Research on the application of UV/Peroxone technology for treating TNT-containing wastewater generated from bomb and explosives deployment processes

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ABSTRACT

Wastewater from dismantling level-5 bombs, explosives, and munitions contains high levels of 2,4,6-trinitrotoluene (TNT), intense color, and exhibits high toxicity and environmental persistence, making it difficult to treat by conventional methods. This study investigates the application of the UV/Peroxone process for TNT and color removal. Key factors, including pH, H_2O_2 concentration, UV intensity, reaction time, and recirculation rate, were examined. Treatment efficiency increased with H_2O_2 concentration, UV intensity, and recirculation rate, while initial pH had a negligible impact. TNT and color removals of 96% and 93%, respectively, were achieved, meeting QCVN 40:2025/BTNMT (column C) and TCVN/QS 658:2011 (column B) standards, demonstrating the process's potential for practical application.

Keywords: TNT; UV/Peroxone; Bombs and explosives; Level-5 munitions; Advanced oxidation processes (AOPs).

1. INTRODUCTION

The clearance, dismantling, and disposal of bombs and explosives are among the primary tasks of combat engineering units. The dismantling process generates large volumes of wastewater containing toxic chemicals, particularly 2,4,6-trinitrotoluene (TNT), a characteristic military explosive. Wastewater contaminated with TNT typically exhibits high color intensity, strong toxicity, and low biodegradability under ambient conditions. Various methods have been studied for treating wastewater containing explosive compounds, including adsorption, electrochemical processes, biological treatments, and the use of higher organisms [1-3]. In recent years, advanced oxidation processes (AOPs) have emerged as a promising technology for the treatment of wastewater contaminated with recalcitrant organic compounds [1-8]. Examples include Fenton, photo-Fenton, ozone, Peroxone, and photo-Peroxone processes [9]. Some studies have shown that Fenton-based processes can achieve high treatment efficiency for a wide range of pollutants [4]. However, Fenton oxidation has limitations, such as complex reaction conditions and the requirement for large amounts of Fe^{2+}, which leads to secondary waste generation in the form of sludge, thus restricting its practical applicability [1, 5, 7-11]. The Peroxone process overcomes many of these drawbacks, as it does not require complicated reaction conditions and produces minimal sludge, making it a promising option for large-scale applications. The fundamental reaction equation for the photo-Peroxone process is as follows [2, 6]:

$$O_3 + H_2O \rightarrow 2^{\bullet}OH + 4O_2 \quad (1)$$

$$H_2O_2 + 2O_3 \rightarrow 2^{\bullet}OH + 3O_2 \quad (2)$$

$$H_2O_2 + 2O_3 + H_2O + hv \rightarrow 4^{\bullet}OH + O_2 \quad (3)$$

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + hv \rightarrow 2^{\bullet}OH \quad (5)$$

However, research on the applicability of the photo-Peroxone process for the degradation of

TNT in wastewater from defense-related operations remains limited. Therefore, the objective of this study is to evaluate the effectiveness of the photo-Peroxone process in removing TNT and reducing the color of wastewater generated during the dismantling of bombs and explosives. In addition, the study investigates several factors influencing the photo-Peroxone reaction, including pH, concentration of H_2O_2, UV irradiation power, and wastewater recirculation rate.

2. MATERIALS AND METHODS

2.1. Wastewater samples

The study material was wastewater collected from storage tanks after the dismantling of explosives. The wastewater had the following characteristics:

Table 1. *Characteristic parameters of the wastewater.*

No.	Parameter	Unit	Value	QCVN 40:2025/BTNMT (C)	TCVN/QS 658:2012 (B)
1	pH		7.8	6 to 9	5.6 to 9
2	Color	Pt-Co	1,115	150	-
3	COD	mg/L	120	130	100
4	TNT	mg/L	12.88	-	1

Compared to the maximum permissible values specified in Column C of QCVN 40:2025/BTNMT – the National Technical Regulation on Industrial Wastewater, the wastewater generated after the dismantling of explosives exhibited a color value approximately 7.5 times higher than the standard limit, and a TNT concentration about 13 times higher than the limit set by TCVN/QS 658:2014 (B).

