



Inhibiting the regeneration of *N*-nitrosodimethylamine in drinking water by UV photolysis combined with ozonation

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ABSTRACT

N-Nitrosodimethylamine (NDMA) is a highly carcinogenic compound that is suspected of carcinogenic activity in the human body. A variety of methods are used to remove NDMA from water, but the main degradation products, dimethylamine (DMA) and NO₂⁻, are also precursors for NDMA formation. UV irradiation combined with ozonation (UV/O₃) was examined in this investigation for its ability to inhibit the regeneration of NDMA after degradation. Both the degradation products and the regeneration potential of NDMA were compared between UV irradiation alone and UV/O₃. The yields of DMA and NO₂⁻ in the UV/O₃ process were less than for UV irradiation alone. Yields of DMA and NO₂⁻ were 2.25 mg L⁻¹ and 3.22 mg L⁻¹ from UV irradiation, while they were 0.92 mg L⁻¹ and 0.45 mg L⁻¹ from the UV/O₃ process. Furthermore, the regeneration of NDMA was also less after the UV/O₃ process than after UV irradiation. The concentration of regenerated NDMA was more than 51.8 μg L⁻¹ after UV irradiation regardless of the dosage of Cl₂. However, the concentration of regenerated NDMA in the UV/O₃ process was less than 7.37 μg L⁻¹ under the same conditions. Consequently, the UV/O₃ process was more effective than UV irradiation alone in inhibiting NDMA regeneration. The inhibition of NDMA regeneration was due to a decrease in DMA and NO₂⁻ produced by the UV/O₃ process. As the major products generated from NDMA, NO₂⁻ and DMA were likely to be oxidized by ozone and hydroxyl radicals (*OH). In addition, the reaction between NDMA and *OH would possibly generate methylamine as the only product, leading to a decrease in the production of DMA by the UV/O₃ process.

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1. Introduction

Nitrosamines, particularly *N*-nitrosodimethylamine (NDMA) is highly carcinogenic, mutagenic and teratogenic [1,2]. The US Environmental Protection Agency (US EPA) classified these compounds into group B2, which indicates that these compounds are probably carcinogenic to humans [3]. The esophagus and liver are the primary tumor formation sites for nitrosamines. Other organs, such as the bladder, brain and lungs, are also targets for nitrosamines. Previous research into NDMA focused on its presence in food, beverages, consumer products, tobacco and polluted air [4]. NDMA has received much attention as a potential drinking water pollutant since it was detected in groundwater [5]. NDMA was also found in drinking water that had been treated with the disinfectants

chlorine and chloramine. Accordingly, NDMA is considered a novel disinfection byproduct [6–13].

NDMA cannot be biodegraded, adsorbed to particulate matter or volatilized due to its physical and chemical properties [14]. However, this compound is sensitive to ultraviolet (UV) light and undergoes a rapid photolytic degradation reaction. UV irradiation is the most common method for NDMA degradation, and the mechanism and the pathway of this process have been well studied [1,2,15,16]. One study utilized low- and medium-pressure Hg lamps for direct UV photodegradation and H₂O₂-assisted UV photodegradation of NDMA in simulated drinking water [17]. The results of that study showed that H₂O₂ enhanced the time-based rate constant only in the low-pressure system. The effectiveness of NDMA removal and the mechanism of NDMA reduction in the presence of granular iron and nickel-catalyzed granular iron were reported by Gui and co-workers [18,19]. The rate of the reduction reaction in that process was too low, and the catalyst was easily poisoned. Fenton reagent proved to be effective for the removal of NDMA from water [20]. Furthermore, Lee et al. [21] investigated the photocatalytic degradation of NDMA with pure and surface-modified

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TiO₂. The photocatalytic degradation products were methylamine (MA), dimethylamine (DMA), nitrite, nitrate and ammonium. The distribution of products changed in response to modifications to the surface of TiO₂. The degradation of NDMA has been reported to occur as a result of conventional ozonation and the advanced oxidation process O₃/H₂O₂ [22]. The results of that study showed that reaction with hydroxyl radicals ($\cdot\text{OH}$) dominated NDMA oxidation during ozonation. The self-decomposition of the carbon-centered NDMA radical resulting from the attack of hydroxyl radicals on the methyl group was suggested as the main oxidative pathway of NDMA to MA.

Previous studies focused mainly on finding effective methods for NDMA removal and on the pathways of NDMA degradation, whereas the fates of the degradation products of NDMA have rarely been discussed. DMA and NO₂⁻ are the main products of NDMA degradation, while they are also precursors of NDMA formation [1,17,21]. The formation of NDMA can occur during chloramine disinfection through a reaction between monochloramine and organic nitrogen-containing precursors. NDMA is generated from the reaction of DMA and monochloramine through a mechanism involving the formation and the oxidation of 1,1-dimethylhydrazine (UDMH). NDMA can also be generated by the nitrosation of DMA with various nitric oxides including nitrite [7,11,12,23]. Choi and Valente reported that the formation of NDMA by the nitrosation of DMA was greatly enhanced by free chlorine (HOCl) [24]. However, several studies found an additional novel pathway of NDMA formation [25,26]. A reaction between dichloramine and DMA can form chlorinated UDMH that is subsequently transformed to NDMA by dissolved oxygen. Although it has been shown that the DMA concentration in nature is not high enough to account for NDMA formation, tertiary amines containing DMA functional groups could be transformed to DMA by dealkylation [27]. Thus, DMA is one of the direct and essential precursors of NDMA formation [23–25]. Accordingly, it is necessary to examine the generation of DMA and NO₂⁻ in the NDMA degradation process. The reaction between DMA and NO₂⁻ is likely to result in the regeneration of NDMA [11,12]. In order to reduce the possibility of NDMA regeneration, decreasing the formation of DMA and NO₂⁻ becomes the key problem.

