	0	2.38	0	0	0	85
40	1	-1	1	1	1	97.9
41	2.38	0	0	0	0	94.04
42	0	0	0	0	0	80
43	-2.38	0	0	0	0	91.08
44	-1	1	1	-1	1	95.83
45	0	0	0	0	0	82
46	0	0	0	2.38	0	85.3
47	-1	-1	-1	-1	1	92.89
48	-1	1	1	1	1	88
49	1	-1	-1	1	1	95.5
50	-1	-1	1	1	-1	65
	R^2	0.9558				
	Adjusted R2	0.9231				

Steps for Measuring PNT Using an Analytical Balance:

1. Calibrate the Balance – Use the Mettler Toledo XS205 (or similar analytical balance) with standard weights and place it on a stable surface.
2. Prepare the Weighing Container – Place a clean dish or weighing paper on the balance and press Tare to reset to zero.
3. Add PNT Carefully – Use a clean spoon or tweezers to transfer PNT, avoiding direct contact.
4. Record the Weight – Wait for the reading to stabilize, then adjust as needed for precision.

Notes: Work in a dry environment, store PNT in a sealed container, and use a fume hood if necessary.

3. Result and Discussion

3.1. Coded empirical model

The experimental observations are shown in Table (2), in which the PNT removal efficiency values range between 47- 99.5 %, according to each experiment condition except the result for run number 34; it is 0.0005% and this is a logical value due to the absence of ozone in other words no reaction was taking place, and it was neglected for analysis of variance ANOVA analysis. The summary of the ANOVA is shown in Table (3), which shows the correlation coefficient (R2) was 0.9558, which means that 95.58% of the total variance can be said to depend on the independent variables studied.

The results were analyzed through RSM combined with CCRD to get the empirical model for response (PNT removal efficiency) as a function of the studied variables (PNT initial concentration, ZnO concentration, pH Ozone flow rate, and UV exposure time), which are below:

$$Y = 82.32 + 0.7598X_1 - 1{,}84X_2 + 2.98X_3 + 3.14X_4 + 5.51X_5 - 2.87X_1X_2 + 2.46X_1X_3 + 6.09X_1X_4 - 0.4403X_1X_5 + 2.76X_2X_3 + 4.12X_2X_4 + 1.72X_2X_5 - 1.41X_3X_4 - 1.15X_3X_5 + 0.1933X_4X_5 + 1.81X_1^2 + 0.9166X_2^2 + 1.08X_3^2 - 3.06X_4^2 - 0.8954X_5^2 \quad (5)$$

Where Y is PNT removal efficiency, X_1 is initial PNT concentration, X_2 is ZnO concentration, X_3 is solution pH, X_4 is ozone flow rate and X_5 is UV exposure time.

Table (3): Results of ANOVA for Y (response)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5224.27	20	261.21	29.19	< 0.0001	significant
X_1-PNT initial Conc.	25.01	1	25.01	2.79	0.1061	
X_2-Zno Concentration	146.14	1	146.14	16.33	0.0004	
X_3-PH	384.22	1	384.22	42.94	< 0.0001	
X_4-Flow O_3	315.89	1	315.89	35.3	< 0.0001	
X_5-Time (UV exposure)	1313.18	1	1313.18	146.76	< 0.0001	
X_1X_2	264.37	1	264.37	29.55	< 0.0001	
X_1X_3	193.73	1	193.73	21.65	< 0.0001	
X_1X_4	1186.44	1	1186.44	132.6	< 0.0001	
X_1X_4	6.2	1	6.2	0.6933	0.4124	
X_2X_3	243.38	1	243.38	27.2	< 0.0001	
X_2X_4	542.13	1	542.13	60.59	< 0.0001	
X_2X_5	94.47	1	94.47	10.56	0.0031	
X_3X_4	63.5	1	63.5	7.1	0.0129	
X_3X_5	42.37	1	42.37	4.74	0.0385	
X_4X_5	1.2	1	1.2	0.1336	0.7176	
X_1^2	167.85	1	167.85	18.76	0.0002	
X_2^2	43.01	1	43.01	4.81	0.0371	
X_3^2	59.75	1	59.75	6.68	0.0155	
X_4^2	123.82	1	123.82	13.84	0.0009	
X_5^2	41.05	1	41.05	4.59	0.0414	

It was noted from Table (3) that the F-value for regression was 29.19, and this is greater than that tabulated (F20, 5, 0,05 = 4.56), which indicated that the assumed second-order polynomial is highly significant. The significance for each term was determined by examined P-values, which are listed in Table (3); the terms X_3, X_4, X_5, X_1X_2, X_1X_3, X_1X_4, X_2X_3 and X_2X_4 were highly significant through a very small P-value. The final empirical model, according to ANOVA analysis, will be in the following form:

A comparison between predicted and experimental data points for the response was shown in Figure (1), as seen in the distribution of points around 45º lines, which indicates an accurate depiction of scientific findings by a good fit for the assumed model. Removal efficiency as a function of the factors under investigation was ordered according to importance as follows: UV time exposure, pH, ozone flow rate, ZnO concentration, and initial PNT concentration via their F-values 146.76, 42.94, 35.3, 16.33, and 2.79, respectively.

