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The use of response surface methodology for modeling and optimizing of pnitrophenol contaminated water treatment process conducted by the nonthermal plasma discharge technology

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GRAPHICAL ABSTRACT



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1. Introduction

In recent years, the rapid growth of industrial development has led to the significant production of various organic compounds, particularly those derived from petroleum sources. These petroleum-based compounds, which are often present in refinery wastewater, pose a serious environmental challenge. Due to their toxic nature and persistence in the environment, these compounds are classified as priority pollutants, demanding urgent attention for effective *Corresponding author Email: F.Qaderi@nit.ac.ir

ABSTRACT

In the realm of industrial development, a variety of organic pollutants, including petroleum compounds, have emerged as persistent environmental concerns due to their non-degradable nature. To effectively address this issue, plasma technology has garnered significant attention as a promising approach for wastewater treatment, offering the capability to eliminate a wide spectrum of contaminants. This research capitalizes on Response surface methodology (RSM) to explore the independent and combined effects of key factors such as initial concentration, pH, applied voltage, and time on the degradation of a specific pollutant known as PNP, utilizing non-thermal discharge plasma technology. The outcomes of this investigation unveiled several noteworthy trends. Enhancing the initial pH, applied voltage, and reaction time while reducing the initial concentration exhibited a positive influence on the removal efficiency. Additionally, the study examined the interactions among these variables, revealing both antagonistic and synergistic effects. Specifically, antagonistic relationships were observed between initial concentration and initial pH, initial concentration and applied voltage, as well as applied voltage and time. On the other hand, a synergistic effect was noted between initial concentration and time. By employing an optimization approach, the optimal conditions for achieving PNP degradation were determined to be as follows: an initial concentration of 50 mg/L, pH of 9.7, applied voltage of 13.75 kV, and a reaction time of 8 min, resulting in an impressive removal efficiency of 96.503%. The findings of this study underscore the immense potential of non-thermal discharge plasma technology and the utilization of RSM in advancing the optimization of advanced oxidation processes for effective wastewater treatment.

management and treatment (Mrayyan and Battikhi, 2005; Wake, 2005). The release of these biodegradable materials into the environment can cause significant environmental risks (Babanezhad et al. 2017; Dabbaghi et al. 2021).

Phenolic compounds, recognized as highly hazardous industrial pollutants, have garnered significant attention due to their remarkable toxicity (Meng et al. 2016; Zhao et al. 2021). These versatile compounds find extensive use in a wide range of industries, including oil refining, steel production, pharmaceuticals, textiles, plastics, paper

Cite this article: A, Khourshidi, F. Qaderi The use of response surface methodology for modeling and optimizing of p-nitrophenol contaminated water treatment process conducted by the non-thermal plasma discharge technology, *Journal of Applied Research in Water and Wastewater*, 10 (1), 2023, 80-90. https://doi.org/10.22126/arww.2023.8527.1275 manufacturing, as well as in the production of disinfectants, chemical reactants, paints, and resins (Boruah et al., 2017; Taghizadeh et al. 2019; Ebrahimi & Qaderi 2021). Phenol and its derivatives pose a substantial risk to human and animal health due to their toxic nature. biodegradability, extended shelf life, (Liu et al., 2016), mutagenicity, carcinogenicity, high water solubility, and ability to bioaccumulate (Lai et al. 2014; Suarasan et al. 2002; Zhao et al. 2021). Therefore, developing effective techniques to eliminate harmful contaminants from water is crucial, whether through complete mineralization or the conversion of these contaminants into less harmful intermediate forms (Ebrahimi Ghadi et al. 2019; Yavari & Qaderi 2020). In this study, P-4nitrophenol (also referred to as 4-nitrophenol or hydroxynitrobenzene), a phenolic compound with a nitro group opposite the hydroxyl group on the benzene ring, is used as a representative of phenolic compounds.

There are numerous methods that have been proposed for treating wastewater containing PNP, including adsorption on adsorbents (Rushdi I.Yousef, El-Eswed and Al-Muhtaseb, 2011), solvent extraction, microwave irradiation, oxidation or chemical reduction (Ji, Yuefei et al., 2017), distillation (Busca et al., 2008), and removal by biological and physical methods. Each of these methods has its own limitations and disadvantages. The biological method is not suitable for phenol removal due to its toxicity (John wiley & Sons, 2003) and requires a longer purification time. The physical method does not completely remove impurities, but rather only transfers them from one phase to another (Boruah et al., 2017). Advanced oxidation processes are a type of chemical oxidation process that is divided into various categories, including H_2O_2/O_3 , homogeneous photolysis, heterogeneous photolysis, radiolysis, sonolysis, anodic oxidation, and photon reactants.

Non-thermal plasma discharge technology, specifically the dielectric barrier discharge (DBD), is widely recognized as an advanced oxidation process with numerous advantages in the field of wastewater treatment (Lai et al., 2014). One key advantage of this technology is its ability to generate potent active species, including OH• and O₃, which exhibit exceptional efficiency in wastewater treatment. These species play a pivotal role in the degradation and elimination of organic pollutants, thereby significantly enhancing the overall effectiveness of non-thermal plasma discharge technology in various wastewater treatment applications (Sun, Sato and Sid Clements, 1997a; Lukeš, 2001; Lukes, Appleton and Locke, 2004). Other characteristics include low energy consumption, independence from temperature and pressure, and environmental compatibility (Bruggeman and Leys, 2009). There has been extensive research on the structure of discharge reactors and their types, including needle-shaped electrodes to plate (Wang, Li and Quan, 2006), line to plate (Sano et al., 2002; Faungnawakij et al., 2006; Grabowski et al., 2006) line to tube (Faungnawakij et al., 2006) line to line (Shao et al., 2004) ring to the tube (Tri Sugiarto, Ohshima and Sato, 2002) are classified. Plasma electric discharge is also classified into three main groups based on the distribution of the phases: 1) electric discharge above the liquid surface, 2) direct electric discharge in the liquid phase, and 3) electric discharge in air/vapor bubbles in the liquid environment (Locke et al., 2006). Research shows that the efficiency of electrical discharge in the gas phase for decomposing organic material is usually higher than in the liquid phase (Malik, 2010; Hijosa-Valsero et al., 2013).