A pulsed UV system using a small amount of H₂O₂ is able to control the formation of by-products and inhibit the regeneration of NDMA after chlorinated and chloraminated disinfection [17], however the amount of H₂O₂ used in the UV/H₂O₂ system significantly decreases the effectiveness of NDMA removal [2]. A large amount of H₂O₂ will decrease the effectiveness of NDMA removal in the UV/H₂O₂ system, and residual H₂O₂ becomes a problem. By comparison, the combination of ozonation with UV irradiation is

considered a more effective process for removing organics [28–30]. Hydroxyl radicals ($\cdot\text{OH}$) that are generated in the UV/O₃ process are non-selective and vigorous oxidants. The rate constants for $\cdot\text{OH}$ reacting with most organic compounds are within the range of 10⁶–10⁹ L mol⁻¹ s⁻¹ [31]. The degradation of resistant compounds can be accelerated by free radicals. Moreover, ozone is unstable in water, so it will not have a negative impact on the human body.

In this investigation, UV/O₃ was used to remove NDMA and decrease the regeneration of NDMA in drinking water after chlorination. The aims of this paper were to assess the ability of UV/O₃ to decrease the regeneration of NDMA by decreasing the formation of DMA and NO₂⁻, as well as to discuss the possible inhibiting mechanisms and pathways of the regeneration of NDMA.

2. Materials and methods

2.1. Reagents

NDMA was synthesized using the method described by Hu and Ma [32]. The purity of NDMA was greater than 95%, as confirmed by HPLC. Other chemicals (MA, DMA, benzensulfonyl chloride, dichloromethane, NaNO₂, NaNO₃, NaHCO₃, Na₂SO₄, Na₂SO₃, NaOH and H₂SO₄) were of analytical grade and were used without further purification. All stock solutions were prepared in distilled water.

All glassware used in the experiments was soaked in a solution of H₂SO₄–K₂Cr₂O₇ overnight, and then washed three times in both tap water and distilled water.

2.2. Experimental procedure

The NDMA degradation experiments using UV alone and UV/O₃ were performed in a cylindrical glass reactor (see Fig. 1). The valid sample bulk of the reactor was 700 mL. The solution of NDMA was exposed to UV irradiation using a low-pressure Hg lamp (8 W, emission at 253.7 nm, Tianjin Xinjing Co. China). In the NDMA degradation experiments using UV/O₃, ozone was produced by a laboratory ozonizer (DHX-SS-1G, Harbin Jiujiu Electrochemistry Engineering Ltd. China), which had a maximum ozone production of 9 g h⁻¹, using pure oxygen as feed gas. Dissolved ozone concentration in the reactor was controlled by varying the oxygen flux, the voltage of ozone production and the time at which ozone was introduced into the reactor. The ozone was introduced into the reactor in a single addition before the beginning of the experiment. The stock solution of NDMA was then dropped into the reactor immediately following the introduction of the ozone, and the low-pressure Hg lamp was turned on at the same time. Reaction solution pH was adjusted by H₂SO₄ and NaOH solution (0.1 mol L⁻¹). Samples were collected at predetermined time intervals, and were analyzed quickly after sampling. The ozone oxidation reaction was quenched with Na₂SO₃ solution (0.1 mol L⁻¹).

Chlorination was performed after the UV and UV/O₃ processes. Reactions were performed in 120 mL vials, which were kept in the dark at room temperature for 24 h. The concentration of the chlorine stock was standardized iodometrically (2.15 g L⁻¹ as Cl₂). Reactions were halted by the addition of excess Na₂SO₃ solution (0.1 mol L⁻¹) to quench the residual free chlorine prior to the analysis of NDMA.

2.3. Analysis

NDMA was analyzed by HPLC (LC-10A, Shimadzu, Japan) with UV detection at 230 nm. Separation was performed with a Venusil Mp-C₁₈ column (150 mm × 4.6 mm, 5 μm, Agela Technologies Inc.) using isocratic elution of 95% water and 5% methane at a flow rate of 1.0 mL min⁻¹. The detection limit (DL) of NDMA was approximately 8.04 ng L⁻¹, and the relative standard deviation (RSD) was approximately 2.31%.

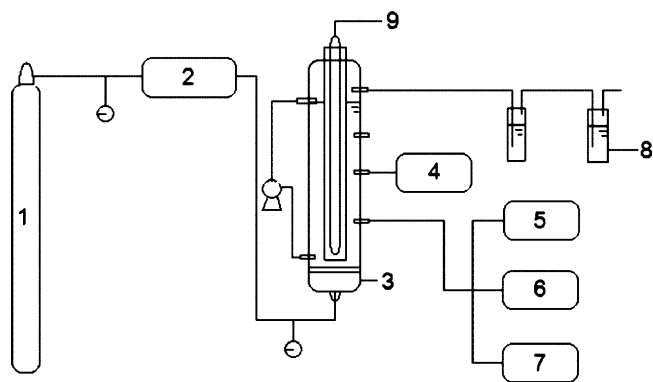


Fig. 1. Schematic diagram of UV and UV/O₃ systems. (1) Oxygen bottle, (2) ozone generator, (3) reactor, (4) dissolved ozone analysis, (5) HPLC, (6) GC-MS, (7) IC, (8) KI solution, (9) UV lamp.