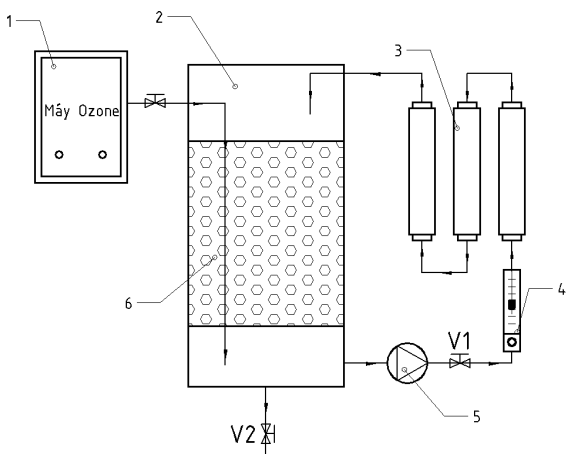
2.2. Chemicals, equipment and experimental setup

a) Chemicals

- H_2SO_4, purity ≥ 98.0%, Xilong Scientific Co., Ltd – China;
- H_2O_2 solution, 30.0%, Guangdong Guanghua Sci-Tech Co., Ltd – China.
- NaOH, purity ≥ 98,0%, Xilong Scientific Co., Ltd – China;

b) Equipment and experimental model

The equipment and experimental model were installed at the laboratory of the Institute of Materials, Biology and Environment/Academy of Military Science and Technology. The experimental setup included a wastewater treatment model based on the photo-Peroxone process, as shown in figure 1.



Notes:

1: Ozone generator, manufactured by Ozonemaxx, Vietnam (Power: 50 W/220 V; O_3 output: 2 g/h);

2: Reaction unit (capacity: 15 L; material: SUS 304 stainless steel);

3: UV lamps, manufactured by Sterilizer, China (Power: 15 W/lamp; wavelength: 254 nm; quantity: 03 units)

4: Flow meter, manufactured by Zyia, China (Inline type; range: up to 18 L/min);

5: Recirculation pump, manufactured by Wilo, China (Power: 500 W/220V; head: 2.1 m; adjustable flow rate: 0.4 – 4 m^3/h);

6: Plastic cushion material, wheel-shaped, 25 mm in diameter × 10 mm thick

Figure 1. *Photo-Peroxone reaction system model.*

The treatment model operates on the following principle: Wastewater samples in the reaction unit (2) are supplied with oxidizing agents, including O_3 (from the ozone generator (1)) and 30% H_2O_2 solution. O_3 gas is introduced from the bottom of the reaction unit and evenly dispersed in the solution through a layer of plastic cushion material. A recirculation pump (5) is used to mix the solution within the system and to convey the wastewater through the UV lamp, enabling the photo-Peroxone reaction. Valve V1 is used to adjust the recirculation flow rate of the system. After the reaction period, samples are taken via valve V2 for analysis and evaluation of the reaction system's performance.

2.3. Experimental methods

Use 10 L of wastewater for each reaction. To evaluate the factors affecting the Peroxone photoreaction, the study was conducted with the following experimental contents:

- Investigation of the effect of pH (at pH = 3, 7, and 10);

- Investigation of the effect of H_2O_2 concentration (ranging from 10 to 50 mmol/L);

- Investigation of the effect of UV lamp power (ranging from 1.5 to 4.5 W/L) at a wavelength of 254 nm;

- Investigation of the effect of recirculation rate (ranging from 0.2 to 0.6 times/min).

The O_3 dosage in each reaction was maintained at 2 g/h. The experiments were conducted over a 180-minute period, with samples collected at 0, 30, 60, 90, 120, 150, and 180 minutes. Each collected sample was adjusted to neutral pH before analysis. The evaluated parameters included color and TNT concentration. The experimental procedure is summarized in table 2.

Table 2. *Experimental parameters of the photo-Peroxone reaction.*

No.	Experiment	Reaction parameters						
		pH	Wastewater volume (L)	Ozone dosage (g/h)	H_2O_2 concentration (mmol/Lit)	UV lamp power (W/Lit)	Recirculation rate (times /min)	Sampling time (min)
1	Investigation of pH effect	3 - 7 - 10	10	2	20	3	0.4	30; 60; 90; 120; 150; 180
2	Investigation of H_2O_2 concentration effect	6.5 - 7.5	10	2	10; 20; 30; 40; 50	3	0.4	30; 60; 90; 120; 150; 180
3	Investigation of UV irradiation effect	6.5 - 7.5	10	2	Optimized after TN2	1.5; 3; 4,5	0.4	30; 60; 90; 120; 150; 180
4	Investigation of the recirculation rate effect	6.5 - 7.5	10	2	Optimized after TN2	Optimized after TN3	0.2; 0.4; 0.6	30; 60; 90; 120; 150; 180