Previous studies have demonstrated the effectiveness of DBD in eliminating pollutants associated with petroleum, medical, and dye sources. These studies have investigated various parameters, including initial solution concentration, ozone dosage, initial pH, and reaction time, to assess their influence on the efficiency of pollutant removal. (Amano and Tezuka, 2007; Gu et al., 2009; Wang et al., 2012; Mirzaei et al., 2018; Ahmadi et al., 2020; Crema et al., 2020; Liu, Liu and Gu, 2020). However, the simultaneous effect of two arbitrary variables on the removal efficiency has not been reported.

Response surface methodology (RSM) optimizes complex systems by analyzing the relationship between input variables and output response (Sheikholeslami et al. 2020). Through experiments, a mathematical model (response surface) is created to predict and optimize the system's performance. RSM reduces the number of experiments needed, saving time and resources (Bezerra et al., 2008; Jin et al., 2014; Mirzaei et al., 2018; Moghadam & Qaderi, 2019).

This study aimed to develop a new mathematical model to examine the combined impact of two variables on the removal efficiency of p-Nitrophenol pollutants. The model also explored the interaction effects, including synergistic and antagonistic effects, between these variables. By analyzing the data using analysis of variance (ANOVA) and evaluating the significance of each variable, the study identified optimal conditions for pollutant removal, taking into account the combined and individual effects of the variables.

2. Materials and methods 2.1. Materials and equipment

For tests, P-nitrophenol as a contaminant, sodium hydroxide 0.01 molar, and hydrochloric acid 0.01 molar for pH adjustment were purchased from Merck Company. Lutron multifunction instrument model WA-2017SD was used to adjust the pH of the solution before purification and to measure the final pH of the solution, and a digital balance (Radwag AS 120.R2) was used Also, it is Used a digital stirrer (Alpha analog model HS860) to keep the solution homogeneous during the tests.

In this study, a cylindrical DBD reactor is used for plasma formation, which is one of the most commonly used among the various geometries of plasma reactors in water and wastewater treatment (Jiang et al., 2014). The high-voltage electrode employed in this setup is a stainlesssteel plate with a diameter of 77 mm and a thickness of 1 mm. A Plexiglas plate 130 mm in diameter and 2 mm thick located below the high-pressure electrode acts as a dielectric coating. The ground connection electrode is made of stainless steel and has the same dimensions as the high-pressure electrode, which is in contact with the solution at the bottom of the cylindrical reactor. The cylinder has an inner diameter of 110 mm, an outer diameter of 120 mm, and a height of 22.7 mm. Fig. 1 illustrates the schematic view of the reactor. The distance between the water surface and the dielectric coating was considered to be 5 mm, and this value was constant in all experiments according to the previous studies (Crema et al., 2020; Farzinfar and Qaderi, 2022). With this configuration, the volume of the solution that could be treated in the reactor was 200 ml., which is thoroughly mixed by a magnetic stirrer during the purification process. The pilot power supply consists of a Variac Transformer Adjustable Manual Voltage Regulator and a neon transformer connected in series. The Variac variable transformer is powered by 220 volts AC and its output voltage is adjustable from 0 to 300 volts. The function of the neon transformer is to amplify the input voltage of the Variac (at 220 volts, the input and output voltage of the device is 12 kV at a constant frequency of 50 Hz) and to supply the plasma reactor (Fig. 1).



Fig. 1. Schematic of the electric plasma discharge system.

2.2. Dependent and independent parameters; experiments

Voltmeter was utilized for voltage control, which enables precise and dependable measurements of voltage in electrical circuits, ensuring their safe and efficient operation. Also, in order to monitor and regulate the pH of the solution, a pH meter was employed both before and after every experiment. One of the key aspects of effective experimental design is the precise selection of the independent variables to be tested. This should be followed by the identification of the range of changes to be applied to each variable Previous research has shown that applied voltage, initial pH of the solution, initial concentration of the pollutant, and treatment time are important factors that can impact plasma treatment processes (Mirzaei et al., 2018). To inform the design of the central composite design (CCD), the range of changes for each independent variable can be determined through preliminary testing, based on previous studies and the maximum power capacity of the reactor (Chen et al. 2019; Farzinfar and Qaderi 2022; Shang et al. 2019; Zhao et al. 2021)

Split-plot designs are useful for incorporating Hard-to-Change (HTC) factors, which remain constant for a group of experimental runs. However, this restricted randomization reduces precision for estimating HTC factors. Split-plot Central Composite designs, similar to

(1)

randomized versions, are employed to fit and test quadratic models. They require adjustments to accommodate HTC factors but offer robust testing and excellent statistical properties. Maintaining the central composite structure while restricting randomization necessitates a larger number of runs, leading to the consideration of split-plot optimal designs. Central Composite designs are preferred for accurately estimating response surface curvature, allowing for response variable optimization. Unlike designs with limited levels, Central Composite designs are of data by starting at the top three levels and extending slightly beyond upper and lower levels, facilitating a comprehensive analysis of experimental factors (Jin et al. 2014).

Table 1. Range of variables

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_	Variable Name	Unit	-α	-1	0	+1	+α
	Initial concentration	mg/L	25	50	75	100	125
	Initial pH	_	2	5	8	11	14
	Applied voltage	kV	11	12	13	14	15
	Time	min	10	20	30	40	50

RSM is utilized to investigate mathematical and statistical techniques, and to plan tests by aligning the experimental model with the collected data. In order to optimize, model, and describe the system function, functions based on Eqs. 1-3 are employed (Bezerra et al. 2008; Tamadoni and Qaderi 2019).