DMA and MA were quantified by GC–MS (Agilent 6890–5973N, USA) after derivatization with benz磺onyl chloride [33]. The sample (20 mL) was diluted to 200 mL in a 250 mL round-bottomed flask, then mixed with 10 mol L⁻¹ NaOH solution (8 mL) and benz磺onyl chloride (2 mL). The flask was closed and stirred for 10 min at room temperature. After that, another solution of 10 mL NaOH (10 mol L⁻¹) was added and the mixture was stirred for another 10 min at 80 °C to hydrolyze the excess derivatization reagent. Subsequently, the solution was cooled to room temperature with ice water, and was then acidified using 18.5% HCl solution to pH 5.5. The mixture was extracted twice with 10 mL dichloromethane. The aqueous solution was discarded and the organic phase was washed once with 15 mL NaHCO₃ solution (0.05 mol L⁻¹) and dried with anhydrous Na₂SO₄. The solvent (1 μL) was then injected into the GC–MS to determine DMA and MA concentrations. All GC–MS data were obtained from an Agilent 6890/5973N instrument equipped with a column (DB–1MS, 30 m × 0.25 mm i.d. × 0.25 μm, J & W Scientific, Folsom, CA). The oven temperature was varied according to the following program. The initial oven temperature was 80 °C (held for 5 min). It was then increased to 150 °C (held for 10 min) at 10 °C min⁻¹, and then to 300 °C (held for 1 min) at 50 °C min⁻¹. The injection port was in splitless mode and the temperature was 290 °C. High purity He gas was used as carrier gas, and the column flow rate was 0.5 mL min⁻¹. The ion source of the mass spectra was operated in the electron-impact mode (EI; electron energy 70 eV, 230 °C). Full-scan mass (*m/z* 40–500) was recorded for the identification of the analytes at high concentration. The identification of trace chemicals was achieved by the use of SIM mode. As the quantitative ion, *m/z* 77 was selected for DMA derivatives and MA derivatives. The qualitative ions for DMA derivatives were *m/z* 44 and *m/z* 185. The qualitative ions for MA derivatives were *m/z* 141 and *m/z* 171.

The anions NO₂⁻ and NO₃⁻ were analyzed by ion chromatography (ICS–3000, Dionex, USA) with an Ion Pac ASII–HC (Dionex, USA) ion-exchange column, using KOH solution (30.0 mmol L⁻¹) as the eluent at a flow rate of 1.2 mL min⁻¹.

The aqueous ozone concentration was measured by the indigo method [34].

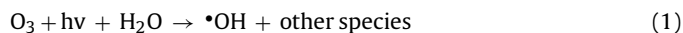
The incident irradiance value (μW cm⁻²) was measured in separated experiments by a ferrioxalate actinometry experiment, as described by Murov et al. [35].

3. Results and discussion

3.1. NDMA degradation by UV and UV/O₃

The results of the NDMA-removal experiments using UV and UV/O₃ are shown in Fig. 2. UV irradiation is well known as an effective method of NDMA degradation. Irradiation with UV for 20 min achieved up to 99% removal of NDMA, meaning that NDMA was almost completely removed within 20 min. The introduction of ozone over a range from 2.6 mg L⁻¹ to 6.6 mg L⁻¹, resulted in a similar degree of NDMA removal in the UV/O₃ process. The removal of NDMA was greater than 99% in all cases, which confirmed that both UV and UV/O₃ were effective methods for NDMA removal from water.

The combination of ozonation with UV irradiation is considered a more effective process for removing organics than the use of UV alone. When UV irradiation is combined with ozonation, ozone decomposition is enhanced to yield more free radicals, thus allowing a higher rate of oxidation to be attained (Formula (1)):



It was found in this study that introducing O₃ into the UV process did not enhance significantly the effectiveness of NDMA removal

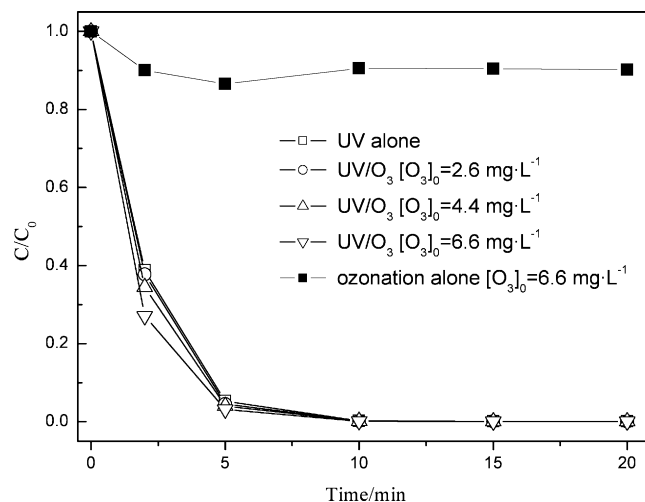


Fig. 2. Removal efficiency of NDMA degradation by UV and UV/O₃ processes. [NDMA]₀ = 0.1 mmol L⁻¹, pH 6.0, irradiation 1000 μW cm⁻².

Table 1

Kinetic parameters of NDMA degradation by UV/O₃.

| O ₃ dosage (mg L ⁻¹) | K (min ⁻¹) | R ² |
|---|------------------------|----------------|
| 0 | 0.6168 | 0.9948 |
| 2.6 | 0.6191 | 0.9968 |
| 4.4 | 0.6319 | 0.9982 |
| 6.6 | 0.6642 | 0.9991 |

from water. The rates of NDMA degradation by UV/O₃ with different O₃ dosages were only a little faster than that attained by UV irradiation alone (see Table 1). This demonstrated that UV played a more important role than the O₃ in NDMA degradation by the UV/O₃ process. The effectiveness of NDMA removal by UV/O₃ was mainly due to the UV irradiation.