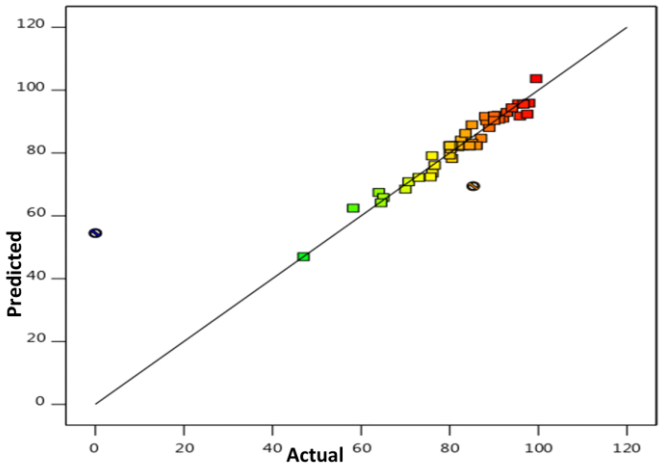

Fig. (2): Comparison between the actual and predicted response values for PNT removal efficiency

3.2. Effect of studied variables

The impact of each investigated variable on the effectiveness of PNT elimination is explained in Figure (2), in which PNT removal efficiency increases with pH, and this agrees with S. Song's report [7]. The initial PNT concentration with a higher value triggered a decrease in efficiency in removing PNTs, while the presence of ZnO concentration inversely affected efficiency in removing PNTs, and this may be due to the ZnO particle tendency to agglomerate at its concentration increase. Effect of ozone flow rate, as seen with increasing ozone flow rate which leads to the increasing area of gas-liquid interface and this will cause increasing ozone concentration resulting more and more free radicals required for PNT degradation reaction, and this agrees with S. Song report [7] until reached the maximum value for PNT removal efficiency at about 2.56 g/L, and via elevation of the ozone flow more than this value the response started decreasing. The increase in time will be caused by PNT removal efficiency due to increasing contact time between reactants.