2.4. Analytical methods

The parameters used to evaluate treatment efficiency and their corresponding analytical methods were as follows:

- Color: Determined according to TCVN 6185:2015 using a Hanna HI97727 colorimeter (Romania);

- pH: Determined according to TCVN 6492:2011 using a HandyLab 680 pH meter (Germany);

- COD: Determined according to SMEWW 5220.C:2017 using a Hanna HI 839800 digestion reactor (Romania);

- TNT: Determined according to TCVN/QS 658:2012 using a high-performance liquid chromatography (HPLC) system (Agilent 1100) with a Hypersil C18 column (200 × 4 mm); Detector: diode array, scanning range 0–1100 nm; Mobile phase: acetonitrile/water = 65/35 (v/v); flow rate: 0.5 mL/min; Pressure: 280 bar; Detection wavelength: 227 nm.

3. RESULTS AND DISCUSSION

3.1. Investigation of the effect of pH

The study was conducted using wastewater from explosive dismantling with the following characteristics: pH = 7.8, color = 1,115 Pt-Co, TNT concentration = 12.88 mg/L, and COD = 120 mg/L. The reaction pH was adjusted to three levels: pH = 3, pH = 7, and pH = 10. The ozone dosage was maintained at 2 g/h, H_2O_2 concentration at 20 mmol/L, UV irradiation power at 3 W/L, and recirculation rate at 0.4 times/min (equivalent to 4 L/min). The reaction time was set at 120 minutes. The experimental results are as follows:

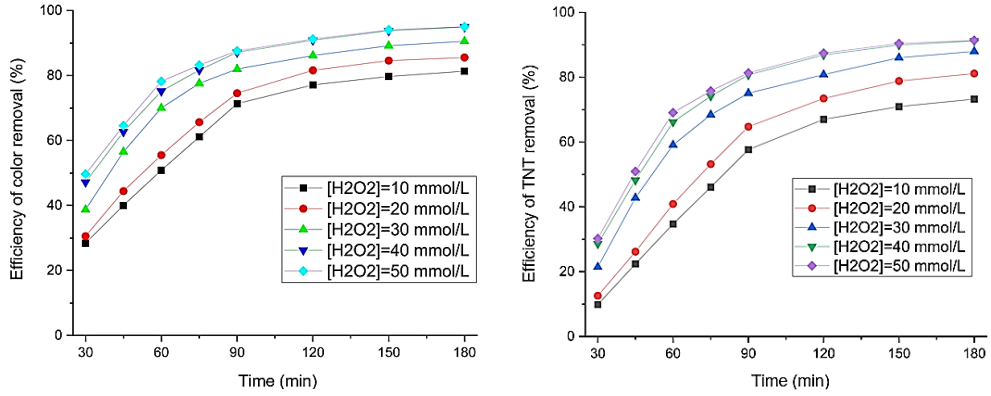
Table 3. *Effect of pH on the efficiency of the Peroxone reaction.*

Parameter	Effect of pH			
	Initial	**pH = 3.2**	**pH = 7.8**	**pH = 10.1**
Color (Pt-Co)	1,115	770	780	765
Removal efficiency (%)	0	31.1	30.2	31.6
TNT (mg/L)	12.88	3.42	3.34	3.51
Removal efficiency (%)	0	73.4	74.1	72.7

The results presented in table 3 indicate that changes in the reaction medium pH (acidic, neutral, and alkaline conditions) led to minimal variation in the removal efficiency of both color and TNT in the Peroxone reaction. TNT removal efficiency ranged from 72.7% to 74.1%, while color removal efficiency ranged from 30.2% to 31.6%. Therefore, the effect of reaction medium pH on the performance of the Peroxone process is considered negligible.