Previous studies on the mechanism of NDMA photolysis indicated that the principal products of NDMA degradation were DMA, MA, NO₂⁻ and NO₃⁻ [15]. Small amounts of N₂O, N₂, HCHO and HCOOH were also formed by UV irradiation [1]. The yields of DMA, MA, NO₂⁻ and NO₃⁻ formed in the UV process are shown in Fig. 3. It was clear that the yields of DMA and NO₂⁻ were much greater than the yields of MA and NO₃⁻, respectively. An imbalance of nitrogen mass was maintained throughout the reaction. Results suggested

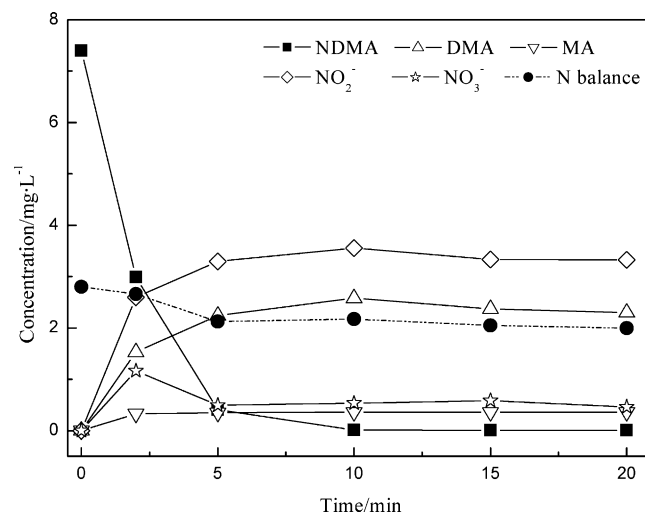


Fig. 3. Reaction of NDMA degradation by UV irradiation. [NDMA]₀ = 0.1 mmol L⁻¹, pH 6.0, irradiation 1000 μW cm⁻².

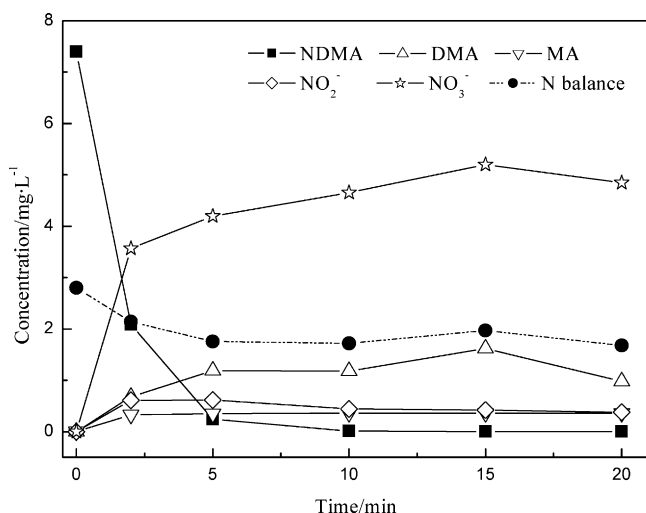


Fig. 4. Reaction of NDMA degradation by UV/O₃. [NDMA]₀ = 0.1 mmol L⁻¹, [O₃]₀ = 6.6 mg L⁻¹, pH 6.0, irradiation 1000 μW cm⁻².

that some undetected species containing nitrogen were generated by UV irradiation. Lee et al. [16] confirmed, using GC-MS, that *N*-methylformamide (NMF) was a novel photolysis product of NDMA, and they used this to explain the nitrogen imbalance in the process of NDMA degradation by UV.

The products of the UV/O₃ process were quite different from those of UV irradiation alone (see Fig. 4). DMA and NO₂⁻ decreased markedly in the UV/O₃ process compared with UV irradiation. In the UV/O₃ process, yields of MA and NO₃⁻ were greater than the yields of DMA and NO₂⁻. The nitrogen imbalance was also more marked in the UV/O₃ process, which indicated that more nitrogen-containing products of NDMA were generated. In other words, it was easy for other nitrogen-containing species to form, and the pathway of NDMA degradation was changed in the UV/O₃ process.

The aim of this study was not to explain the imbalance of nitrogen, but to focus on the yields of the dominant nitrogen-containing products of NDMA degradation as a result of the UV irradiation and UV/O₃ processes. As products generated from NDMA, DMA and NO₂⁻ were well known as the ubiquitous precursors of NDMA formation. Their presence in water creates a risk of NDMA regeneration, so the yields of DMA and NO₂⁻ are of particular concern.

3.2. Regeneration of NDMA

It is well known that NDMA can be produced by both chlorination and chloramination in the presence of DMA in water [11,12]. The formation of NDMA can also occur by DMA nitrosation with NO₂⁻ [7,11,12,23]. DMA and NO₂⁻ are considered to be the ubiquitous precursors of NDMA formation in water, while they are also the primary products of NDMA photolysis [1,15]. The presence of DMA and NO₂⁻ in water may lead to the regeneration of NDMA. Moreover, disinfection using such processes as chlorination and chloramination is an essential part of drinking water and wastewater treatment. Accordingly, it is of particular concern to know whether the degradation products DMA and NO₂⁻ will cause the regeneration of NDMA.