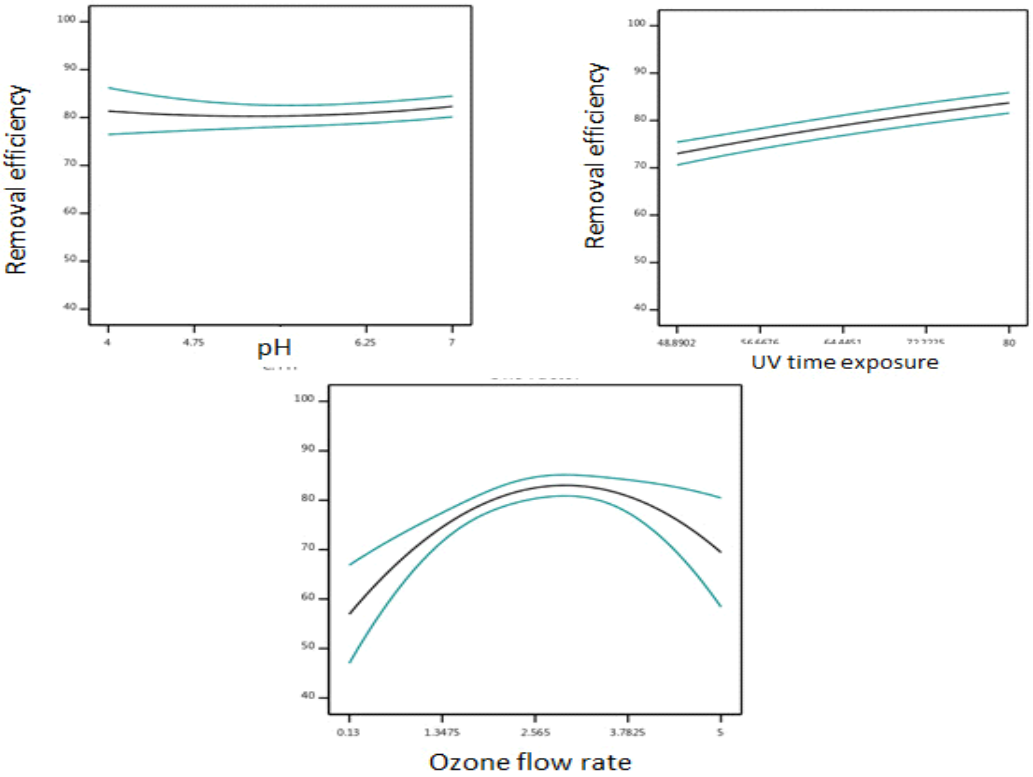

Fig. (2): Effect of more significant individual variables (pH solution, ozone flow rate, and UV time exposure) on PNT removal efficiency

3.3. Interactions effect of studied variables

The interaction between terms in the model via their significance was illustrated by plotting at the same time two variables on a contour chart (two dimensions) and the response surface. The final empirical model shows the reduced model for response (PNT removal efficiency), as it was noted that the response depends on three individual variables (X_3, X_4 and X_5) and five interaction factors (X_1X_2, X_1X_3, X_1X_4, X_2X_3 and X_2X_4) through their significance.

$$Y = 82.32 + 2.98X_3 + 3.14X_4 + 5.51X_5 - 2.87X_1X_2 + 2.46X_1X_3 + 6.09X_1X_4 + 2.76X_2X_3 + 4.12X_2X_4 \quad (6)$$

Figure (3) shows the interaction effect between initial PNT concentration and ZnO concentration on the contour chart. The removal efficiency increases when the initial PNT concentration is reduced from 100 to 62.5 ppm at any ZnO concentration at the range of 0.2 to 0.16 g/l, while The interaction between initial PNT concentration and pH solution is presented in Figure (4), the PNT removal efficiency was increased by initial PNT concentration from 100 to 62.5 ppm at any constant value for pH within the range from 4 to 6.25, figures reveals that maximum response more than 81 %.

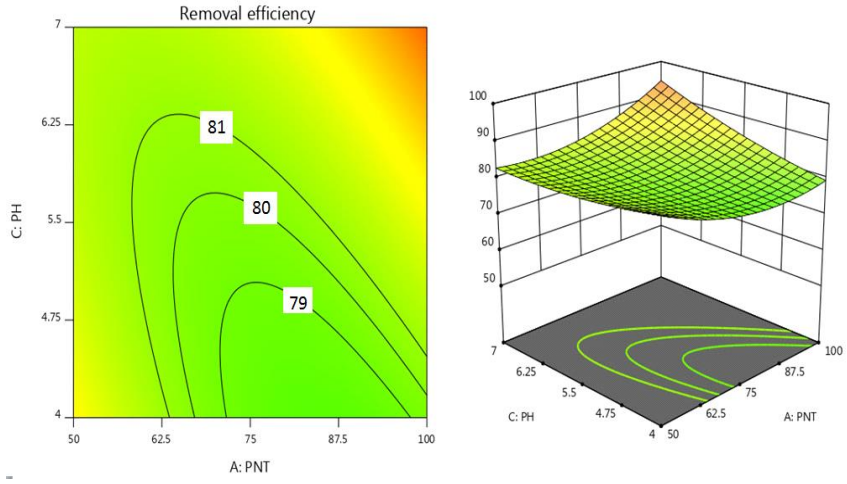

Fig. (3): Contour plot (left) and response surface (right) representing the combined effect of initial PNT concentration and ZnO concentration on PNT removal efficiency

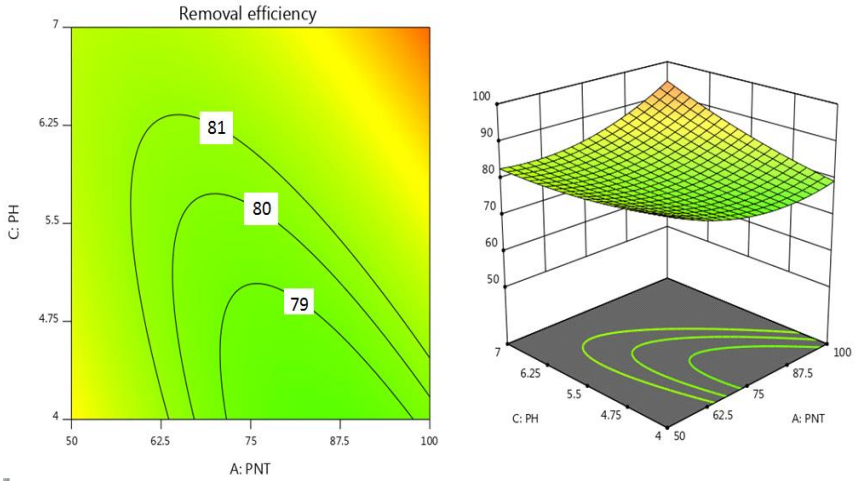

Fig. (4): Contour plot (left) and response surface (right) representing the combined effect of initial PNT concentration and pH solution on PNT removal efficiency