3.2. Investigation of the effect of H_2O_2 concentration

The experiment was conducted under the following conditions: ozone dosage of 2 g/h, UV irradiation power of 3 W/L, and recirculation rate of 0.4 times/min (equivalent to 4 L/min). The effect of H_2O_2 concentration on the removal efficiency of color and TNT in the wastewater is illustrated in the chart shown in figure 2.



a) Efficiency of color removal. *b) Efficiency of TNT removal.*

Figure 2. *Effect of H_2O_2 concentration on treatment efficiency.*

The color removal results shown in figure 2(a) indicate that treatment efficiency is directly

proportional to the H_2O_2 concentration. Specifically, within the first 60 minutes of the reaction, at H_2O_2 concentrations of 10 mmol/L and 20 mmol/L, the color removal efficiency was approximately equal, reaching around 35%. At higher H_2O_2 concentrations, the efficiency increased to about 60%, and at 40 mmol/L and 50 mmol/L, it reached approximately 70% within the same 60-minute period. After 120 minutes of reaction, the color of the wastewater continued to decrease, further demonstrating the role of H_2O_2 concentration in color removal. At 120 minutes, color removal efficiencies for H_2O_2 concentrations of 10 mmol/L and 20 mmol/L were 67% and 73%, respectively, whereas at 40 mmol/L and 50 mmol/L, efficiencies were approximately 90%. After 120 minutes, color removal continued to increase, but the improvement was marginal. The TNT removal results presented in figure 2(b) exhibited a similar trend to that of color removal, with reaction time and H_2O_2 concentration being directly proportional to removal efficiency. For example, at 90 minutes, TNT removal efficiencies were over 81% and 83% for H_2O_2 concentrations of 40 mmol/L and 50 mmol/L, respectively. In the same period, efficiencies for concentrations of 10 mmol/L, 20 mmol/L, and 30 mmol/L were 61%, 65%, and 77%, respectively. At 150 minutes, TNT removal efficiencies increased across all concentrations, with the highest efficiency of 95% achieved at 50 mmol/L and the lowest efficiency of 81% at 10 mmol/L. These results highlight the significant role of H_2O_2 concentration in both color and TNT removal. This can be explained by the fact that increasing H_2O_2 concentration raises the availability of oxidizing agents capable of generating hydroxyl radicals (●OH), thereby enhancing removal efficiency. However, beyond a certain threshold, excess H_2O_2 can lead to reduced performance. Previous studies have shown that excessive H_2O_2 promotes the recombination of hydroxyl radicals into H_2O_2 (reaction (6)) and the reaction between hydroxyl radicals and H_2O_2 to form hydroperoxyl radicals (HO_2●) (reaction (7)), which possess a lower oxidation potential than hydroxyl radicals, thereby decreasing overall treatment efficiency.

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (6)$$

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2{}^{\bullet} \quad (7)$$

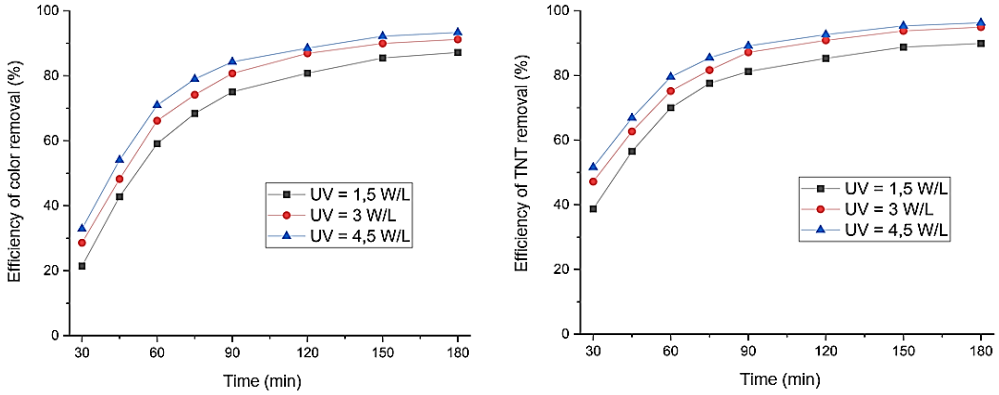
From the above charts, in addition to the effect of H_2O_2 concentration, it is evident that reaction time plays an important role in treatment efficiency. This can be explained by the fact that as the reaction time increases, the oxidizing agents have sufficient time to react, leading to better degradation of organic compounds and consequently higher removal efficiencies for both color and TNT. Furthermore, the data in figure 2 show that the removal efficiencies for color and TNT at H_2O_2 concentrations of 40 mmol/L and 50 mmol/L are nearly identical. At 150 minutes, with H_2O_2 concentrations of 40 mmol/L and 50 mmol/L, the process achieved high performance, with both color and TNT levels falling below the maximum permissible limits. Therefore, it can be concluded that for this reaction system, the optimal H_2O_2 concentration is 40 mmol/L, and the optimal reaction time at this concentration is 150 minutes, resulting in color and TNT levels of 112 Pt-Co and 0.8 mg/L, respectively, both meeting the regulatory standards. The H_2O_2 concentration selected for subsequent experiments was 40 mmol/L.