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_1^2 + b_{12} x_{12} x_2 + \dots$$

$$\frac{\partial y}{\partial x_1} = b_1 + 2b_{11}x_1 + b_{12}x_2 + \dots = 0$$
(2)

$$\frac{\partial y}{\partial x_2} = b_2 + 2b_{22}x_2 + b_{12}x_2 + \dots = 0$$
(3)

There are several terms used in these equations: "y" is the principal function, "x_i" is the independent variable, and "b_i" is the constant term. Also, "b_i" is the interaction coefficient, and "b_i" is the coefficient of each parameter. Tests were designed using Design-Expert 13.0.0 software and results were analyzed using it. In this study, the pH, applied voltage (kV), initial concentration (mg/L), and duration (min) of the experiment have been evaluated by using them as independent variables. The experiments were designed using CCD is a very suitable design for fitting quadratic models in the experimental space (Jin et al. 2014). In this type of experimental design, the axial points of the experimental design considering the four independent variables as shown in the figure below are in the range of - α to + α and the points of the factorial experimental design are in the range of -1 to +1. The rotation mode is used to calculate the value α based on the default settings of the software.

Statistical indicators such as R-squared, Adjusted R², Predicted R², P-value, and ANOVA are used to evaluate the model's fit after utilizing Design expert software. ANOVA analyzes the relationship between the independent variables (initial concentration, applied voltage, initial pH, and degradation time) and the dependent variable (PNP degradation/removal) using RSM. RSM is also employed for optimizing PNP pollutant removal using utility equations.

2.3. Experimental sections

In this study, 30 experiments were conducted using a 200 ml solution of PNP and water for each trial. The conditions and removal efficiencies of PNP for each experiment are presented in the Table 2. To measure the concentration of PNP in the water, a spectroscopic method was utilized with a spectrophotometer. PNP exhibits maximum absorption at wavelengths of 317 and 401 nm (Ye et al., 2016; Zhang et al., 2018; Zhao et al., 2021b). As PNP is mostly in the protonated state at pH values less than 6, an absorption peak is observed at the wavelength of 317 nm. This means that at pH values of 3.5 and below, all PNP molecules are in the protonated state. On the other hand, at pH values of 10 and above, the maximum absorption of PNP occurs at 401 nm, indicating that the molecules have changed into an anionic state at high pH values (Syedd-León et al., 2020). Thus, to measure the concentration of PNP in the water, the pH of the solution needs to be adjusted to either acidic or basic conditions. For analysis, 5 ml aliquots were taken from the solution both before and after purification.

3. Results and discussions

The relationship between four independent variables (initial concentration, applied voltage, initial pH, and degradation time) and the dependent variable (PNP removal) was analyzed using RSM.

To evaluate the statistical significance of the model, the p-value was employed. In RSM, a high p-value suggests that certain independent variables in the model do not significantly affect the response variable. This means that, at the chosen significance level, the null hypothesis of no effect for these variables cannot be rejected. The model displayed an F-value of 116.35, indicating its statistical significance. The probability of obtaining such a high F-value due to noise alone is merely 0.01%.

By comparing the p-values to the significance level, typically set at 0.05 or 0.1, we can determine the significance of a factor. If the p-value is lower than the significance level, the factor is considered significant, indicating that its effect on the response is statistically significant.

Conversely, if the p-value is greater than the significance level, the factor is considered non-significant, and its effect on the response is deemed to be due to chance. Model terms A^2 , B^2 , C^2 , and D^2 , as well as interactions AB, AC, BD, CD were found to be significant, as their p-values were less than 0.050. It can be stated that parameters AD (0.3939) and BC (0.8843) hold no significant value as their p-values exceed 0.1.

Table 2 CCD to examine th	o four experimenta	I factors and the (htsingd regulte
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Dun	С,	ъЦ	٧,	t,	Predicted	Removal,
Kull	mg/L	рп	kV	min	value	%
1	50	11	14	20	83.67	90
2	50	5	12	20	42.91	44.24
3	100	5	12	20	9.53	10.04
4	100	11	14	20	70.56	68.32
5	50	5	14	20	69.00	67.10
6	75	8	13	50	78.74	79.13
7	75	8	13	30	79.20	79.27
8	75	8	15	30	82.63	80.77
9	50	5	14	40	76.10	77.10
10	75	14	13	30	83.06	81.54
11	75	8	11	30	27.66	28.38
12	25	8	13	30	81.60	79.91
13	75	8	13	30	79.20	80.10
14	100	5	14	20	46.71	47.87
15	75	8	13	30	79.20	76.71
16	100	5	14	40	56.41	57.59
17	100	11	14	40	86.75	87.91
18	100	11	12	40	57.87	58.38
19	75	8	13	30	79.20	75.65
20	75	2	13	30	37.61	38.002
21	100	5	12	40	27.09	23.26
22	75	8	13	30	79.27	79.27
23	50	11	12	20	58.03	55.46
24	100	11	12	20	33.81	35.30
25	75	8	13	30	79.20	81.006
26	50	11	12	40	79.49	80.82
27	75	8	13	10	47.57	46.05
28	50	5	12	40	57.88	58.73
29	125	8	13	30	37.69	38.25
30	50	11	14	40	97.28	95.38

According to the table Table 3 the Lack of Fit F-value of 1.47 suggests that the lack of fit is not statistically significant compared to the pure error, with a probability of 35.26%. This indicates that the proposed model fits the design space well, even in the presence of a non-significant lack of fit. The results of ANOVA show that the F Fisher values for all regressions were high, with a particularly large value of 237.44. This suggests that the main changes in the response can be explained by the regression equation.

