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Advanced Oxidation Process for DNAN Using UV/H_2O_2

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ABSTRACT

2,4-Dinitroanisole (DNAN) is an important component of insensitive munitions that is anticipated to replace 2,4,6-trinitrotoluene (TNT) in munitions formulations. Photocatalyzed hydrogen peroxide (H_2O_2) oxidation experiments and chemical analyses were conducted to study the effect of initial pH and H_2O_2 dosage on the kinetics of DNAN decomposition and the reaction pathways. The results show that DNAN degradation followed zero-order kinetics when a 250 ppm DNAN solution was treated with ultraviolet (UV) light and 1500–4500 ppm H_2O_2 in an initial pH range of 4–7. However, when the H_2O_2 concentration was 750 ppm, DNAN degradation followed pseudo-first-order kinetics. The results indicate that DNAN can easily be oxidized by UV/H_2O_2 treatment. When the H_2O_2 dosage was 1500 ppm and the initial pH was 7, DNAN was reduced from 250 ppm to less than 1 ppm in 3 h. However, the total organic carbon (TOC) and total carbon (TC) concentrations were reduced slowly from 100 to less than 70 ppm carbon (C) in 3 h, and decreased to about 5 ppm after 9 h of treatment, suggesting the formation of other organic compounds. Those reaction intermediates were oxidized to carbon dioxide (CO_2) at a slower rate than the oxidation of DNAN. CO_2 was emitted from the solution because the solution pH decreased rapidly to about 3 during the UV/H_2O_2 oxidation. Most of the nitrogen in DNAN was converted to nitrate by UV/H_2O_2 oxidation after 9 h of treatment. The research results indicate that UV/H_2O_2 oxidation is a promising technique for the treatment of DNAN in wastewater.

1. Introduction

2,4-Dinitroanisole (DNAN) is an important constituent of insensitive munitions that is intended to replace 2,4,6-trinitrotoluene (TNT) in munitions formulations. It is also used for the synthesis of dyes and insecticides [1]. Therefore, the production, transport, storage, and use of DNAN is expected to increase, which will result in large amounts of wastewater containing DNAN. Accordingly, increased concern has been raised regarding the environmental fate and impacts of DNAN.

DNAN is poorly soluble in water (about 276 $mg \cdot L^{-1}$ at room temperature), and produces rod-shaped crystals at higher concentrations, with adsorption to clay and organic soils [2]. DNAN has been found to be toxic to aquatic organisms, such as algae, cladocerans, and fish, and lethal to earthworms in soil [3–5]. Studies on rats have indicated that the acute toxicity of DNAN (lethal dose (LD50) = 199 $mg \cdot kg^{-1}$) could be even higher than that of TNT (LD50 = 794–1320 $mg \cdot kg^{-1}$) [6]. Moreover, the degradation products of DNAN, such as 2,4-dinitrophenol and nitrite, are even more toxic than DNAN itself. Furthermore, DNAN can result in a persistent yellow color in wastewater, which must be removed by a pretreatment process.

Only a few studies have been conducted to characterize the environmental fate and behavior of DNAN, and to examine the biological transformation of DNAN under aerobic and anaerobic conditions. In this research, the relevant sensitivity, chemical compatibility, and thermal properties of DNAN have been determined through a literature review and experimental work [6].

Advanced oxidation processes (AOPs) appear to be some of the most promising methods for the treatment of wastewater containing nitroaromatic compounds. AOPs are associated with the generation of radical species (e.g., hydroxyl radical (·OH)), which, given sufficient contact time and proper conditions, can mineralize the target pollutants to carbon dioxide (CO_2) [7]. Ultraviolet (UV)

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photolysis in combination with hydrogen peroxide (H_2O_2) oxidation is an important AOP technology that has been used to treat wastewater contaminated with nitroaromatic compounds [8]. H_2O_2 is readily available and relatively inexpensive, and the photolysis of H_2O_2 results in the generation of ·OH, which may degrade contaminants. UV/H_2O_2 has been shown to be an effective degradation and mineralization treatment for most organic compounds [9–13].

Thus far, studies have examined the degradation of DNAN using the Fenton oxidation process [1], biotic or abiotic transformation [14–18], alkaline hydrolysis [19,20], and bimetal reductive treatment [21]. Only a few studies have been conducted on the oxidation of DNAN with UV/H_2O_2 [22], and the results have shown that photo-oxidation is the main mechanism for DNAN degradation, with the formation of nitrite and nitrate as major nitrogen (N) species and 2,4-dinitrophenol as a minor species [22]. An evaluation of treatment technologies for industrial process wastewater containing insensitive munitions (i.e., DNAN) has been summarized [23], but the optimal conditions for the design and operating parameters for a UV/H_2O_2 degradation process need to be determined. The objective of this study was to investigate the feasibility of treating DNAN-contaminated water by means of UV/H_2O_2 advanced oxidation, and to determine the optimal oxidation conditions for DNAN degradation, including H_2O_2 dosage and initial pH. This study has fundamental implications for the treatment of wastewater containing DNAN.

2. Materials and methods

Aqueous DNAN stock solutions were prepared by dissolving reagent-grade DNAN ($C_7H_6N_2O_5$; 98% purity, Sigma Aldrich LLC., USA) in tap water. Considering that the solubility of DNAN in water at room temperature is about 260 ppm, the initial concentration of the DNAN solutions prepared in this study was about 250 ppm. The UV lamp used for the treatment was an LSE Lighting UV Bulb (254 nm, 13 W for Pura 1GPM 10–212 UV10 UV11). H_2O_2 solution (30%) was used in the oxidation process (reagent grade, Thermo Fisher Scientific Inc., USA). Sodium hydroxide (NaOH) was used to adjust the initial pH of the DNAN solutions (reagent grade, Thermo Fisher Scientific Inc., USA).

Oxidation experiments of DNAN by UV/H_2O_2 were conducted using a 1000 mL glass beaker. The 1000 mL beaker, which had a diameter of 8.9 cm and a height of 18.7 cm, was used as the reactor. The UV lamp was fixed in the center of the beaker, with most of it under the surface. A magnetic mixer with a length of 3 cm was used to mix the solutions. The UV intensity measured during the oxidation process was about 4500 lx. In order to determine the optimal conditions for the treatment of DNAN, batch experiments were conducted with different H_2O_2 dosages (1500, 2250, 3000, and 4500 ppm) at a fixed pH of 7 and at different initial pH (4, 5, 6, and 7) using a fixed H_2O_2 dosage (1500 ppm). For each experiment, 800 mL DNAN solution was used, and the initial concentration of DNAN was about 250 ppm, or 35 ppm as DNAN-N. Next, the solutions were exposed to the UV light for a total time of 9 h while being continuously mixed by magnetic mixers. Samples were collected (25 mL) from the reactor at specific time intervals during the degradation process for analysis. Data were checked for deviations from normality and homogeneity of variance before performing statistical analyses. Pearson pair-wise correlation coefficients between the N-concentrations and carbon (C)-concentrations were determined using SPSS software (Statistics 21, IBM, USA).

The analysis of DNAN was performed with a high-performance liquid chromatography (HPLC) system (Varian Inc., USA; equipped with a ProStar 410 Auto-sampler and a 330 UV–Vis PDA detector). A Dionex Acclaim™ 120 C18 column (15 μm, 4.6 mm × 250 mm, Thermo Fisher Scientific Inc., USA) was used. The eluent was an isocratic methanol–water mixture at a ratio of 70:30 (v/v). It was pumped at a flow rate of 1 mL·min^{-1}. The analytical wavelength was 284 nm and the sample injection volume of was 10 μL. Under these conditions, DNAN elutes at 4.9 min.

The total-N and nitrite-nitrogen (NO_2-N) of the samples were analyzed using UV spectrophotometry (DR2800, Type LPG422.99.00012, 15 V, 30 VA, HACH, USA). The concentrations of H_2O_2 were measured using a H_2O_2 test kit (Model HYP-1, HACH, USA). The nitrate-nitrogen (NO_3-N) concentrations of the samples were measured by means of an ion chromatography system (Dionex, Thermo Fisher Scientific Inc., USA) equipped with an anion separation column (AS16). Total organic carbon (TOC) and total carbon (TC) were measured using a Phoenix 8000 UV–Persulfate TOC analyzer, equipped with a TOC boat sampler (Rosemount Dohrmann Model 183), and TOC Talk software (Teledyne Tekmar Company, USA). A TOC and TC concentration range of 0.1–20 ppm C were used to calibrate the instrument.