The interaction effect between initial PNT concentrations and ozone flow rate presented in Figure (5), the efficiency of removing PNTs rose for the ozone flow rate range from about 0.25 g/l until they reached value of 2.56 g/l for any value for initial PNT concentration, and suddenly response started decreasing from a maximum value at ozone flow rate 2.56 to 3.78 g/l. It is clear that effect of the ozone flow rate on the removal efficiency has overcome the effect of the initial PNT concentration, and this may be because the rate of ozone flow is of greater importance according to the value of F in the ANOVA analysis, the same situation that we will get when examining the reaction outcome of both the ozone flow rate and concentration ZnO, (see Figures (6), (7)) where The pace of ozone flow is more critical than the ZnO concentration.

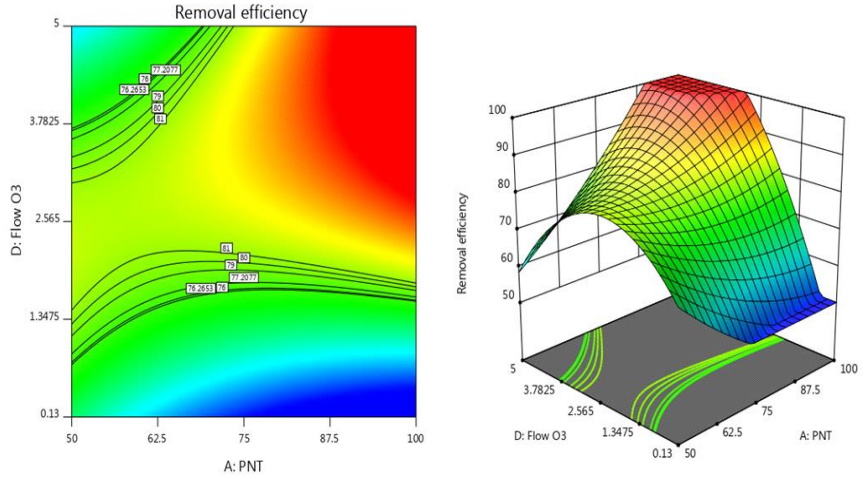

Fig. (5): Contour plot (left) and response surface (right) representing the combined effect of initial PNT concentration and ozone flow rate on PNT removal efficiency

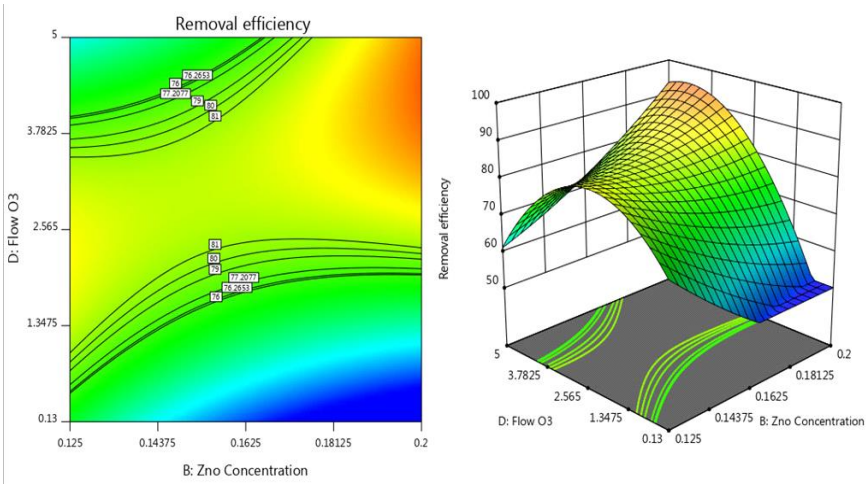

Fig. (6): Contour plot (left) and response surface (right) representing the combined effect of initial PNT concentration and ozone flow rate on PNT removal efficiency