One way to assess the suitability of the model is to examine the coefficient of determination (R^2). The adjusted R^2 can be used to compare the number of parameters in the model to the number of points in the design. A value of R^2 within roughly 0.20 of the predicted R^2 is considered acceptable, indicating that the model accurately predicts the response value. In this case, the adjusted R^2 is 0.982, indicating a difference of less than 0.2 between the predicted (0.957) and adjusted R^2 . Another measure of model suitability is the signal-to-noise ratio, which can be calculated using the Adequate Precision (AP) statistic. A ratio of greater than 4 is considered ideal. In this case, the ratio is 42.009, indicating that the model is acceptable for navigating within the design space. The AP value is calculated by comparing the residual error of the model with the average standard deviation (Here, the calculated SD value is 2.95) of the response variable. The formula for AP is:

$$AP = |MSPE / SD|$$
(4)

where MSPE is the mean square of the prediction error, which is calculated as the sum of the squared differences between the predicted and actual response values divided by the degrees of freedom. A lower MSPE value indicates that the response surface model is more accurate in predicting the response variable. SD is the average standard deviation of the response variable, which is calculated as the square root of the mean of the squared standard deviations of the response value indicates that the response variable is more precise, meaning that it has less variability around its mean (Bezerra et al. 2008). Fig. 2. shows a plot of the predicted response

values and the actual values from the experiments, which can be used to evaluate the accuracy of the proposed model. The fig suggests that the model accurately predicts the PNP removal efficiency values based on the agreement with the experimental data.



Fig. 2. A Comparison of actual and model results for PNP deletion in the plasma process alone.

	Table 3.	ANOVA anal	vsis associated	with the	RSM model.
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Source	Sum of squares	df	Mean square	F-value	p-value	
Model	14214.27	14	1015.30	116.35	< 0.0001	Significant
Residual	130.90	15	8.73			
Lack of Fit	97.60	10	9.76	1.47	0.3526	Not significant
Pure Error	33.29	5	6.66			
Cor Total	14345.16	29				

Fig. 3 illustrates the CCD for the four variables in this study, including the range of factors and the degradation efficiency at the boundaries. The best-fitting model for the data is a quadratic polynomial model that describes the relationship between the response and purification variables. The coded equation and the resulting actual equation are presented in Eqs. 5 and 6, respectively, to optimize the response. The coded equation allows us to predict the response at given levels of each factor, where +1 represents high levels and -1 represents low levels. Moreover, coded formula in RSM can be useful to transform the original experimental variables into dimensionless values that are more convenient for statistical analysis. It also enables researchers to work with standardized factor values that are free from the units of measurement and have similar ranges, regardless of the original measurement scale of each factor. This transformation simplifies the analysis and interpretation of experimental results and makes it easier to compare the effects of different factors on the response variable.





Fig. 3. Cube degradation efficiency (%): Conceptual model of CCD test design, predicted values are shown.

It is important to note that the levels of factors should be specified in their original units. The coefficients in the equations are scaled to match the units of each factor, and the intercept is not located at the center of the design space. As a result, these equations cannot be used to determine the relative impact of each factor on the response.

$$\begin{split} Y(\%) &= -1185.193 - 1.030 [Initial Concentration] + \\ 8.728 [initial pH] + 167.959 [Applied voltage] + \\ 5.113 [Time] + 0.030 [Initial Concentration * \\ initial pH] + 0.110 [Initial Concentration * \\ Applied voltage] + 0.002 [Initial Concentration * \\ Time] - 0.036 [Initial pH * Applied voltage] + \\ 0.054 [initial pH * Time] - 0.196 [Applied voltage * \\ Time] - 0.007 [Initial Concentration]^2 - \\ 0.523 [initial pH]^2 - 6.013 [Applied voltage]^2 - \\ 0.040 [Time]^2 \end{split}$$

In the equations presented here, Y represents the removal efficiency of PNP after t min of purification, expressed as a percentage. A, B, C, and D correspond to the independent variables of applied voltage, initial concentration of PNP, pH, and time, respectively. Positive values in these equations indicate an increasing effect on the response, while negative values indicate a decreasing effect on the response.

3.1. Individual effect of each variable on PNP degradation

The effect of each independent variable on removal efficiency can be visualized in Fig4. a-d.





Fig. 4. The effect of the changes in each independent variable on the degradation efficiency of PNP. Each diagram shows the changing of a variable and the other variables are at the center point; (a) Effect of initial concentration (mg/L), (b) Effect of initial pH, (c) Effect of applied voltage (kV), (d) Effect of degradation time (min) [initial concentration = 75 mg/L, initial pH = 8, applied voltage = 13 kV and time = 30 min].

3.1.1. Effect of initial concentration

As shown in Fig. 4a, when the discharge time is 30 min, the highest rate of degradation of PNP is achieved at an initial concentration of 50 mg/L PNP, which is 83.10%. Under constant conditions with an applied voltage of 13 kV, pH of 8, and discharge time of 30 min, by increasing the initial concentration of PNP from 50 to 100 mg/L, the degradation rate decreased from 83.10% to 64.31%. The main reason for better PNP removal at lower concentrations is that the amount of chemically active species formed in the plasma discharge process is the same at a constant applied voltage. Therefore, at higher PNP concentrations are fewer chemically active species per PNP molecule, which reduces the removal efficiency. Another reason may be the production of intermediates at high concentrations and their competition with decomposed PNP molecules for reaction with chemical species. As shown in previous studies, if the initial concentration of Acid Orange-7 increases, the removal rate decreases. Acid Orange (AO7) shows a competition effect with reactive species, especially at higher initial dye concentrations (Jiang et al., 2012). Certain degradation intermediates of AO7 are even more competitive than AO7 itself, further reducing the collision probability between AO7 and reactive species (Zhu et al., 2014). In plasma oxidation processes, the hydroxyl radical is recognized as the primary agent, and its concentration and lifespan are critical factors affecting the degradation efficiency (Gao et al., 2003).

3.1.2. Effect of initial pH

The pH of the solution can significantly affect the performance of gasliquid discharge plasma, as it determines the ionization state of organic compounds and how they become activated (Blizanac, Ross and Markovic, 2007; Jiang *et al.*, 2014). Optical emission spectra have shown that pulsed streamer discharges generate OH• emissions whose intensity increases under neutral and alkaline conditions (Sun et al. 1997). In addition, the formation of hydrogen peroxide in the solution is influenced by pH (Thagard, Takashima and Mizuno, 2009).