3. Results and discussion

3.1. Effect of H_2O_2 dosage on kinetics of DNAN removal

The kinetics of DNAN removal under four different H_2O_2 dosages is shown in Fig. 1. The DNAN removal rate depends markedly on H_2O_2 dosage, indicating that H_2O_2 dosage has a strong effect on the degradation rate of DNAN. For dosages of 1500–3000 ppm, the degradation rate increased with increasing dosage. This is because the increasing H_2O_2 concentration can promote the formation of ·OH, which can accelerate the DNAN degradation process. However, studies on the photo-degradation of some organics have shown that excessive H_2O_2 may reduce the degradation rate because it acts as a scavenger for ·OH [24–26]. From Fig. 1, it can be seen that the DNAN removal rate at 4500 ppm H_2O_2 is slower than that at 3000 ppm, suggesting that excessive H_2O_2 reduces the DNAN degradation rate. It can be concluded that excessive H_2O_2 may compete with DNAN for reaction with ·OH, which would decrease the degradation rate of DNAN.

The results show that the optimal H_2O_2 dose for the oxidation of a DNAN solution with an initial concentration of 250 ppm is 3000 ppm. However, a higher H_2O_2 dosage would result in higher treatment costs in engineering applications, and the H_2O_2 remaining in the treated solution must be removed for environmental protection. Thus, it is of great importance to optimize the H_2O_2 dose for the treatment of DNAN solutions.

The results show that DNAN degradation follows zero-order kinetics under our experimental conditions; the rate constants are summarized in Table 1. The zero-order kinetics were different from the reported pseudo-first-order decay kinetics of DNAN under sunlight and UV only, under which the degradation process was much slower [22]. This difference was probably due to the presence of H_2O_2, which can accelerate the DNAN degradation process. Linear regression was developed for the DNAN degradation kinetics; the results are shown in Fig. 1. The points after the degradation was finished were not used in the linear regression.

A lower H_2O_2 dosage of 750 ppm was used to treat the DNAN solution; the DNAN removal kinetics are shown in Fig. 2. It was clear that the kinetics of DNAN degradation were pseudo-first-order decay kinetics. The results in Figs. 1 and 2 indicate that DNAN can easily be oxidized by UV/H_2O_2 in the presence of sufficient H_2O_2, and that the oxidation rate of DNAN is not affected by decreasing DNAN concentration during the treatment. Zero-order decay kinetics for the advanced oxidation process for other organic contaminates, such as nitroguanidine, have also been reported [27].

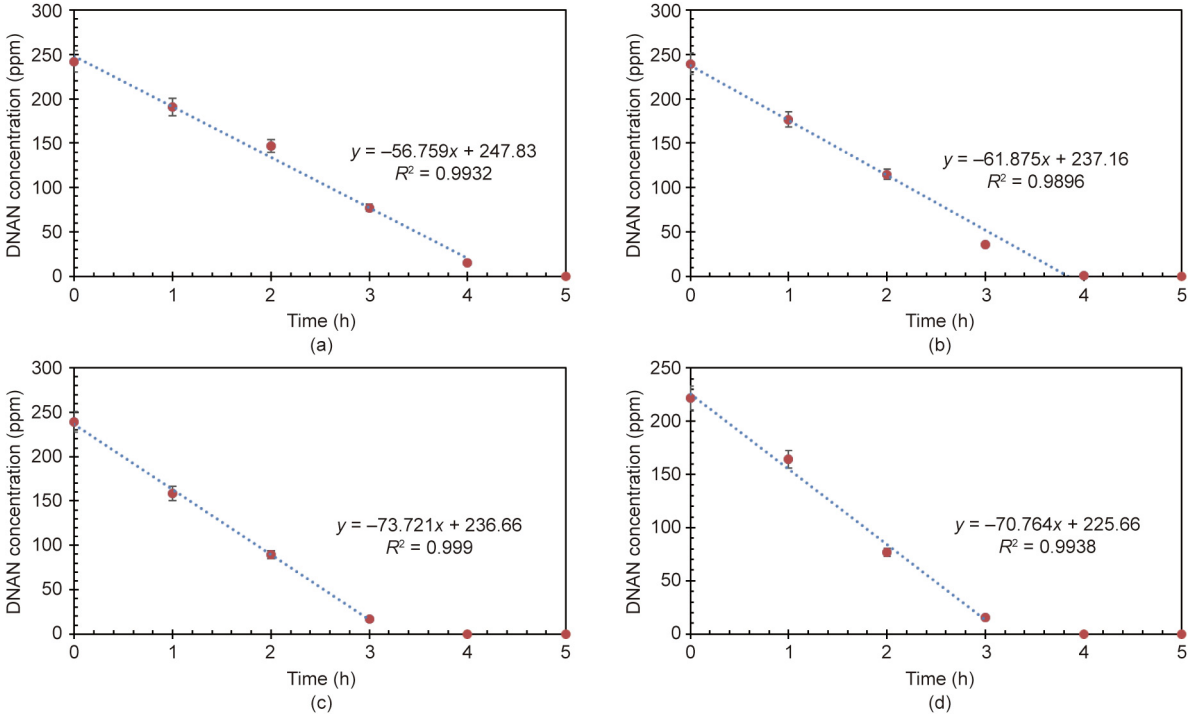

Fig. 1. Kinetics of DNAN removal under four different H_2O_2 dosages: (a) 1500 ppm, (b) 2250 ppm, (c) 3000 ppm, and (d) 4500 ppm. Initial DNAN concentration ≈ 250 ppm, initial pH ≈ 7, under 13 W UV light.

Table 1
Zero-order rate constants of DNAN oxidation kinetics (k_0).

H_2O_2 concentration (ppm)	pH	k_0 (h^{-1})	R^2
1500	7	56.76	0.9932
2250	7	61.88	0.9896
3000	7	73.72	0.999
4500	7	70.76	0.9938
1500	4	53.74	0.9905
1500	5	56.12	0.9889
1500	6	74.99	0.9717
1500	7	75.84	0.9812

Fig. 3 shows the changes in H_2O_2 concentration and TOC during the DNAN oxidation process using 1500 ppm H_2O_2 for 9 h of treatment. While the DNAN degradation process was completed in about 5 h (Fig. 1), it took 9 h to reach about 95% TOC removal (Fig. 3). Considering that 1500 ppm H_2O_2 was completely consumed after 9 h of reaction, this dosage of H_2O_2 is suitable for the oxidation of DNAN solution with an initial DNAN concentration of 250 ppm.

$$C_7N_2O_5H_6 + 17\,H_2O_2 \rightarrow 7\,CO_2 + 2\,HNO_3 + 19\,H_2O \quad (1)$$

Assuming that all the H_2O_2 was used to oxidize DNAN to nitrate (HNO_3) and CO_2, 730 ppm H_2O_2 was needed to completely oxidize 250 ppm DNAN, as calculated based on Eq. (1). Under experimental conditions, only part of the H_2O_2 was consumed to oxidize the DNAN and its degradation products, and the actual demand for H_2O_2 was greater than 730 ppm.

3.2. Effect of initial pH on kinetics of DNAN removal

In addition to H_2O_2 dosage, the effect of initial pH on DNAN degradation was studied. Batch experiments were conducted to treat DNAN solutions at an initial pH of 4, 5, 6, and 7, respectively, with the same H_2O_2 dosage of 1500 ppm. The kinetics of DNAN removal at four different initial pH values are shown in Fig. 4. The results show that DNAN degradation follows zero-order kinetics under the experimental conditions used here; the rate constants are shown in Table 1. Linear regression was developed for the DNAN degradation kinetics, and the results are shown in Fig. 4. The points after the degradation finished were not used in the linear regression.