3.3. Investigation of the effect of UV lamp power

UV irradiation is an important factor influencing the efficiency of the process. The presence of UV light generates more hydroxyl radicals (●OH) through both direct and indirect pathways. In the system, two oxidation processes, direct and indirect, occur simultaneously (as shown in equations (3), (4), and (5)), enhancing the oxidation capacity toward organic compounds in the wastewater. This process is referred to as the photo-Peroxone process. Several studies have reported that, under identical conditions, the treatment efficiency achieved using the Peroxone process combined with UV irradiation is 12–20% higher than that of the conventional Peroxone process.

The experiment was conducted using a UV irradiation source with a wavelength of $\lambda = 254$ nm and power levels ranging from 1.5 to 4.5 W/L of wastewater, with an added H_2O_2 concentration of

40 mmol/L. The results shown in figures 3(a) and 3(b) indicate that, in the photo-Peroxone process, higher UV irradiation power leads to higher removal efficiencies for both color and TNT. After 90 minutes of treatment using a UV power of 4.5 W/L, the removal efficiencies for color and TNT were 80% and 86%, respectively. At the same reaction time, using a UV power of 1.5 W/L resulted in color and TNT removal efficiencies of 68% and 77%, respectively.



a) Efficiency of color removal. *b) Efficiency of TNT removal.*

Figure 3. *Effect of UV irradiation power on treatment efficiency.*

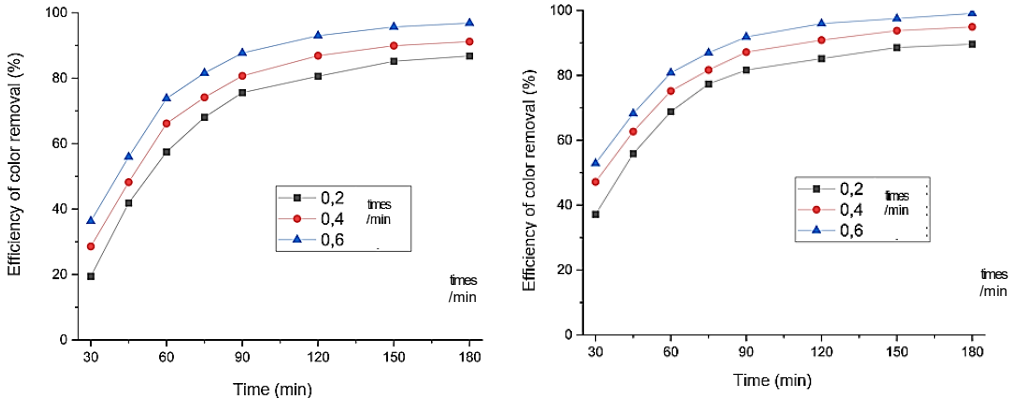
The experimental results also show that during the first 0 - 120 minutes, color and TNT removal occurred at a relatively high rate. After 120 minutes, the efficiencies continued to increase but at a slower rate. At 150 minutes, with a UV power of 4.5 W/L, removal efficiencies reached over 90% for both parameters (specifically, 92% for color and 95% for TNT). At a UV power of 3.0 W/L, the corresponding efficiencies were 90% for color and 94% for TNT, whereas at 1.5 W/L, they were 85% and 88%, respectively. The research results show that the UV radiation intensity affects the treatment efficiency of the process. The mechanism of action is explained as follows: the presence of UV radiation promotes the formation of ●OH radicals, and when the UV radiation power increases, the amount of free ●OH radicals produced also increases accordingly. However, the experimental results show that the treatment efficiency at UV radiation power = 3.0 W/L is not significantly different from the case of power 4.5 W/L. Therefore, the power of 3.0 W/L was chosen for the following experiments to ensure treatment efficiency while optimizing operating conditions.