The equilibrium between various plasma species and acid or base can also influence the degradation reactions of aqueous pollutants. An alkaline solution exhibits different chemical reactivity when it is treated with hydroxyl radicals (OH•), which are oxygen-based oxidizers, compared to a strongly alkaline solution (Jiang et al., 2014). Furthermore, OH• acts as an electrophile when reacting with organic molecules, whereas O- acts as a nucleophile, leading to different reaction pathways (Joshi and Thagard 2013; Varjani et al. 2019). The degradation potential of organic molecules can be influenced by their acid-base equilibrium. In the case of phenol, the basic form exhibits higher reactivity compared to its acidic form during degradation processes (Amano and Tezuka, 2007). This may be due to the enhanced electron liability of the aromatic rings in phenol, which makes the p bonds more likely to accept electrons. This understanding can help explain why different optimal pHs are required for treating different pollutants with plasma technologies (Amano and Tezuka, 2007; Feng et al., 2009). The pH of the solution can also affect the redox potential of the active species. When ozone (O₃) is involved in the degradation reaction, the pH of the solution plays a crucial role in the chemical

stability of $O_3.$ Specifically, O_3 is more prone to decompose into OH+ in an alkaline environment.

Fig. 4b shows that higher PNP degradation efficiency was obtained at neutral and alkaline pH. When the initial pH values are 5.0, 8, and 11, the removal rates of PNP are approximately 65%, less than 80%, and greater than 80.0%, respectively, for a discharge time of 30 min. The increase in the removal rate of PNP with higher initial pH values suggests that the degradation process is influenced by various factors. One possible explanation is that in the NTP reactor, O₃, H₂O₂, and other reactive species are generated (Ahmadi et al., 2020). Under acidic conditions, O₃ can directly degrade organic impurities, whereas under alkaline conditions, it can be converted to OH•, which facilitates the nonselective removal of impurities (Jiang et al., 2014). At higher pH values, such as pH=11.0, the stability of H₂O₂ decreases, leading to its decomposition and the generation of free radicals that can oxidize contaminants and contribute to their degradation (Zhang, Yu and Li, 2005; Shang et al., 2017). The hydroxyl radical can also be produced through the decomposition of H₂O₂ by a plasma depletion process under UV waves (Equation (7)) (Zhao et al., 2021a).

$$0_2 + hv \to 20H^{\bullet} \tag{7}$$

3.1.3. Effect of applied voltage

 H_2

The degradation of organic compounds through plasma oxidation has been found to rely on a specific range of energy input (Zhang *et al.*, 2008; Feng *et al.*, 2009; Jiang *et al.*, 2012). During the formation of plasma in air, accelerated electrons interact with various molecular species present in the air, with particular emphasis on O_2 , N_2 , and H_2O . This encompasses both atmospheric moisture and water molecules at the gas-liquid interface. As the plasma discharge occurs, electrons are released from gas molecules and subsequently engage with N_2 and O_2 , leading to the generation of reactive oxygen and nitrogen species, such as OH', H_2O_2 , O_3 , NO•, HNO₂, and HNO₃ (Joshi and Thagard 2013). Within an air-driven plasma reactor, O3 and NOx species are produced through a series of reaction steps (8) to (14). For these RONS to effectively interact with PNP molecules, they must traverse the gasliquid interface where the reactions take place.

$$0_2 + e^- \to 0^{\bullet} + 0^{\bullet} + e^-$$
 (8)

 $O_2 + O \to O_{3(g)} \tag{9}$

$$N_2 + e^- \rightarrow N^{\bullet} + N^{\bullet} + e^- \tag{10}$$

$$N^{\bullet} + 0^{\bullet} \to NO_{(g)} \tag{11}$$

- $\mathrm{NO}_{(g)} + 0^{\bullet} \to \mathrm{NO}_2 \tag{12}$
- $O_{3(g)} \to O_{3(aq)} \tag{13}$
- $\mathrm{NO}_{2\,(g)} \to \mathrm{NO}_{2\,(aq)} \tag{14}$

Plasma discharge in the aqueous phase results in the generation of various species (Clements, Sato and Davis, 1987). This process produces charged particles with energies ranging from approximately 5-20 eV(Hochanadel, 1952; Holroyd, 1987). This can cause water vibration/rotation reactions, water decomposition, or even ionization of water (Itikawa and Mason 2005; Joshi et al. 1995; Joshi and Thagard 2013). The free electrons discharging into water react with water molecules to generate OH', which combines with water molecules to yield H₂O₂, according to equations (15) and (16). Moreover, when H₂O₂ is present, ozone can react with HO₂⁻ to produce reactive superoxide radical anions (O₂⁻⁻), which is demonstrated in equations (17) and (18). O₂⁻⁻ can either directly participate in the degradation of pollutants or generate more potent oxidative species such as OH' and singlet oxygen. O₂⁻⁻ can either contribute directly to the degradation of pollutants or generate more potent excitation of OH' or singlet oxygen to a greater extent.

$H_2O + e^- \rightarrow OH^{\bullet} + H^{\bullet} + e^-$	(15)
$0H^{\bullet} + 0H^{\bullet} \rightarrow H_2O_2$	(16)
$\mathrm{H}_{2}\mathrm{O}_{2} \rightarrow \mathrm{H}^{+} + \mathrm{H}_{2}\mathrm{O}^{-}$	(17)
$0_3 + HO_2^- \rightarrow 0_2^{\bullet-} + OH^{\bullet} + O_2$	(18)
$0^{\bullet-}_2 + 0H^{\bullet} \rightarrow \frac{1}{1}O_2 + 0H^{-}$	(19)
$20_2^{\bullet-} + 2H^+ \rightarrow {}_1^1O_2 + H_2O_2$	(20)
$0^{\bullet-}_{2} + H_2 O_2 \rightarrow 0 H^{\bullet} + 0 H^{-}$	(21)