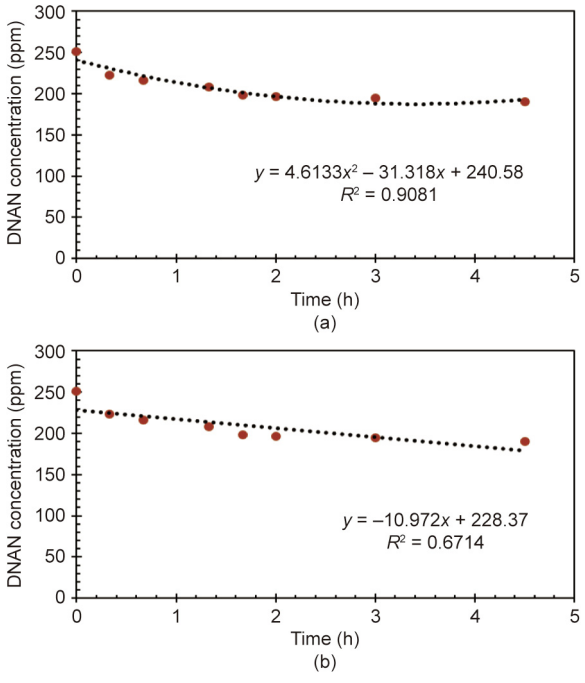

Fig. 2. Kinetics of DNAN removal under an H_2O_2 dosage of 750 ppm. (a) Pseudo-first-order approach fitting result; (b) zero-order approach fitting result. Initial DNAN concentration ≈ 250 ppm, initial pH ≈ 7, 13 W UV light.

Fig. 4 shows that the initial pH can affect the DNAN degradation processes to some extent: The higher the pH, the faster the

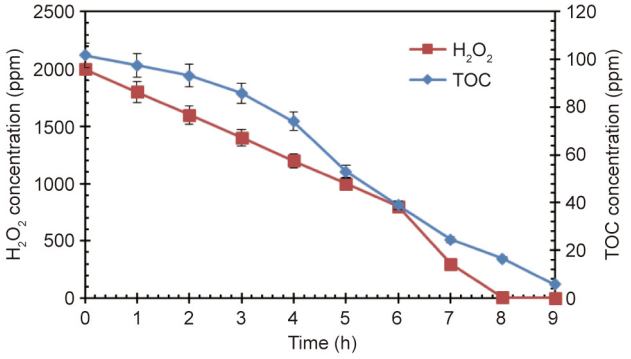

Fig. 3. Variation of H_2O_2 concentration and TOC during oxidation treatment of 250 ppm DNAN solution with 1500 ppm H_2O_2. Initial pH ≈ 7, 13 W UV light.

degradation rate within the pH range of 4–7. When the pH is higher than 7, alkaline hydrolysis of DNAN will take place, which is a different degradation process [19,20]. However, the effect of initial pH on the degradation rate of DNAN is modest compared with the effect of the H_2O_2 dosage. Studies on the phototransformation rate of DNAN in water showed that a variation in the solution pH (pH 6.5–8.0) had only slight effects on the degradation rate of DNAN [22]. Considering that the initial pH of the DNAN solution is about 7, the most suitable pH is 7 for DNAN oxidation, as no pH adjustment is needed and the degradation efficiency is not affected.

Tables 2 and 3 show the changes in pH during the oxidation processes under different initial pH and H_2O_2 dosages. The results show that the pH decreased quickly when the oxidation process of DNAN began, regardless of the initial pH and H_2O_2 dosage, and remained constant at about 2 after the DNAN degradation processes finished. This finding indicates that some acid substances—mostly HNO_3—were formed as a result of DNAN degradation.

Table 2
Changes in pH during the DNAN degradation processes under different initial pH.

Time (h)	pH value			
	Initial pH = 4	Initial pH = 5	Initial pH = 6	Initial pH = 7
0	3.50	4.80	6.10	7.07
1	2.76	2.90	2.53	2.82
2	2.21	2.27	2.03	2.08
3	2.00	1.98	1.81	1.84
4	1.83	1.80	1.75	1.80
5	1.73	1.75	1.77	1.80
6	1.71	1.74	1.84	1.91
7	1.73	1.76	1.96	2.02
8	1.75	1.78	1.91	1.99
9	1.77	1.81	1.86	1.93

Initial DNAN concentration = 250 ppm, 1500 ppm H_2O_2, 13 W UV light.

Table 3
Changes in pH during the DNAN degradation processes under different H_2O_2 dosages.

Time (h)	pH value			
	1500 ppm H_2O_2	2250 ppm H_2O_2	3000 ppm H_2O_2	4500 ppm H_2O_2
0	8.46	8.12	7.76	7.57
1.33	6.04	5.81	3.53	3.65[a]
2	5.43	4.59	2.92	2.42
3	3.61	3.24	2.65	2.08
4	2.98	2.72	2.68	1.93
5	2.78	2.66	2.71	1.93

Initial DNAN concentration = 250 ppm, initial pH ≈ 7, 13 W UV light.
[a] Measured at 1 h.

3.3. N concentrations during the DNAN degradation processes

In order to determine the oxidation products of DNAN, concentrations of the various kinds of N species—including total-N, ammonia, nitrate, and nitrite—formed during the oxidation

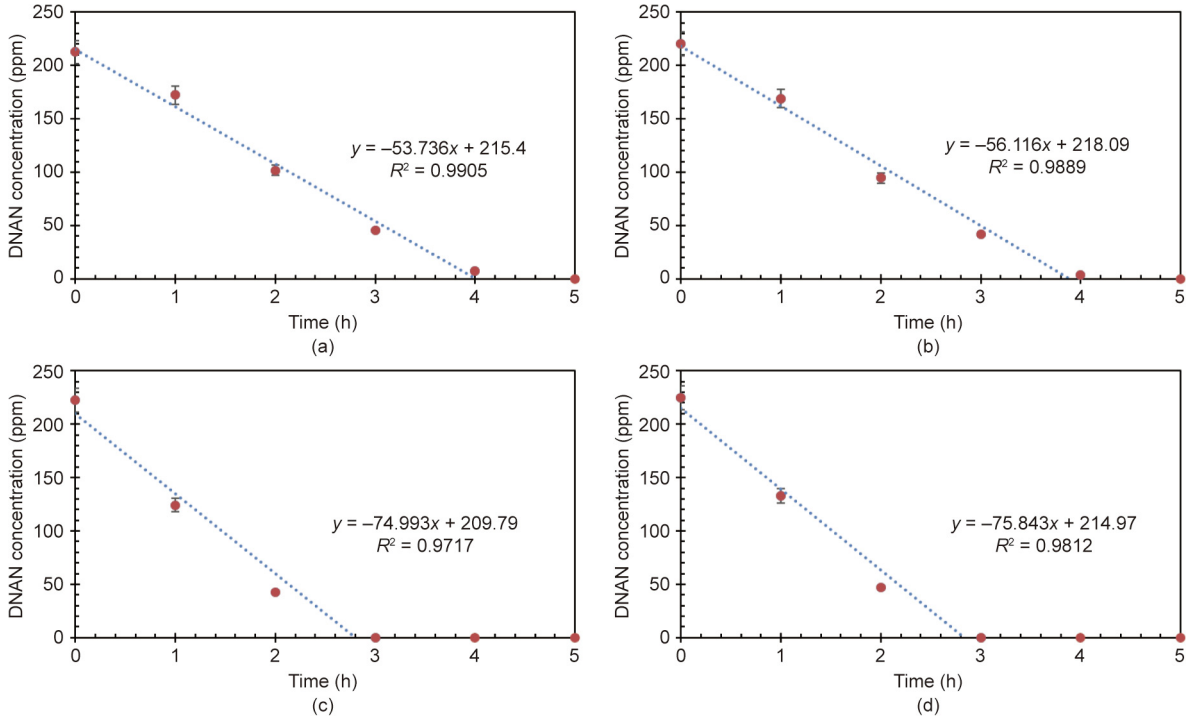

Fig. 4. Kinetics of DNAN removal at four different initial pH values: (a) pH = 4, (b) pH = 5, (c) pH = 6, and (d) pH = 7. Initial DNAN concentration ≈ 250 ppm, 1500 ppm H_2O_2, 13 W UV light.

processes of DNAN were measured in addition to the analysis of DNAN-N.