In China, chlorination is more widely used than chloramination in the treatment of drinking water and wastewater. Therefore, this study assessed the regeneration potential of NDMA using chlorination. The results are shown in Fig. 5. After being degraded by UV irradiation, the regeneration of NDMA increased greatly in the presence of chlorine. Regardless of the dosage of Cl₂, the regeneration of NDMA was greater than 51.8 μg L⁻¹. However, the regeneration of NDMA was less than 7.37 μg L⁻¹ in the UV/O₃ process under the

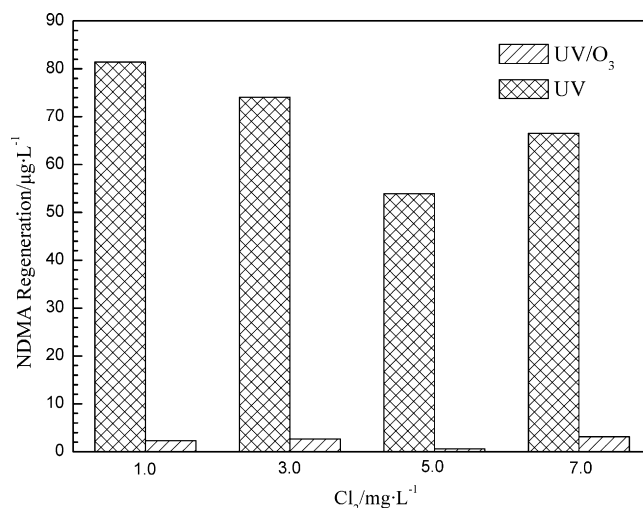


Fig. 5. Regeneration of NDMA. [NDMA]₀ = 0.54 mmol L⁻¹, chlorination 24 h after UV and UV/O₃ processes.

same conditions. That is, the UV/O₃ process was more effective than UV irradiation in inhibiting NDMA regeneration.

The regeneration of NDMA is caused by DMA nitrosation that is greatly enhanced by free chlorine. In addition, the regeneration of NDMA follows the reactions below [24].



DMA and NO₂⁻ are the precursors of NDMA regeneration in UV-irradiated or UV/O₃-treated water. As shown in Fig. 3 and Fig. 4, yields of DMA and NO₂⁻ were 2.25 mg L⁻¹ and 3.22 mg L⁻¹ in the UV irradiation process, while they were 0.92 mg L⁻¹ and 0.45 mg L⁻¹ in the UV/O₃ process. As a result of the yields of DMA and NO₂⁻ being much lower in the UV/O₃ process compared with the UV process, the regeneration of NDMA in UV/O₃-treated water was much less than in UV-treated water. This observation indicated that decreasing the formation of DMA and NO₂⁻ was the key to inhibiting NDMA regeneration.

3.3. Decreasing the formation of DMA and NO₂⁻ by UV/O₃

The product yields from the UV/O₃ process were quite different from those resulting from UV irradiation. In particular, the formation of DMA and NO₂⁻ were markedly decreased in the UV/O₃ process. The combination of UV and ozonation played an important role in decreasing the formation of DMA and NO₂⁻.

Fig. 6 shows the yields of DMA formed during the UV/O₃ process with different dosages of ozone. The yield of DMA from the UV/O₃ process was clearly less than that from UV irradiation. This shows that UV/O₃ was effective in decreasing the formation of DMA. The yields of DMA decreased with increases in the ozone dosage, which suggested that the combination of UV and ozone accounted for the decrease in DMA production. The lowest yield of DMA was observed at an ozone dosage of 6.6 mg L⁻¹.

The influence of ozone dosage on the formation of NO₂⁻ is shown in Fig. 7. When ozone was introduced into the UV irradiation process, the yield of NO₂⁻ decreased abruptly. The yield of NO₂⁻ decreased as the ozone dosage increased. Therefore, UV/O₃ was an effective method of controlling NO₂⁻ formation.

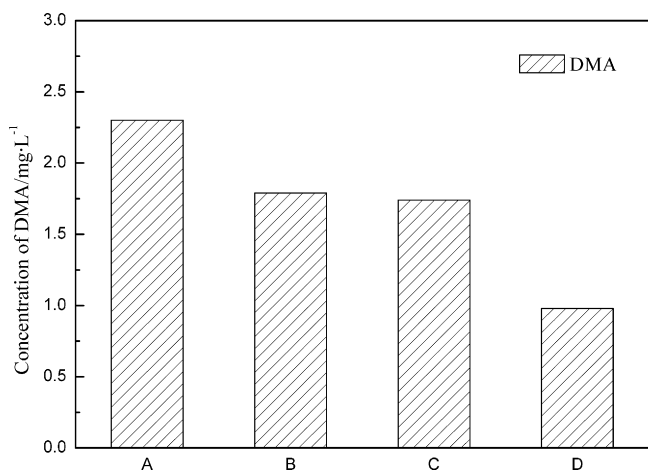


Fig. 6. Effect of O₃ dosage on the control of DMA formation by UV/O₃. [NDMA]₀ = 0.1 mmol L⁻¹, (A) UV, (B) UV/O₃ [O₃]₀ = 2.6 mg L⁻¹, (C) UV/O₃ [O₃]₀ = 4.4 mg L⁻¹, (D) UV/O₃ [O₃]₀ = 6.6 mg L⁻¹, pH 6.0, irradiation 1000 μW cm⁻².

3.4. Mechanism for decreasing the formation of DMA and NO₂⁻ by UV/O₃

There are two possible reaction pathways by which ozone may attack pollutants: (1) direct ozonation by the ozone molecule, or (2) oxidation by highly oxidative free radicals such as •OH, which are formed by the decomposition of ozone in aqueous solution. In the UV/O₃ process, the decomposition of ozone was enhanced (see Fig. 8). Accordingly, UV irradiation, ozone and •OH were all able to assist in the UV/O₃ process.

The nitrogen in the NO₂⁻ group is in the middle valence state, allowing it to be oxidized further. Both ozone and •OH are strong oxidants, and their oxidation–reduction standard potentials are 2.07 V and 2.80 V, respectively. Therefore, both ozone and •OH can oxidize NO₂⁻ to NO₃⁻ easily. As a result, UV/O₃ is an effective method for decreasing the formation of NO₂⁻ that is generated from NDMA degradation.