Water molecules stabilize in the low-energy state in the vibrational/rotational excited state, which may produce some active radicals (Lukeš, 2001). When oxygen is exposed to electrical discharge, the oxygen atom can be generated by the decomposition of O_2 and increase the production of OH (Malik, Ghaffar and Malik, 2001). In addition, the O atom can react directly with pollutants as well as with 0_2 , producing 0_3 (Malik, Ghaffar and Malik, 2001). So, it is possible to vary either the voltage or the frequency introduced into the discharge system to evaluate the different requirements of the experiments. Generally, higher electron densities lead to the production of more OH-O-, H₂O⁻, H₂O₂, and O₃ (Joshi et al. 1995; Joshi and Thagard 2013; Sun et al. 1997). Fig. 4c shows the effect of applied voltage. Under constant conditions of PNP concentration (75 mg/L), pH (8), and time (30 min), the efficiency of PNP removal increases with increasing applied voltage (from 12 to 14 kV). The removal efficiency of PNP at the optimal voltage is more than 98%. The enhancing effect of applied voltage on removal efficiency is due to the production of more free electrons and the intensity of chemically active species formed in the reactor, which increases the probability of collisions with PNP molecules and initiates decomposition reactions. On the other hand, plasma discharge over time decreases the pH of the solution, which negatively impacts the efficiency of PNP removal (the reasons for this are explained in the "pH effect" section). Therefore, the efficiency of PNP removal tends to increase with increasing voltage from 10 to 14 kV, and the amplifying effect of applied voltage on the changes in removal efficiency is greater than the effect of decreasing pH. As a result, the combination of these two factors has a negative impact on PNP removal efficiency.

3.1.4. Effect of time passage

As shown in Fig. 4d the efficiency of PNP degradation increases with time (from 20 to 40 min) at constant PNP concentration (75 mg/L), pH (8), and applied voltage (13 kV). The highest degradation rate of PNP is achieved at 40 min, which is 83.21%. The main reason for this could be the production of more active species over time.

3.2. Simultaneous effect of two variables on pollutant removal

In Fig. 5 the simultaneous effects of the variables in this study are illustrated on degradation efficiency. These variables can be interpreted simultaneously using these three-dimensional Figs.

3.2.1. Simultaneous effect of initial concentration and initial pH

Fig. 5a shows the effect of simultaneous changes in the two variables initial concentration and initial pH of the solution on the PNP removal efficiency in the plasma process. These curves are plotted at a constant voltage of 13 kV and a purification time of 30 min. As can be seen in Fig. 5 a, the removal efficiency increases with increasing initial pH and increasing the amount of hydroxyl radicals, while decreasing the initial concentration until the best removal efficiency is observed at an initial concentration of 50 and a pH of 11. The lowest removal efficiencies are obtained at a pH of 5 and an initial concentration of 100 mg/L. Thus, the slope of the concentration curve is greater than that of the pH curve, indicating that the concentration parameter is more influential.

3.2.2. Simultaneous effect of applied voltage and initial concentration

The removal of PNP during the plasma process was found to be greatly influenced by the applied voltage and the initial concentration of PNP in the solution. In Fig. 5b, it can be observed that the degradation efficiency of PNP varied as these variables changed, while keeping the pH constant at 8 and the purification time at 30 min. The results demonstrated that the highest degradation efficiency was achieved at the optimal voltage of 14 kV for all initial concentrations of PNP. However, the initial concentration of PNP had a negative impact on the removal efficiency across all applied voltages. Specifically, the highest efficiency was obtained when the initial concentration of PNP was at its lowest value of 50 mg/L, while the lowest efficiency was observed at an initial concentration of 100 mg/L and an applied voltage of 12 kV. Conversely, the highest removal efficiency was observed when the initial concentration of PNP was 50 mg/L and the applied voltage was 14 kV. Notably, increasing the applied voltage had a more pronounced effect on the removal efficiency compared to reducing the initial concentration of PNP.

3.2.3. Simultaneous effect of initial concentration and degradation time

Fig. 5c the relationship between the initial concentration of PNP, treatment time, and the efficiency of PNP removal in the plasma process is depicted, while maintaining a constant voltage of 13 kV and a pH of 8. It illustrates that increasing the initial concentration of PNP has a negative influence on the removal efficiency, while increasing the treatment time has a positive effect. The highest removal efficiency was attained at an initial concentration of 50 mg/L and a treatment time of 40 min, whereas the lowest efficiency was observed at an initial concentration of 100 mg/L and a treatment time of 10 min. Furthermore, it can be noted that the curve representing the initial concentration has a steeper slope compared to the curve for the treatment impact on the removal efficiency as compared to the treatment time.

3.2.4. Simultaneous effect of applied voltage and initial pH

Fig. 5 d illustrates the impact of the initial pH of the solution and applied voltage on the degradation efficiency of PNP in the plasma process at a constant time of 30 min and an initial concentration of 75 mg/L. It demonstrates the positive effect of increasing the initial pH of the solution and the purification time on the degradation efficiency. The lowest efficiency was observed at an initial pH of 5 and a treatment time of 10 min, while the highest efficiency was achieved at a treatment time of 40 min and an initial pH of 11. It also shows that the slope of the curve for the initial pH has a greater influence on the degradation efficiency compared to the treatment time.

3.2.5. Simultaneous effect of initial pH and degradation time

Fig. 5e displays the effect of the initial pH of the solution and the purification time on the degradation efficiency of PNP in the plasma process at a constant applied voltage of 13 kV and an initial concentration of 75 mg/L. It shows the positive effect of increasing the initial pH of the solution and the applied voltage on the degradation efficiency. The slope of the curve for the initial pH is steeper than the slope for the applied voltage, indicating that the initial pH has a greater influence on the degradation efficiency compared to applied voltage. These results demonstrate the importance of considering the initial pH and applied voltage when optimizing the PNP removal process in the plasma process.