The results (Fig. 5) show that during the DNAN degradation processes, nitrate and nitrite were formed and no ammonia was detected. The concentration of NO_2-N was very low and disappeared after the DNAN degradation processes finished, indicating that NO_2-N is one of the major intermediates. Nitrite was oxidized to nitrate immediately after being generated from the decomposition of DNAN. The concentration of NO_3-N continued to increase during the degradation processes, and the final concentration of NO_3-N was similar to the initial DNAN-N concentration. This result suggests that NO_3-N was the end product, and that almost all of the DNAN-N was transformed into NO_3-N, similar to the other nitroaromatics treated with UV/H_2O_2 [8,28]. These results are consistent with those of other studies that have been conducted on the UV photolysis of DNAN [22], and suggest that photo-oxidation is a promising technique for the treatment of DNAN in wastewater.

The total-N remained constant during the DNAN degradation process, indicating that no gaseous N was formed (Fig. 6). Furthermore, the N compounds showed similar change trends at a different initial pH within the range of 4–7. However, the DNAN-N decreased faster and the nitrate increased faster with a higher initial pH, as a higher pH increases the rate of the DNAN degradation progress. After 9 h of treatment, the NO_3-N was still a little lower than the total-N, suggesting that there was a small portion of N remaining in the form of nitro-organics. Similarly, Fig. 7 shows that the TOC was about 5 ppm after 9 h of treatment, indicating that some organics containing N were present in the reacted solutions. This probably occurred because the very low concentration of H_2O_2 that remained after 9 h (Fig. 3) was unable to oxidize the residual nitro-organics into nitrate and CO_2.

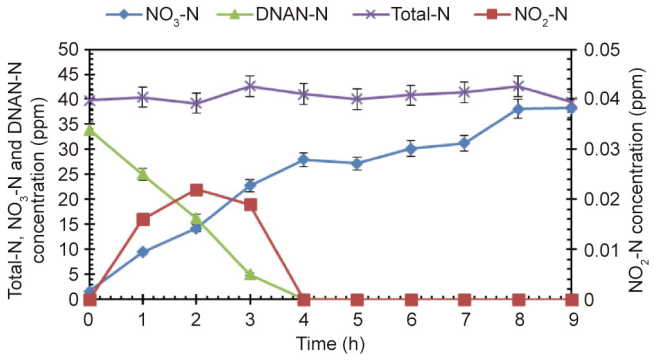

Fig. 5. Variation of N compounds during the oxidation process of 250 ppm DNAN solution. Initial pH ≈ 7, 1500 ppm H_2O_2, 13 W UV light.

3.4. C concentrations during the DNAN degradation processes

TOC and TC were measured during the degradation process of DNAN in order to investigate the changes of carbon species; the results are shown in Fig. 7. The TOC concentrations are almost the same as the TC concentrations, and both the TOC and TC decrease during the degradation process of DNAN. This result indicates that gaseous carbon (probably CO_2) was generated during the DNAN degradation process, and that no carbonate or bicarbonate was present in the treated water. As discussed before, the pH decreased quickly during the oxidation processes when the oxidation process of DNAN began, regardless of the initial pH and the H_2O_2 dosage, and remained constant at about 2 after the DNAN degradation processes finished. This result indicates that some acid substances—mostly HNO_3—were formed as a result of DNAN degradation, which also explains why no carbonate or bicarbonate was present in the treated water.

The results show that complete mineralization of DNAN can be achieved with UV/H_2O_2, as the TC and TOC decreased to about 5 ppm after 9 h of treatment. As the DNAN degradation finished in about 4 h, DNAN was converted to other organic compounds, which were subsequently degraded. The degradation process of DNAN may follow parts of the decomposition pathway of 2,4-dinitrotoluene by UV/H_2O_2, in which some lower molecular weight carboxylic acids are produced and then oxidized into CO_2 [29]. This would explain why the pH increased slightly after the DNAN degradation was complete.

Fig. 6 shows that the rate of increase of nitrate was faster during the degradation process of DNAN than after the DNAN degradation

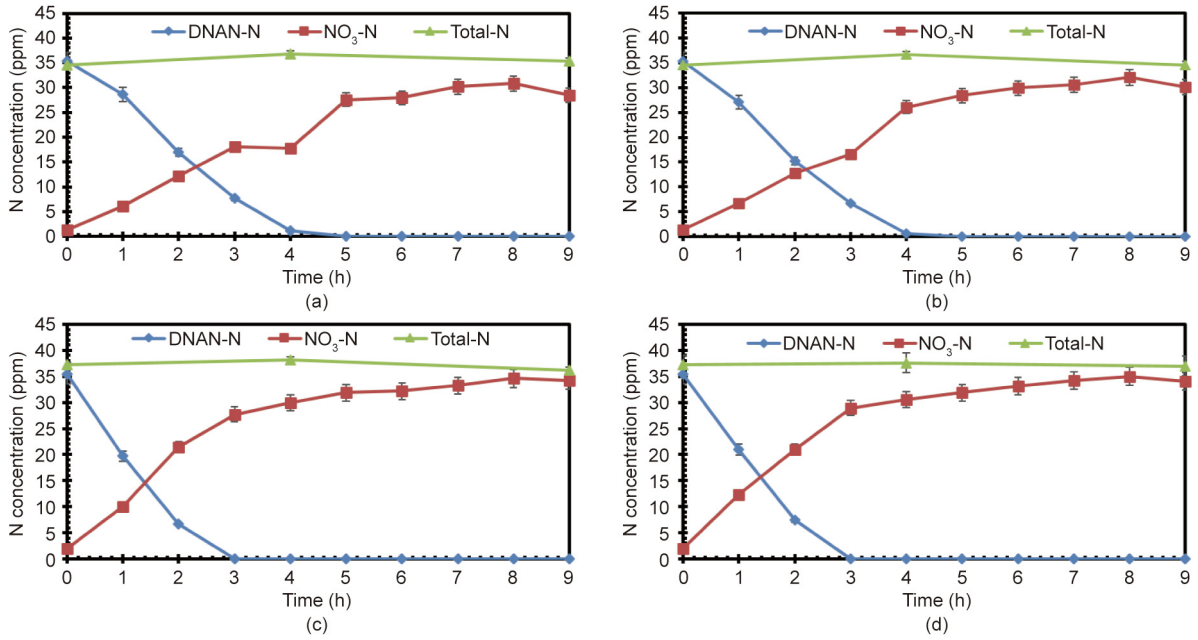

Fig. 6. Variation of N concentrations under different initial pH: (a) pH = 4, (b) pH = 5, (c) pH = 6 and (d) pH = 7. Initial DNAN concentration = 250 ppm, 1500 ppm H_2O_2, 13 W UV light.

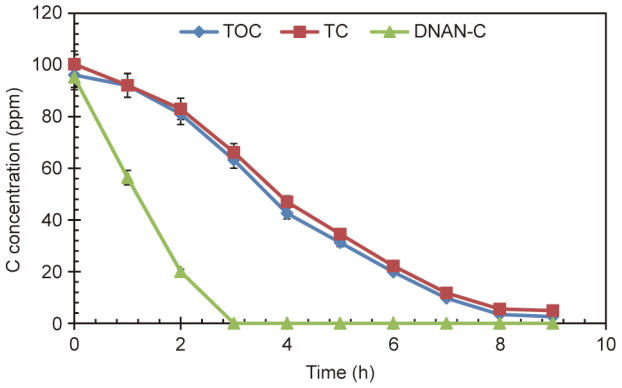

Fig. 7. Variation of C concentrations under different initial pH for 250 ppm DNAN solutions. 1500 ppm H_2O_2, 13 W UV light.

finished, indicating that the cleavage of nitro groups took place in the early stages of DNAN decomposition. When the DNAN degradation was complete, about 77% of the N had been transformed into nitrate, suggesting that 23% of the N remained in the form of nitro-organics. Meanwhile, Fig. 7 shows that about 65% of the TOC remained at that time, which indicates that the nitrification process is faster than mineralization during DNAN degradation.