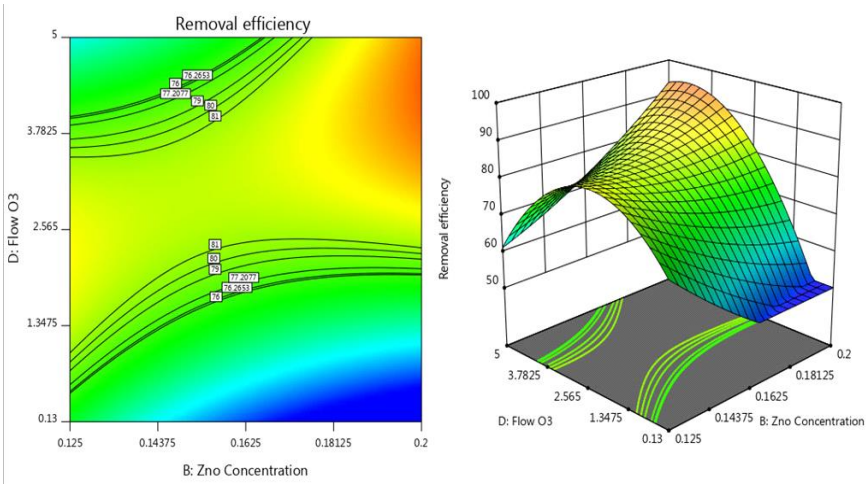

Fig. (7): Contour plot (left) and response surface (right) representing the combined effect of pH solution and ZnO concentration on PNT removal efficiency

3.4. Process optimization

In order to discover values for all variables that meet specified requirements, Optimization is one of the most significant capabilities offered by Design Expert program (version 11). The desired response and the limitations of each variable are displayed in Table (4). The solution that met all response criteria (PNT removal efficiency) is shown in Table (5). The suggested statistical model is satisfactory for PNT removal efficiency by photocatalytic ozonation reaction; therefore, as per the Design Expert software solution, the ideal circumstances are 100 solutions, and one was chosen as an example, as shown in Table (5).

Table (4): Constraints each variable for numerical optimization of response

Type of variable	Goal	Lower limit	Upper limit
Initial PNT concentration (ppm)	is in range	46.7332	78.2668
ZnO Concentration (g/l)	is in range	0.128978	0.171022
PH (-)	is in range	5.73866	8.26134
Ozone flow rate (g /l)	is in range	1.44888	3.55112
UV time exposure (min)	is in range	56.0798	93.9202
PNT removal efficiency (%)	maximize	47	99.5

Table (5): Constraints each variable for numerical optimization of response

No.	Initial PNT concentration (ppm)	ZnO Concentration (g /l)	PH	Ozone flow rate (g /l)	UV time exposure (min)	PNT removal efficiency (%)	Desirability
1	76.701	0.160	8.235	3.516	93.854	99.548	1.000

The experimental findings confirmed the effective degradation of PNT through ozonation in the presence of ZnO as a catalyst. Optimum conditions were determined using RSM for selected experimental runs, with removal efficiency ranging between 47–99.5%. ANOVA analysis indicates that the studied variables significantly influenced the response in the following order: UV time exposure, pH, ozone flow rate, ZnO concentration, and initial PNT concentration, with F-values of 146.76, 42.94, 35.3, 16.33, and 2.79, respectively.

Using software to design a test, especially The reaction surface method's implementation to examine the consequence of different factors on PNT degradation and their interactions increases accuracy and efficiency while reducing costs, time, and energy consumption. This method allows for the optimization of the process by considering effective factors, achieving the highest degradation with the lowest cost.

Considering the outcomes of the planned experiments, the reported numbers and outcomes align well with the model provided by the software. By analyzing the influencing factors and reported graphs, it was found that changes in pH significantly affect PNT degradation. The maximum removal efficiency was achieved under the following conditions:

Initial PNT concentration: 76.7 ppm

ZnO concentration: 0.16 g/L

pH: 8.235

Ozone flow rate: 3.516 g/L

UV exposure time: 93.854 minutes

Using ultraviolet radiation, which has the energy to break the PNT structure, along with nano-catalysts, is an effective approach to eliminating or reducing hazardous detergents from textile waste. This method, in addition to its high efficiency in reducing contamination from textile and dyeing industries, is clean and poses minimal risk to the environment and living organisms.

4. Conclusion

The study shows that the removal (degradation) of PNT by ozonation reaction in the presence of ZnO as a catalyst was successful. Optimum conditions were established by using RSM for some experimental runs, with removal efficiency results of 47-99.5%. ANOVA analysis shows that the studied variables have significance on response with order: UV time exposure, pH, ozone flow rate, ZnO concentration, and initial PNT concentration via their F-values 146.76, 42.94, 35.3, 16.33, and 2.79, respectively.

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