3.2.6. Simultaneous effect of applied voltage and degradation time

Fig. 5 f the impact of the applied voltage and treatment time on the efficiency of PNP removal in the plasma process is depicted, while maintaining a constant solution concentration of 75 mg/L and pH of 8. It illustrates that increasing the treatment time has a positive effect on the removal efficiency across all applied voltages. Additionally, as the applied voltage increases from 12 to 14 kV and the treatment time extends from 10 to 40 min, the removal efficiency also increases. Furthermore, it is observed that the slope of the curve representing the treatment time is shallower compared to the slope for the applied voltage. This suggests that the applied voltage has a greater influence on the removal efficiency as compared to the treatment time. These findings highlight the importance of precise control over the applied voltage and treatment time in order to enhance the efficiency of PNP removal in the plasma process

Khourshidi and Qaderi. / Journal of Applied Research in Water and Wastewater 10 (2023) 80-90



Fig. 5. Simultaneous effect of (a) Initial concentration (mg/L) and Initial pH, (b) Initial concentration (mg/L) and Applied voltage, (c) Initial concentration (mg/L) and purification time, (d) applied voltage (kV) and initial pH, (e) initial pH and purification time (min), (f) applied voltage (kV) and purification time (min), [Constant conditions: Initial concentration = 75 mg/L, applied voltage = 13 kV, time = 30 min, Initial pH = 8].

3.3. Interaction of variables

An interaction diagram, like Fig. 6, is a graphical representation of the relationship between two levels of a variable (such as high and low values) and two independent variables. These diagrams can help to visualize how different parameters interact with each other, either synergistically or antagonistically. If the removal efficiency changes

slope when one of the parameters is varied, it indicates a significant interaction between the two parameters. On the other hand, if the removal efficiency does not change slope, it suggests that the two parameters have a neutral effect on each other. Interaction diagrams can be useful for identifying and understanding the influence of different parameters on a given process or outcome.

90

100





Fig. 6. The interaction effects of variables on the PNP removal efficiency (a): Initial concentration (mg/L) and Applied voltage (kV), (b): Initial pH and Applied Voltage (kV), (c): Initial pH and time (min), (d): Initial concentration (mg/L) and Initial pH, (e): Initial concentration (mg/L) and time (min), (f): Initial pH and time (min), [Constant conditions: Initial concentration = 75 mg/L, applied voltage = 13 kV, time = 30 min and Initial pH = 8].

3.3.1. The interaction between initial concentration and time

Based on the information provided in Fig. 6a, it appears that the reaction time and the initial concentration had a barely interacted with each other. The graph shows that the efficiency of PNP removal decreased slightly from 74.13% to 50.88% when the processing time was 10 min and the initial concentration increased from 50 to 100 mg/L. Similarly, the efficiency decreased from 88.417% to 67.76% when the processing time was 40 min and the initial concentration increased from 50 to 100 mg/L. Thus, these two parameters did not have much influence on the efficiency of PNP degradation. The results indicate that the pollutant concentration is not impacted by the duration of exposure at either high levels (40 min) or low levels (20 min), and only the passage of time has a nearly equal effect on removal efficiency. This suggests that the variables of time and initial concentration are independent of each other, provided that the variables of applied voltage and acidity remain constant.

3.3.2. The interaction between initial concentration and applied voltage

Based on the information provided in Fig. 6b, it appears that the applied voltage and the initial concentration of the solution had an interactive effect on the efficiency of PNP removal. The graph shows that, for an initial concentration of 50 mg/L and a reaction time of 30 min, the PNP elimination efficiency decreased from 68.303% to 44.959% as the applied voltage increased. Similarly, for an initial concentration of 100 mg/L, the efficiency decreased from 90.23% to 73.834% as the applied voltage increased. These results suggest that increasing the applied voltage had a negative impact on the efficiency of PNP removal, possibly due to the increased production of hydroxyl radicals, which may counteract the negative effect of increasing the concentration.

3.3.3. The interaction between initial concentration and initial pH

In Fig. 6c, the interaction between the pH of the solution and the initial concentration of PNP on the efficiency of PNP removal is presented. The conditions for this analysis include an applied voltage of 13 kV and a reaction time of 30 min, with a water volume of 200 mL. The graph demonstrates that as the pH of the solution increases from 5 to 11, the efficiency of PNP removal decreases. Specifically, at an initial concentration of 50 mg/L, the removal efficiency decreases from 71.497% to 44.959% with the increase in pH. Similarly, at an initial concentration of 100 mg/L, the removal efficiency decreases from 89.641% to 72.271% as the pH increases. These findings suggest that there is an antagonistic relationship between the pH and the initial concentration of the solution, wherein an increase in pH leads to a decrease in the efficiency of PNP removal. This phenomenon may be attributed to the production of more hydroxyl radicals at high pH levels, which can have a negative impact on the removal efficiency by increasing their concentration.

3.3.4. The interaction between initial pH and applied voltage

In Fig. 6d, the interaction between the reaction time and the applied voltage on the efficiency of PNP removal is depicted. It reveals that the reaction time has a lesser impact on the percentage of PNP removal at higher applied voltages. More specifically, at an applied voltage of 12 kV, the efficiency of PNP removal increases from 42.658% to 77.088% as the reaction time increases. Similarly, at an applied voltage of 14 kV, the efficiency increases from 65.187% to 88.740% with an increase in the reaction time. These results suggest that higher applied voltages, longer reaction times have a greater impact on increasing the efficiency of PNP removal. In other words, at higher applied voltages, longer reaction times have a greater impact on increasing the efficiency of PNP removal.

applied voltage have an antagonistic effect on each other, with an increase in the reaction time leading to a decrease in the efficiency at higher applied voltages. One possible explanation for this is that the production of hydroxyl radicals may decrease after a certain time, which can have a negative impact on the efficiency by increasing the applied voltage.

3.3.5. The interaction between initial pH and reaction time

As previously mentioned, a high pH can have a positive effect on the efficiency of PNP removal, while a low pH may lead to the formation of fewer hydroxyl radicals and lower degradability of the pollutant. Fig. 6 (e) illustrates how the reaction time is affected by the pH of the pollutant solution. It shows that the efficiency of PNP removal is influenced more by the reaction time at higher pH values. Specifically, the efficiency increases from 52.938% to 72.418% when the reaction time increases at a pH of 5, and from 65.273% to 91.25% when the reaction time increases at an initial pH of 11. These results suggest that the reaction time and pH have a synergistic effect on each other, with an increase in the reaction time leading to an increase in the efficiency at higher pH values.