4. Conclusions

The research results indicate that UV/H_2O_2 oxidation is a promising technique for the treatment of DNAN in solutions, as most of the DNAN can be oxidized to CO_2 and nitrate. During the oxidation treatment, the total-N concentration remained almost constant, suggesting that no gaseous N compounds (i.e., nitric oxide, nitrous oxide, nitrogen gas, and ammonia) were formed. Nitrite was one of the major oxidation intermediates. The rate of DNAN oxidation was affected by the H_2O_2 dosage and pH. An H_2O_2 dosage of 1500 ppm and an initial pH of 7 were the optimal conditions for the treatment of 250 ppm DNAN solution.

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Compliance with ethics guidelines

Hailei Su, Christos Christodoulatos, Benjamin Smolinski, Per Arienti, Greg O'Connor, and Xiaoguang Meng declare that they have no conflict of interest or financial conflicts to disclose.

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DNAN 的高级氧化过程研究

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摘要

2,4-二硝基茴香醚（DNAN）是用于替代2,4,6-三硝基甲苯（TNT）的钝感炸药的一种重要成分。为了研究初始pH和过氧化氢（H_2O_2）剂量对DNAN降解动力学和降解途径的影响，开展了DNAN的光催化H_2O_2氧化实验。结果显示，初始pH为4~7且H_2O_2剂量为1500~4500 ppm，使用UV/ H_2O_2处理浓度为250 ppm的DNAN溶液时，DNAN的降解服从零级反应动力学。但是，当H_2O_2剂量为750 ppm时，DNAN的降解服从类一级反应动力学。结果表明，DNAN易于被UV/H_2O_2氧化降解。当H_2O_2剂量为1500 ppm且初始pH为7时，3 h内DNAN浓度从250 ppm降到1 ppm以内；但3 h内总有机碳（TOC）和总碳（TC）浓度从100 ppm降到70 ppm以下，9 h后降到5 ppm以下，说明生成了其他有机化合物。这些中间产物氧化为CO_2的速度慢于DNAN的氧化速度。UV/H_2O_2氧化过程中，生成的CO_2释放到空气中，因为溶液pH迅速降低到3左右。9 h的UV/H_2O_2处理后，DNAN中的N绝大多数转化为硝态氮。研究表明，UV/H_2O_2氧化是处理DNAN废水的有效技术。

1. 引言

2,4-二硝基茴香醚（2,4-dinitroanisole, DNAN）是炸药合成中取代2,4,6-三硝基甲苯（2,4,6-trinitrotoluene, TNT）的钝感炸药的重要成分之一，也可以用于合成染料和杀虫剂[1]。近年来，DNAN的生产、运输、储存和使用逐渐增多，过程中产生了大量的含DNAN的工业废水。因此，DNAN的环境行为和影响也受到了越来越多的关注。

室温下DNAN在水中的溶解度很低，约为276 $mg \cdot L^{-1}$，浓度较高时会吸附在颗粒或有机质上形成针状晶体[2]。研究表明，DNAN对藻类、水蚤类动物和鱼类等水生生物有一定的毒性，对土壤中的蚯蚓有致死效应[3−5]。对老鼠的毒性实验显示，DNAN的急性毒性（LD_{50} = 199 $mg \cdot kg^{-1}$）比TNT（LD_{50} = 794~1320 $mg \cdot kg^{-1}$）还要强[6]。另外，DNAN的降解产物，如2,4-二硝基苯酚和亚硝酸根等，毒性比DNAN更大。其次，DNAN在废水中会产生持久性的黄色，必须在污水的预处理阶段中去除。

目前，关于DNAN的环境归趋和行为表征，以及厌氧和好氧条件下的生物转化研究较少。通过文献综述和实验工作，有学者研究了DNAN的相对敏感性、化学相容性和热力学性质等[6]。

高级氧化过程（AOP）是处理含硝基芳香化合物废水的最有效方法之一。AOP通过产生自由基（OH·），在适当的条件和充分的接触下，将目标污染物矿化为

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CO_2 [7]。紫外线光解结合H_2O_2氧化是一种重要的高级氧化技术，广泛用于处理含硝基芳香化合物的废水[8]。H_2O_2价格便宜，容易获得，且光解后产生的羟基自由基可以降解污染物。研究表明，UV/H_2O_2是一种可以有效降解和矿化多种有机化合物的处理方法[9−13]。

目前，已有学者开展了使用Fenton氧化[1]、生物和非生物转化[14−18]、碱性水解[19−20]和双金属还原[21]等方法降解DNAN的研究。但使用UV/H_2O_2氧化DNAN的研究很少[22]。研究显示，光氧化是DNAN降解的主要机制，生成的主要含氮物质是硝酸根和亚硝酸根，以及少量的2,4-二硝基苯酚[22]。有学者总结评估了含有DNAN等钝感炸药成分废水的工业过程处理技术[23]，认为降解过程的设计最优条件和操作参数需要进一步研究确定。本研究的目标是，研究UV/H_2O_2高级氧化处理含DNAN废水的可行性，并确定DNAN降解的最优氧化条件，包括H_2O_2剂量和初始pH。研究对含DNAN废水的处理提供基本的技术指导。

2. 实验材料和实验方法

将试剂级的DNAN固体（$C_7H_6N_2O_5$，纯度为98%，Sigma Aldrich LLC., USA）溶解于自来水中制备DNAN溶液。考虑到室温下DNAN在水中的溶解度约为260 ppm，实验过程中制备的DNAN溶液浓度为250 ppm。DNAN氧化降解实验中使用的紫外灯为LSE Lighting UV Bulb（254 nm, 13 W for Pura 1GPM 10-212 UV10 UV11），以及30%的H_2O_2溶液（试剂级，Thermo Fisher Scientific Inc., USA）。另外，使用氢氧化钠溶液调节DNAN溶液（试剂级，Thermo Fisher Scientific Inc., USA）的pH。

使用UV/H_2O_2氧化DNAN的实验在1000 mL烧杯（内径为8.9 cm，高18.7 cm）中进行。UV灯固定在烧杯中部，且大部分位于液面下。使用一个3 cm长的磁力搅拌器搅拌溶液。搅拌过程中，紫外线的强度约为4500 lx。为了确定DNAN处理的最佳条件，开展了一系列不同H_2O_2剂量水平（1500 ppm、2250 ppm、3000 ppm和4500 ppm，pH固定为7）和不同初始pH（4、5、6和7，H_2O_2剂量为1500 ppm）的批处理实验。每组实验使用800 mL初始浓度约为250 ppm的DNAN溶液（35 ppm DNAN-N）。将DNAN溶液暴露于紫外灯下9 h，同时不停搅拌。降解过程中每隔特定的时间间隔取样25 mL用于分析。统计分析前对数据进行正态检验。

溶液中DNAN浓度的分析使用高效液相色谱（Varian Inc., USA；配备ProStar 410自动采样器和330 UV-vis PDA探测器），色谱柱为Dionex Acclaim™ 120 C18（15 μm , 4.6 mm × 250 mm, Thermo Fisher Scientific Inc., USA）。洗脱液为等度乙醇和水按70:30体积比的混合液。泵的流速是1 mL·min^{-1}，分析波长为284 nm，样品注射体积为10 μL。实验条件下，DNAN的洗脱时间为4.9 min。

样品中总氮（total-N）和亚硝态氮（NO_2-N）的测定使用紫外分光光度计（DR2800, Type LPG422.99.00012, 15 V, 30 V·A, HACH, USA）。H_2O_2的浓度使用H_2O_2试剂盒测定（Model HYP-1, HACH, USA）。硝态氮（NO_3-N）的测定使用离子色谱（Dionex, Thermo Fisher Scientific Inc., USA），色谱柱为阴离子分离柱AS16。总有机碳（TOC）和总碳（TC）的测定使用Phoenix 8000 UV-过硫酸钠TOC分析仪，配有TOC进样器（Rosemount Dohrmann Model 183）和TOC软件（Teledyne Tekmar Company, USA）。TOC和TC的标线浓度范围为0.1~20 ppm。