The mechanism by which UV/O₃ decreased the formation of DMA is complicated by the presence of UV, ozone and •OH. Two possible mechanisms are proposed. First, as a product generated from NDMA, DMA was oxidized by ozone and •OH in the UV/O₃ process. To confirm this hypothesis, DMA degradation experiments by UV irradiation, ozonation and UV/O₃ were performed. The

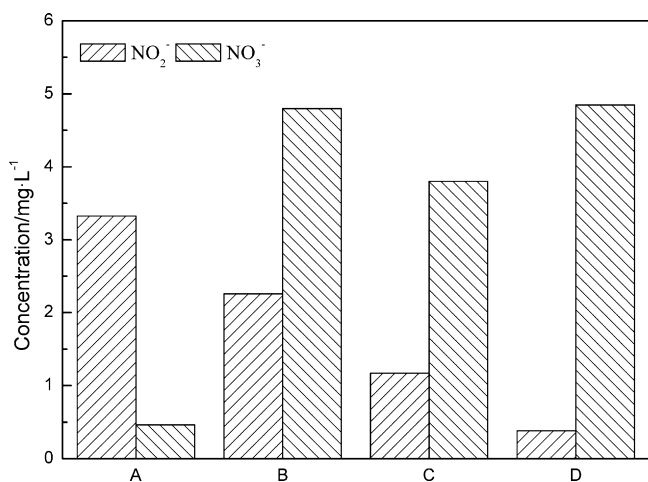


Fig. 7. Effect of O₃ dosage on control of NO₂⁻ formation by UV/O₃. [NDMA]₀ = 0.1 mmol L⁻¹, (A) UV, (B) UV/O₃ [O₃]₀ = 2.6 mg L⁻¹, (C) UV/O₃ [O₃]₀ = 4.4 mg L⁻¹, (D) UV/O₃ [O₃]₀ = 6.6 mg L⁻¹, pH 6.0, irradiation 1000 μW cm⁻².

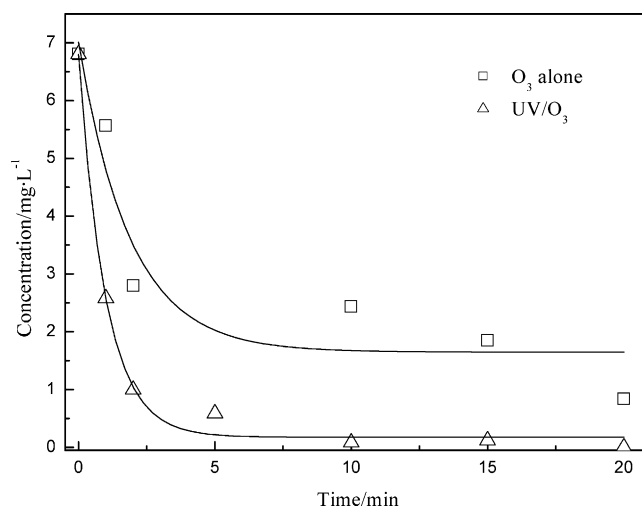


Fig. 8. Ozone decay in O₃ alone and UV/O₃. [O₃]₀ = 6.6 mg L⁻¹, pH 6.0, irradiation 1000 μW cm⁻².

concentration–time profiles are shown in Fig. 9, which show that DMA was not likely to be degraded effectively by UV irradiation. According to the published literature, rate constants of DMA reacting with ozone and •OH were 1.9×10^7 (mol L⁻¹)⁻¹ s⁻¹ [36] and 8.9×10^9 (mol L⁻¹)⁻¹ s⁻¹ [37], respectively. Therefore, both ozone and UV/O₃ were able to enhance DMA degradation compared with UV irradiation. From Fig. 9, the residual concentration of DMA in both ozonation and UV/O₃ was much lower than in UV irradiation. These results suggest that both ozone and •OH played a role in decreasing the formation of DMA in the UV/O₃ process. Furthermore, •OH played a more important role than ozone in decreasing the formation of DMA in the UV/O₃ process.

In the second possible mechanism, the pathway of NDMA degradation was changed by introducing ozone into the UV irradiation process. The reaction between NDMA and •OH generated MA as the only product, resulting in a decrease in DMA yields. The reaction between •OH and NDMA has been already studied by Heur et al. [38] (see Fig. 10). The authors proposed a mechanism where denitrosation occurred through self-decomposition of the carbon-centered radical that was produced from the methyl group of NDMA by hydrogen abstraction of the attacking hydroxyl radical. Mezyk et al. [39] used γ-radiolysis to demonstrate the production of a carbon-centered radical in NDMA oxidation with •OH.

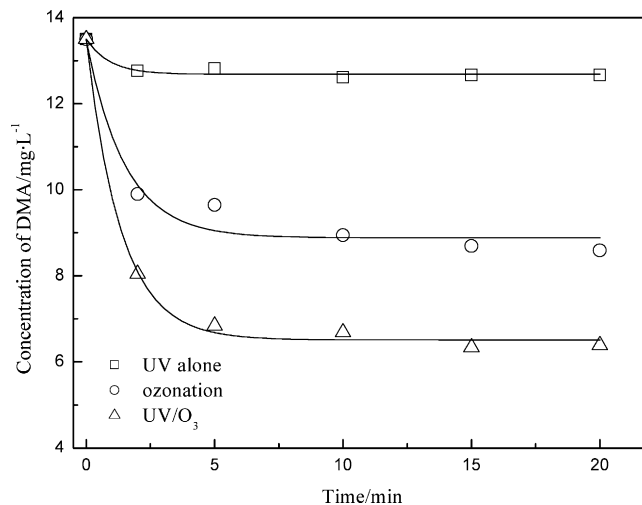


Fig. 9. DMA degradation by UV alone, O₃ alone and UV/O₃. [DMA]₀ = 0.3 mmol L⁻¹, [O₃]₀ = 6.6 mg L⁻¹, pH 6.0, irradiation 1000 μW cm⁻².