3.3.6. The interaction between applied voltage and time

Fig. 6 f demonstrates the relationship between the applied voltage and the reaction time on the efficiency of PNP removal. It shows that, over time, the decomposition of PNP increased from 45.672% to 77.088% for an applied voltage of 12 kV, and from 65.187% to 88.740% for an applied voltage of 14 kV. These results suggest that the applied voltage and the reaction time have an antagonistic effect on each other, with an increase in the reaction time leading to a decrease in the efficiency at higher applied voltages. This may be due to the fact that, as the pollutants are decomposed by the plasma, there are fewer decomposed

chemical species present over time, and this process occurs more quickly at high applied voltages. **3.4. Response surface optimization**

Response surface analysis is a statistical technique employed to ascertain the optimal conditions and the extrema of a process or system. This analysis is particularly valuable when multiple responses or criteria necessitate simultaneous consideration (Khalegh & Qaderi 2019). One approach to determining the optimal conditions involves plotting the contours of response surfaces derived from regression models in an overlay plot. This graphical representation illustrates the range of feasible response values within the factor space and identifies regions that satisfy the optimization criteria. The purpose of optimization of this research is to maximize the removal of PNP according to the changes of independent parameters within the specified range. In the provided report, two tables are mentioned: one containing criteria constraint and the other containing optimal solutions for the process. It is plausible that these optimal solutions were determined based on the criteria constraints outlined in the first table, utilizing response surface analysis or a comparable optimization technique (Ghafari et al., 2009). The weight parameter has a customizable range spanning from 0.10 to 10, serving to fine-tune the optimization process's pursuit of the optimal solution. Employing a lower weight value, such as around 0.10, accommodates a broader array of solutions that may not precisely align with the optimal objective. Conversely, a higher weight value, approximating 10, prompts the optimization process to actively target a solution in proximity to or surpassing the defined objective. From an applied perspective, a pragmatic initial approach entails retaining the weight value at 1.0. Additionally, the concept of importance comes into play, allowing for the specification of the relative significance attributed to distinct objectives. While certain objectives might be deemed critical, others could possess moderate significance and some might bear the lowest level of importance. As a default, all objectives are commonly set to for their importance rating.

 Table 4. A summary spreadsheet showing all of the criteria used to determine the optimal settings would be helpful.

Parameters	Goal	Lower weight	Upper weight	Lower Limit	Upper Limit	Importance
C, mg/L	in range	1	1	50	100	3
pН	in range	1	1	5	11	3
V, kV	in range	1	1	12	14	3
t, min	in range	1	1	20	40	3
Removal	max	1	1	10.04	95.38	3

A desirability score of 1.00 is commonly employed as a benchmark for optimal performance or results in response surface analysis and other optimization techniques. Typically, such a score signifies that the process or system goals or criteria have been comfortably met or surpassed, and further improvements can be pursued by intensifying the objectives or introducing new criteria for less crucial responses or factors. In essence, a desirability score of 1.00 implies room for enhancement within the process or system, warranting adjustments to the criteria or inclusion of additional factors to optimize performance and outcomes. It is crucial to meticulously consider the goals and criteria of the process or system in order to identify the optimal conditions and attain the desired results.

Table 5. For Looking through all the given solutions to see which ones best meet the specified criteria.

C, mg/L	рН	V, kV	T, min	Removal	Desirability	Std Dev
50.32	9.73	13.75	38.41	96.503	1.000	2.954

The ultimate aim of response surface analysis and other optimization techniques is not solely to maximize the desirability score, but to carefully consider other factors and trade-offs. It may be feasible to identify a limited "island" of acceptable outcomes among the factor settings that yield the highest desirability scores. Numerical optimization involves a mathematical approach to determining optimal values for factors or responses, and it is important to define the minimum and maximum values for each parameter during this process. Specific goals and constraints of the process or system must be taken into account to accurately identify the optimal conditions.

RSM is a statistical technique that can effectively optimize a process or system by identifying the optimal combination of factors or variables that yield the desired responses or outcomes. In the specific case described, RSM was utilized to optimize the degradation of PNP, resulting in the determination of optimal conditions that yielded a PNP degradation of 96.503%, with an initial concentration of 50.322 mg/L, a pH of 9.733, an applied voltage of 13.753 kV, and a reaction time of 38.418 min. To validate the model's validity, three additional experiments were conducted under these optimal conditions, leading to

an average maximum removal efficiency of 83.648%. These findings indicate the successful optimization of the PNP removal process through the application of RSM.

4. Conclusions

The findings of the study indicate that non-thermal plasma discharge technology represents a viable and eco-friendly approach for advanced oxidation processes. The application of RSM proved effective in optimizing this process. Through the analysis of initial concentration, applied voltage, initial pH, and removal time using RSM, it was determined that increasing the initial pH, applied voltage, and time while decreasing the initial concentration positively influenced removal efficiency. The individual effects of these variables on removal efficiency ranked as follows: applied voltage had the most significant impact, followed by initial pH, initial concentration, and time, which had the least impact. Interaction plots revealed that certain variables exhibited antagonistic effects (initial concentration and initial pH, initial concentration and applied voltage, applied voltage and time), while others showed synergistic effects (initial concentration and time). No significant interaction was observed between initial pH and applied voltage, as well as between initial concentration and time. Based on the optimal variables, the study identified an optimal PNP degradation rate of 96.503%. These results demonstrate the potential of non-thermal plasma discharge technology and RSM as valuable tools for optimizing advanced oxidation processes and enhancing removal efficiency.

Author Contributions

Amirhossein Khourshidi: Doing experiments, Empirical validation, Analysis by software, Writing draft of manuscript.

Farhad Qaderi: Conceptual elucidation, Methodological framework construction, Rigorous analytical scrutiny, Ideational conceptualization, Correction of manuscript and editorial and Supervisory role.

Conflict of Interest

The authors affirm that they possess no recognizable conflicting financial affiliations or individual associations that might have appeared to exert an impact on the findings detailed within this manuscript.

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Data Availability Statement

All data used in the article are provided in the text and are available.

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