3. 结果和讨论

3.1. H_2O_2剂量对DNAN去除动力学的影响

4种不同H_2O_2剂量水平下DNAN的去除动力学如图1所示。由图1可以看出，DNAN的去除速率明显依赖于H_2O_2剂量，表明H_2O_2剂量对DNAN降解有显著的影响。在1500~3000 ppm的H_2O_2剂量范围内，DNAN的降解速率随着H_2O_2剂量的增加而增加。这是由于增加的H_2O_2剂量可以促进羟基自由基的生成，从而加速DNAN的降解过程。然而，关于一些有机化合物的光降解研究结果显示，过量的H_2O_2很可能作为羟基自由基的捕获剂，从而降低降解速率[24−26]。从图1中可以看出，H_2O_2剂量为4500 ppm时，DNAN的去除速率比3000 ppm时慢，表明过量的H_2O_2会降低DNAN的降解速率。因此，可以得出结论，过量H_2O_2的存在会与DNAN竞争羟基自由基（·OH），从而降低DNAN的降解速率。

研究结果显示，在实验采用的H_2O_2剂量范围内，DNAN的初始浓度为250 ppm时，DNAN降解的最优H_2O_2剂量是3000 ppm。另外，较高的H_2O_2剂量会导致工业应用中产生较高的处理费用。并且，处理后的溶液

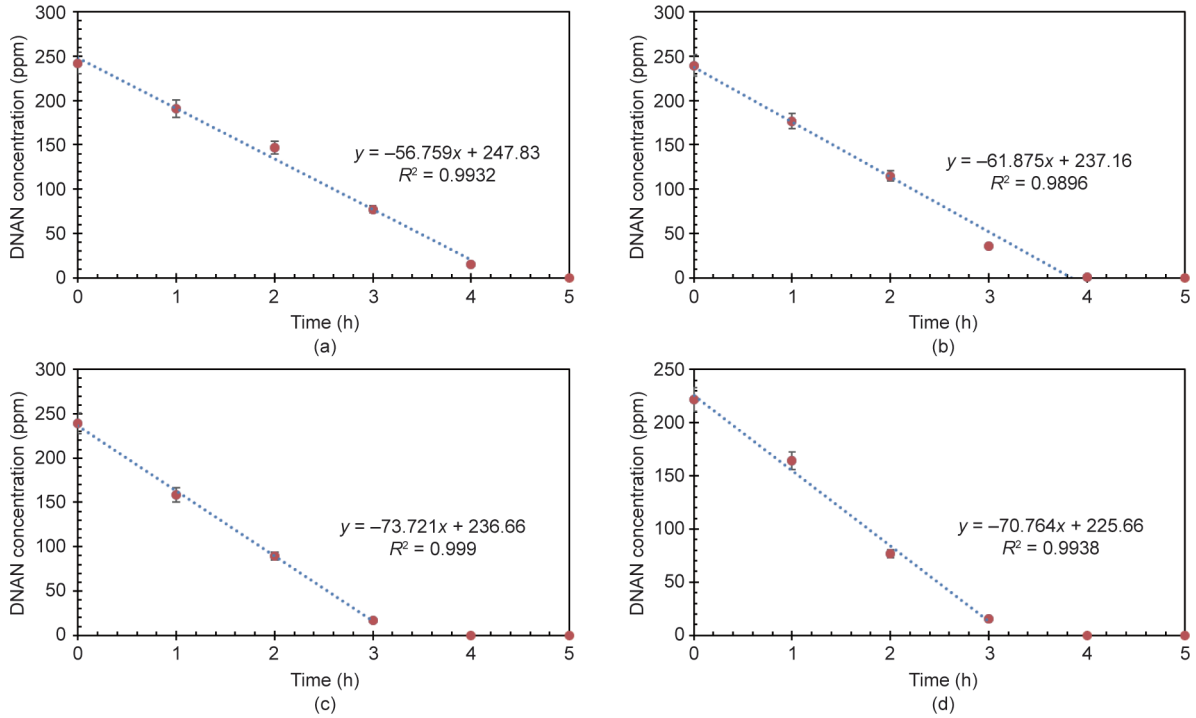

图1. 不同H_2O_2剂量（1500 ppm、2250 ppm、3000 ppm和4500 ppm）条件下DNAN的降解动力学，初始DNAN浓度约为250 ppm，初始pH约为7，13 W紫外线。

中剩余的H_2O_2还需要去除以防治环境污染。因此，最优化DNAN溶液处理中需要的H_2O_2剂量非常重要。

研究结果显示，在本研究中采用的实验条件下，DNAN的降解过程服从零级反应动力学，速率常数如表1中所示。该零级反应动力学不同于文献中报道的太阳光和紫外线下DNAN降解的类一级反应动力学[22]，且本研究中的降解速率明显更快。造成这种差别的原因很有可能是本研究中H_2O_2的存在加速了DNAN的降解过程。对DNAN降解动力学进行线性回归，结果如图1所示。降解过程结束后的点不用于线性回归。

使用较低的H_2O_2剂量（750 ppm）处理DNAN溶液，DNAN的去除动力学如图2所示。由图可知，DNAN的降解动力学服从类一级反应动力学。由图1和图2可知，足量的H_2O_2存在时，DNAN容易被UV/H_2O_2氧化降解，且DNAN的氧化速率不受DNAN浓度的影响。有文献报道了其他有机污染物的高级氧化过程服从零级反应动力学[27]。

图3给出了1500 ppm H_2O_2条件下，DNAN降解过程（9 h）中H_2O_2和TOC的变化情况。尽管DNAN的降解过程在5 h内结束（图1），但是TOC降低95%以下需要9 h（图3）。考虑到1500 ppm的H_2O_2经过9 h的反应后完全被消耗，这个剂量水平适合于氧化处理初始浓度为250 ppm的DNAN溶液。

表1 DNAN降解动力学的零级速率常数（k_0）

H_2O_2 (ppm)	pH	k_0 (h^{-1})	R^2
1500	7	56.76	0.9932
2250	7	61.88	0.9896
3000	7	73.72	0.999
4500	7	70.76	0.9938
1500	4	53.74	0.9905
1500	5	56.12	0.9889
1500	6	74.99	0.9717
1500	7	75.84	0.9812

$$C_7N_2O_5H_6 + 17\ H_2O_2 \rightarrow 7\ CO_2 + 2\ HNO_3 + 19\ H_2O \quad (1)$$

由公式（1）计算可得，假设所有的H_2O_2都用于将DNAN氧化成硝酸盐和CO_2，那么完全氧化250 ppm的DNAN需要730 ppm的H_2O_2。在本研究的实验条件下，只有部分消耗的H_2O_2用于氧化DNAN及其降解产物，所以实际消耗的H_2O_2多于730 ppm。

3.2. 初始 pH 对 DNAN 去除动力学的影响

除了H_2O_2剂量之外，还研究了初始pH对DNAN降解的影响。为了研究初始pH对DNAN降解过程的影响，进行了4、5、6和7等几个不同初始pH的批处理实验，H_2O_2的剂量设定为1500 ppm。在4种不同初始pH条件下，DNAN的去除动力学如图4所示。结果表明，实验

条件下，DNAN的降解服从零级反应动力学，速率常数如表1所示。对DNAN的降解动力学进行线性回归，回归的结果如图4所示。进行线性回归时，降解过程结束后的点没有用于回归。

从图4可知，DNAN溶液的初始pH在一定程度上影响DNAN的降解过程。在研究的pH范围内（pH 4~7），pH越高，DNAN的降解速率越快。当pH大于7时，DNAN在碱性溶液中会发生碱性水解，是一种不同的降解过程[19−20]。尽管如此，与H_2O_2剂量相比，初始pH对DNAN降解速率的影响是比较轻微的。关于水中DNAN光转化的研究表明，溶液pH的差异（pH 6.5~8.0）对DNAN的降解速率有轻微的影响[22]。考虑到DNAN配置溶液的原始pH约为7，认为pH = 7是DNAN氧化的最佳初始pH条件，不需要调节pH也基本不会影响DNAN的降解效率。