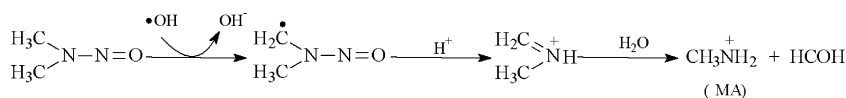


Fig. 10. Possible pathway of NDMA oxidation initiated by hydroxyl radicals.

This result was confirmed by the DMPO spin trapping EPR technique. The second-order rate constants for the reaction of $\bullet\text{OH}$ and NDMA were found to be $(4.30 \pm 0.11) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ [40] and $(4.50 \pm 0.21) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ [22].

The reaction of NDMA and $\bullet\text{OH}$ generated by a hydrogen atom by abstraction from one of its methyl groups. NDMA was oxidized to MA through the self-decomposition of the carbon-centered NDMA radical. Lee et al. [22] found that MA and ammonium (AM) were produced as oxidation products of NDMA oxidation by conventional ozonation and an advanced oxidation process ($\text{O}_3/\text{H}_2\text{O}_2$), finding no formation of DMA in either case. However, DMA was still found to be one of the products of NDMA degradation by UV/ O_3 in the present investigation. The fission of the N–N bond in NDMA by UV irradiation was accounted for by the formation of DMA. Therefore, both UV irradiation and $\bullet\text{OH}$ were able to remove NDMA during the UV/ O_3 process. The reaction between NDMA and $\bullet\text{OH}$ generated MA as the only product, rather than DMA. Therefore, the degradation of NDMA was observed in the UV/ O_3 process, and the formation of DMA was decreased.

4. Conclusions

UV irradiation and the UV/ O_3 combination are effective methods for NDMA removal from drinking water. The introduction of ozone into the UV process had little influence on the effectiveness of NDMA removal. However, it had a great influence on the formation of particular degradation products from NDMA. As the main products, DMA and NO_2^- decreased markedly in the UV/ O_3 process compared with UV irradiation.

Chlorination was performed after NDMA degradation by the UV and UV/ O_3 processes, resulting in NDMA regeneration. The regeneration of NDMA in the presence of chlorine after the UV/ O_3 process was much less than that observed after the UV process. The UV/ O_3 process was more effective than UV irradiation alone in inhibiting the regeneration of NDMA.

Decreasing the formation of DMA and NO_2^- was the key to inhibiting the regeneration of NDMA. In the UV/ O_3 process, the yields of DMA and NO_2^- decreased with increases in the ozone dosage. The presence of ozone and $\bullet\text{OH}$ allowed the oxidation of NO_2^- to NO_3^- . There were two possible mechanisms for the decreased formation of DMA in the UV/ O_3 process. In the first mechanism, DMA was oxidized by ozone and $\bullet\text{OH}$. In the second mechanism, the introduction of ozone changed the degradation products of NDMA so that the reaction between NDMA and $\bullet\text{OH}$ generated MA as the only product, thus decreasing DMA formation.

It is concluded that the UV/ O_3 process is an effective method for degrading NDMA in drinking water and for inhibiting the regeneration of NDMA. However, it may be preferable for the water treatment process to avoid forming NDMA in the first place rather than having to implement these advanced water treatment processes, which are expensive and consume energy.