3.4. Investigation of the effect of recirculation rate

The study examined the effect of recirculation rate on treatment performance. Although the recirculation rate is not an oxidizing agent like H_2O_2 or UV light, the results shown in figure 4 demonstrate that it has a notable influence on removal efficiency. Based on the data in figure 4, at a reaction time of 120 minutes, a recirculation rate of 0.6 times/min achieved color and TNT removal efficiencies of over 95% and 97%, respectively. In contrast, at a recirculation rate of 0.2 times/min, the corresponding removal efficiencies were only slightly above 85% for color and 88% for TNT. While these values are relatively high, the post-treatment color and TNT concentrations still did not meet regulatory standards. Specifically, at a color removal efficiency of 85%, the final color value was 165 Pt-Co (compared to the limit of 150 Pt-Co), and at a TNT removal efficiency of 88%, the TNT concentration in the treated sample was 1.47 mg/L (compared to the standard of 1 mg/L). These findings indicate that increasing the recirculation rate improves both color and TNT removal efficiencies. This can be attributed to enhanced mixing and contact between organic compounds and oxidizing agents at higher recirculation rates. Although the recirculation rate itself is not an oxidizing agent and does not directly or indirectly participate in oxidation reactions, it plays a supporting role in facilitating the oxidation process.

The results of this experiment show that, with a recirculation rate of 0.6 times/min, UV

irradiation power of 3 W/L, and H_2O_2 concentration of 40 mmol/L, both color and TNT levels fell below the standard limits after only 120 minutes. Under these conditions, at the 120-minute mark, the color value was 78 Pt-Co (compared to the standard limit of 150 Pt-Co), corresponding to a removal efficiency of 93%, while the residual TNT concentration was 0.52 mg/L (compared to the standard limit of 1 mg/L), corresponding to a removal efficiency of nearly 96%.



(a) Efficiency of color removal. *(b) Efficiency of TNT removal.*

Figure 4. *Effect of recirculation rate on treatment efficiency.*

4. CONCLUSIONS

This study evaluated the effects of pH, H_2O_2 concentration, UV irradiation power, recirculation rate, and reaction time on the treatment of wastewater generated from the dismantling of bombs and explosives using the photo-Peroxone process. The results showed that treatment efficiency was directly proportional to H_2O_2 concentration, UV irradiation intensity, and recirculation rate, while the initial pH had a negligible influence. Under neutral pH conditions (6–9), with an H_2O_2 concentration of 40 mmol/L, UV irradiation power of 3.0 W/L, recirculation rate of 0.6 times/min, and a reaction time of 120 minutes, the TNT concentration in the wastewater was reduced by 96% (from 12.88 mg/L to 0.52 mg/L) and color by 93% (from 1,115 Pt-Co to 78 Pt-Co), meeting the requirements of QCVN 40:2025/BTNMT and TCVN/QS 658:2012. These findings confirm that the photo-Peroxone process, combined with UV irradiation, is an effective solution for TNT and color removal in wastewater from explosive dismantling operations and has strong potential for practical application in combination with other treatment methods to meet environmental protection standards.

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TÓM TẮT

Nghiên cứu ứng dụng công nghệ quang Peroxone để xử lý nước thải chứa TNT phát sinh từ quá trình xì tháo bom mìn, vật nổ

Nước thải phát sinh từ quá trình xì tháo bom mìn, vật nổ, đạn dược cấp 5 có độ màu lớn, chứa hàm lượng cao 2,4,6-Trinitrotoluen (TNT) và các hợp chất khác là thành phần của các loại thuốc phóng, thuốc nổ. Đây là loại nước thải có tính độc hại cao, bền vững với môi trường và rất khó xử lý bằng các phương pháp thông thường. Bài báo này trình bày kết quả nghiên cứu xử lý nước thải xì tháo bom mìn, vật nổ trên cơ sở phản ứng quang Peroxone. Một số yếu tố ảnh hưởng đến hiệu quả xử lý như: pH, nồng độ H_2O_2, cường độ bức xạ UV, thời gian và lưu lượng tuần hoàn đã được nghiên cứu. Kết quả cho thấy, hiệu quả xử lý tỉ lệ thuận với nồng độ H_2O_2, cường độ bức xạ UV, lưu lượng nước tuần hoàn và hầu như không bị ảnh hưởng bởi pH ban đầu của nước thải. Tại nồng độ H_2O_2 = 40 mmol/L, cường độ bức xạ UV = 3,0 W/L, lưu lượng tuần hoàn = 0,6 lần/phút, sau 120 phút xử lý, hiệu quả xử lý TNT giảm 96% (từ 12,88 mg/L giảm còn 0,52 mg/L) và độ màu giảm 93% (giảm từ 1.115 Pt-Co xuống còn 78 Pt-Co) đạt QCVN 40:2025/BTNMT và TCVN/QS 658:2011 mức B.

Từ khóa: TNT; Quang Peroxone; Bom mìn; Đạn nổ cấp 5; AOPs.