不同H_2O_2剂量和初始pH条件下，氧化过程中pH的变化如表2和表3所示。结果显示，不管初始pH和

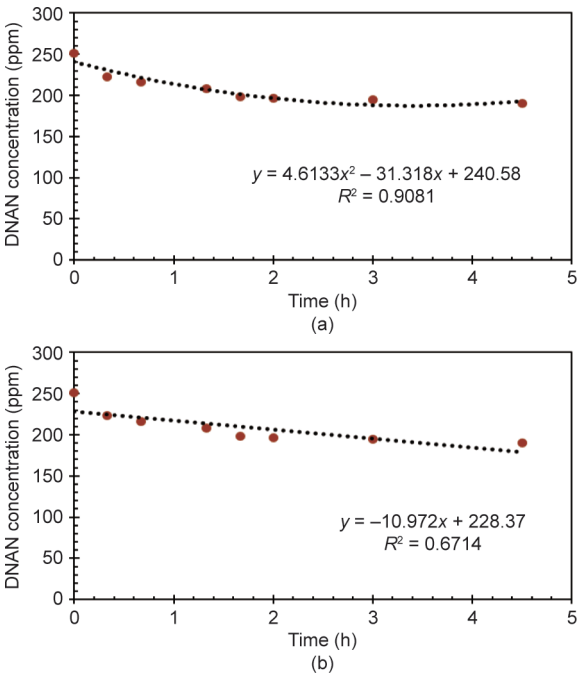

图2. H_2O_2剂量为7500 ppm时的DNAN降解动力学，初始DNAN浓度约为250 ppm，初始pH约为7，13 W紫外线。

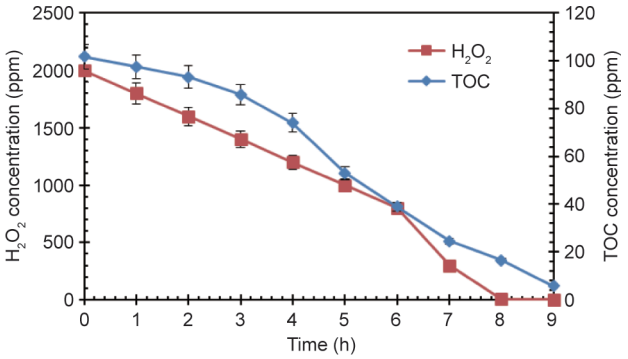

图3. DNAN降解过程中H_2O_2和TOC的变化情况（250 ppm DNAN, 1500 ppm H_2O_2）。初始pH约为7，13 W紫外线。

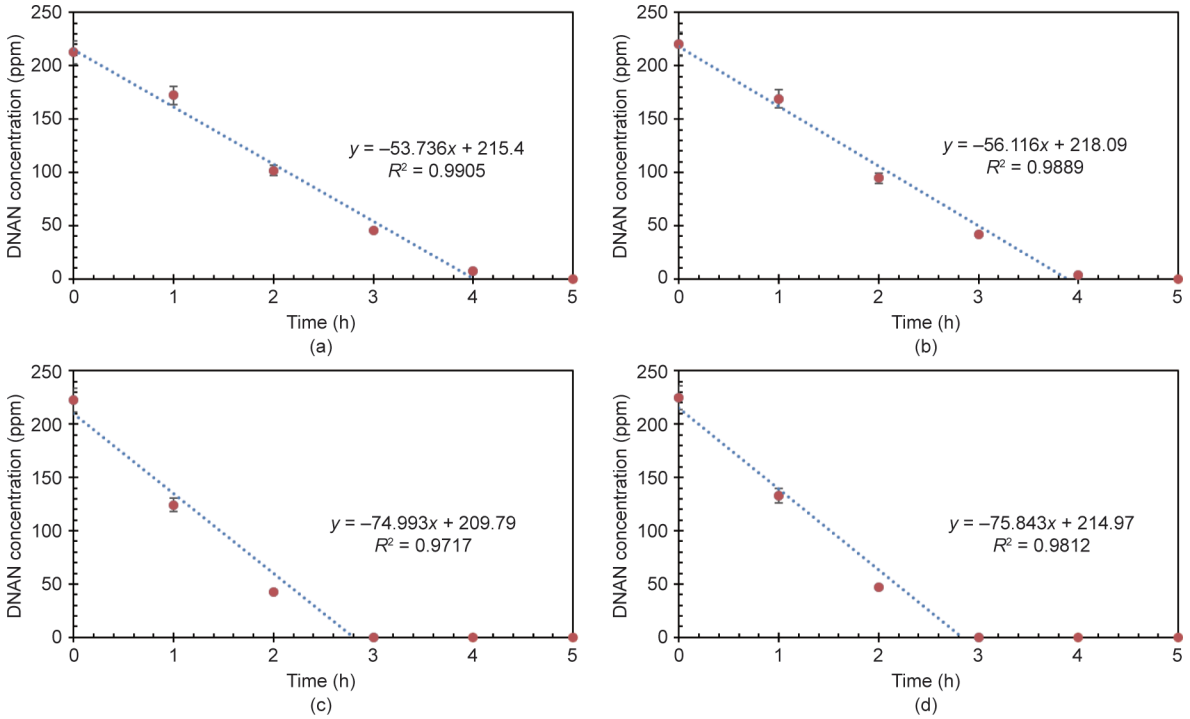

图4. 不同初始pH条件下DNAN的去除动力学，初始DNAN浓度约为250 ppm，1500 ppm H_2O_2，13 W紫外线。（a）pH = 4；（b）pH = 5；（c）pH = 6；（d）pH = 7。

表2 DNAN降解过程中pH的变化

Time (h)	pH value			
	Initial pH = 4	Initial pH = 5	Initial pH = 6	Initial pH = 7
0	3.50	4.80	6.10	7.07
1	2.76	2.90	2.53	2.82
2	2.21	2.27	2.03	2.08
3	2.00	1.98	1.81	1.84
4	1.83	1.80	1.75	1.80
5	1.73	1.75	1.77	1.80
6	1.71	1.74	1.84	1.91
7	1.73	1.76	1.96	2.02
8	1.75	1.78	1.91	1.99
9	1.77	1.81	1.86	1.93

Initial DNAN concentration = 250 ppm, 1500 ppm H_2O_2, 13 W UV light.

表3 不同H_2O_2剂量下DNAN降解过程中pH的变化

Time (h)	pH value			
	1500 ppm H_2O_2	2250 ppm H_2O_2	3000 ppm H_2O_2	4500 ppm H_2O_2
0	8.46	8.12	7.76	7.57
1.33	6.04	5.81	3.53	3.65[a]
2	5.43	4.59	2.92	2.42
3	3.61	3.24	2.65	2.08
4	2.98	2.72	2.68	1.93
5	2.78	2.66	2.71	1.93

Initial DNAN concentration = 250 ppm, initial pH ≈ 7, 13 W UV light.
[a] Measured at 1 h.

H_2O_2剂量条件如何，DNAN的氧化过程中pH都迅速降低，且降解过程结束后维持在2左右的水平。这表明，DNAN降解会产生一些酸类物质，很可能是硝酸等。

3.3. DNAN 降解过程中氮浓度的变化

为了确定DNAN的氧化产物，除了分析DNAN-N外，还测量了降解过程中其他几类含氮化合物的浓度，包括总氮、氨氮、亚硝态氮和硝态氮等。

图5中的结果显示，DNAN的降解过程中产生硝酸根和亚硝酸根，但没有检测到氨氮。亚硝态氮（NO_2-N）的含量很低，且在DNAN降解过程结束后消失，表明NO_2-N是一种主要的中间产物。DNAN降解生成的亚硝态氮会迅速被氧化为硝态氮。降解过程中，硝态氮（NO_3-N）浓度持续增加，且最终的NO_3-N浓度与最初的DNAN-N浓度非常接近。这表明NO_3-N是最终产物，且几乎所有的DNAN-N都转化成为NO_3-N，与UV/H_2O_2处理其他硝基芳香化合物类似[8,28]。这些研究结果与文献报道的使用UV光解DNAN的研究一致[22]，说明光氧化是污水中DNAN降解的一种有效处理技术。

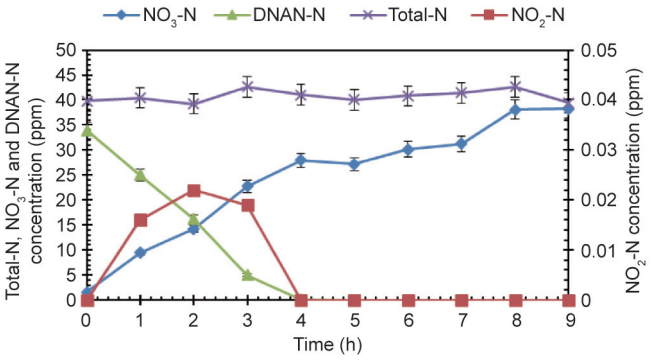

图5. DNAN降解过程中氮浓度的变化情况，初始pH为7，1500 ppm H_2O_2，13 W紫外线。

另外，由图6可以看出，DNAN的降解过程中，总氮（total-N）的浓度基本保持不变，表明此过程中没有气态的含氮化合物生成。同时，在初始pH为4~7的范围下，含氮化合物的浓度变化趋势相似。然而，较高的初始pH条件下，DNAN-N的浓度减少更快，硝态氮的浓度增加较快，因为较高的初始pH促进了DNAN的降解过程。处理9 h后，硝态氮的浓度稍低于总氮，表明仍有少量的含氮有机物存在。同样，图7显示，处理9 h后

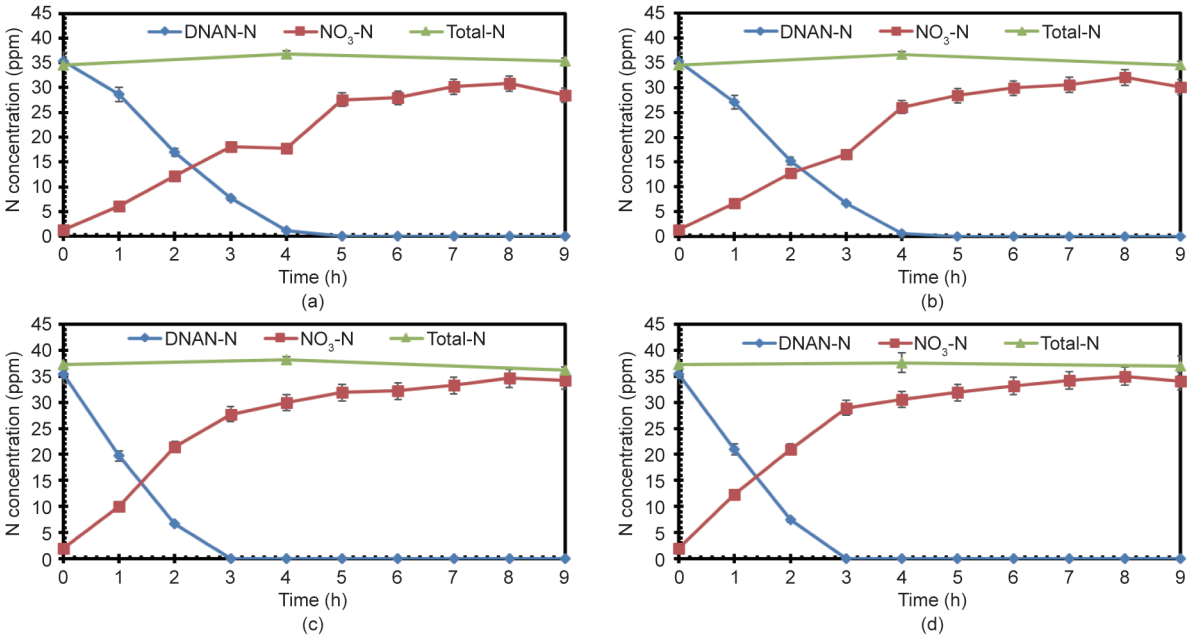

图6. 不同初始pH条件下DNAN降解过程中氮浓度的变化情况，初始DNAN浓度为250 ppm，1500 ppm H_2O_2，13 W紫外线。

的TOC大约为5 ppm，也表明反应后的溶液中还有一小部分的含氮有机物。这很有可能是因为，随着降解过程的进行H_2O_2逐渐消耗（图3），剩余的H_2O_2不足以将剩余的含氮有机物氧化成为硝态氮和CO_2。

3.4. DNAN 降解过程中碳浓度的变化

在DNAN的降解过程中，测量总有机碳（TOC）和总碳（TC）的浓度变化，来研究含碳化合物的变化趋势，结果如图7所示。由图可以看出，DNAN的降解过程中，TOC的浓度与TC的浓度基本一样，且它们的浓度随着DNAN的降解逐渐降低。这表明，DNAN的降解过程中生成了气态碳（CO_2），且溶液中没有碳酸盐或碳酸氢盐。如前文所讨论，当DNAN的氧化过程开始后，氧化过程中pH迅速降低，且DNAN降解过程结束后pH最终维持在2左右的水平。这表明DNAN降解产生了酸类物质（硝酸），也解释了处理后溶液中没有碳酸根或碳酸氢根的原因。

研究结果显示，使用UV/H_2O_2处理的方式，可以实现DNAN的完全碳化，处理9 h后TOC和TC的浓度都降到5 ppm左右。由于DNAN的降解过程在4 h内完成，所以DNAN先转化为其他有机化合物，再进一步降解。DNAN的部分降解过程与2,4-二硝基甲苯在UV/H_2O_2下的降解途径一致，先生成相对分子质量较小的羧酸，再进一步氧化成CO_2 [29]。这也解释了DNAN降解过程结束后溶液pH有一个轻微上升的趋势。

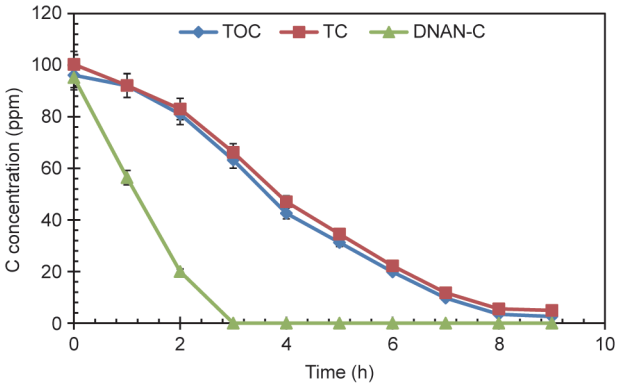

图7. 不同初始pH条件下DNAN降解过程中碳浓度的变化情况，初始DNAN浓度为250 ppm，1500 ppm H_2O_2，13 W紫外线。

图6显示，相比DNAN降解结束后，DNAN降解过程中硝酸根的增加速度更快，说明DNAN降解的早期阶段先脱掉硝基。当DNAN降解结束后，约77%的氮转化为硝态氮，表明还有约23%的氮以硝基有机物形式存在。同时，图7显示，此时还有65%的TOC存在于溶液中，表明DNAN降解过程中硝化过程要快于碳化过程。

4. 结论

研究结果表明，UV/H_2O_2氧化是一种处理溶液中DNAN的有效技术。绝大部分的DNAN可以被氧化为二氧化碳和硝酸根。在氧化过程中，总氮的浓度保持不变，

说明没有生成气态的含氮化合物（NO, N_2O, N_2, NH_3）。亚硝酸根是主要中间产物。DNAN的氧化降解速率主要受H_2O_2剂量和初始pH的影响。对于浓度为250 ppm的DNAN溶液来说，1500 ppm的H_2O_2和初始pH为7是最优降解条件。

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Compliance with ethics guidelines

Hailei Su, Christos Christodoulatos, Benjamin Smolinski, Per Arienti, Greg O'Connor, and Xiaoguang Meng declare that they have no conflict of interest or financial conflicts to disclose.

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