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References

- [1] M.I. Stefan, J.R. Bolton, UV photolysis of *N*-nitrosodimethylamine (NDMA): kinetic and product study, *Helv. Chim. Acta* 85 (2002) 1416–1426.
- [2] S. Liang, J.H. Min, M.K. Davis, J.F. Green, D.S. Remer, Use of pulsed-UV processes to destroy NDMA, *J. Am. Water Works Assoc.* 95 (2003) 121–130.
- [3] P. Andrzejewski, B. Kasprzyk-Hordern, J. Nawrocki, The hazard of *N*-nitrosodimethylamine (NDMA) formation during water disinfection with strong oxidants, *Desalination* 176 (2005) 37–45.
- [4] H. Xu, *N*-Nitrosamines in the Environment, Science Press, Beijing, China, 1988.
- [5] W.A. Mitch, J.O. Sharp, R.R. Trussell, R.L. Valentine, L. Alvarez-Cohen, D.L. Sedlak, *N*-Nitrosodimethylamine (NDMA) as a drinking water contaminant: A review, *Environ. Eng. Sci.* 20 (2003) 389–404.
- [6] S.D. Richardson, Disinfection by-products and other emerging contaminants in drinking water, *Trends Anal. Chem.* 22 (2003) 666–684.
- [7] J. Choi, S.E. Duirk, R.L. Valentine, Mechanistic studies of *N*-nitrosodimethylamine (NDMA) formation in chlorinated drinking water, *J. Environ. Monit.* 4 (2002) 249–252.
- [8] J. Choi, R.L. Valentine, A kinetic model of *N*-nitrosodimethylamine (NDMA) formation during water chlorination/chloramination, *Water Sci. Technol.* 46 (2002) 65–71.
- [9] P. Andrzejewski, B. Kasprzyk-Hordern, J. Nawrocki, Formation of nitrosodimethylamine (NDMA) during chlorine disinfection of wastewater effluents prior to use in irrigation systems, *Water Res.* 40 (2006) 341–347.
- [10] W.A. Mitch, G.L. Oelker, E.L. Hawley, R.A. Deeb, D.L. Sedlak, Minimization of NDMA formation during chlorine disinfection of municipal wastewater by application of pre-formed chloramines, *Environ. Eng. Sci.* 22 (2005) 882–890.
- [11] J. Choi, R.L. Valentine, Formation of *N*-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product, *Water Res.* 36 (2002) 817–824.
- [12] W.A. Mitch, D.L. Sedlak, Formation of *N*-nitrosodimethylamine (NDMA) from dimethylamine during chlorination, *Environ. Sci. Technol.* 36 (2002) 588–595.
- [13] J. Kim, T.E. Clevenger, Prediction of *N*-nitrosodimethylamine (NDMA) formation as a disinfection by-product, *J. Hazard. Mater.* 145 (2007) 270–276.
- [14] M.G. Davie, M. Reinhard, J.R. Shapley, Metal-catalyzed reduction of *N*-nitrosodimethylamine with hydrogen in water, *Environ. Sci. Technol.* 40 (2006) 7329–7335.
- [15] C. Lee, W. Choi, Y.G. Kim, J. Yoon, UV photolytic mechanism of *N*-nitrosodimethylamine in water: dual pathways to methylamine versus dimethylamine, *Environ. Sci. Technol.* 39 (2005) 2101–2106.
- [16] C. Lee, W. Choi, J. Yoon, UV photolytic mechanism of *N*-nitrosodimethylamine in water: roles of dissolved oxygen and solution pH, *Environ. Sci. Technol.* 39 (2005) 9702–9709.
- [17] C.M. Sharpless, K.G. Linden, Experimental and model comparisons of low- and medium-pressure Hg lamps for the direct and H_2O_2 assisted UV photodegradation of *N*-nitrosodimethylamine in simulated drinking water, *Environ. Sci. Technol.* 37 (2003) 1933–1940.
- [18] L. Gui, R.W. Gillham, M.S. Odziemkowski, Reduction of *N*-nitrosodimethylamine with granular iron and nickel-enhanced iron. 1. Pathways and kinetics, *Environ. Sci. Technol.* 34 (2000) 3489–3494.
- [19] M.S. Odziemkowski, L. Gui, R.W. Gillham, Reduction of *N*-nitrosodimethylamine with granular iron and nickel-enhanced iron. 2. Mechanistic studies, *Environ. Sci. Technol.* 34 (2000) 3495–3500.
- [20] K. Hiramoto, Y. Ryuno, K. Kikugawa, Decomposition of *N*-nitrosamines, and concomitant release of nitric oxide by Fenton reagent under physiological conditions, *Mutation Res.* 520 (2002) 103–111.
- [21] J. Lee, W. Choi, Photocatalytic degradation of *N*-nitrosodimethylamine: mechanism, product distribution, and TiO_2 surface modification, *Environ. Sci. Technol.* 39 (2005) 6800–6807.
- [22] C. Lee, F. Yoon, U. Von Gunten, Oxidative degradation of *N*-nitrosodimethylamine by conventional and advanced oxidation process ozone/hydrogen peroxide, *Water Res.* 41 (2007) 581–590.
- [23] A.C. Gerecke, D. Sedlak, Precursors of *N*-nitrosodimethylamine in natural water, *Environ. Sci. Technol.* 37 (2003) 1331–1336.
- [24] J. Choi, R.L. Valentine, *N*-Nitrosodimethylamine formation by free-chlorine-enhanced nitrosation of dimethylamine, *Environ. Sci. Technol.* 37 (2003) 4871–4876.
- [25] I.M. Schreiber, W.A. Mitch, Influence of the order of reagent addition on NDMA formation during chloramination, *Environ. Sci. Technol.* 39 (2005) 3811–3818.
- [26] I.M. Schreiber, W.A. Mitch, Nitrosamine formation pathway revisited: the importance of dichloramine and dissolved oxygen, *Environ. Sci. Technol.* 40 (2006) 6007–6014.
- [27] W.A. Mitch, D.L. Sedlak, Characterization and fate of *N*-nitrosodimethylamine precursors in municipal wastewater treatment plants, *Environ. Sci. Technol.* 38 (2004) 1445–1454.

- [28] J.J. Wu, M. Muruganandham, S.H. Chen, Degradation of DMSO by ozone-based advanced oxidation processes, *J. Hazard. Mater.* 149 (2007) 218–225.
- [29] N.C. Shang, Y.H. Chen, H.W. Ma, C.W. Lee, C.H. Chang, Y.H. Yu, C.H. Lee, Oxidation of methyl methacrylate from semiconductor wastewater by O₃ and O₃/UV processes, *J. Hazard. Mater.* 147 (2007) 307–312.
- [30] S. Irmak, O. Erbatur, A. Akgerman, Degradation of 17β-estradiol and bisphenol A in aqueous medium by using ozone and ozone/UV techniques, *J. Hazard. Mater.* 126 (2005) 54–62.
- [31] J. Staehelin, J. Hoigné, Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, *Environ. Sci. Technol.* 16 (1982) 676–681.
- [32] R. Hu, L. Ma, *Analysis Method of N-Nitro Compounds*, Science Press, Beijing, China, 1980.
- [33] F. Sacher, S. Lenz, H. Brauch, Analysis of primary and secondary aliphatic amines in waste water and surface water by gas chromatography–mass spectrometry after derivatization with 2,4-dinitrofluorobenzene or benzenesulfonyl chloride, *J. Chromatogr. A* 764 (1997) 85–93.
- [34] H. Bader, J. Hoigné, Determination of ozone in water by the indigo method, *Water Res.* 15 (1981) 449–456.
- [35] S.L. Murov, I. Carmichael, G.L. Hug, *Handbook of Photochemistry*, 2nd ed., Marcel Dekker, New York, 1993.
- [36] M.C. Dodd, A.D. Shah, U. Von Gunten, C.H. Huang, Interactions of fluoroquinolone antibacterial agents with aqueous chlorine: reaction kinetics, mechanisms, and transformation pathways, *Environ. Sci. Technol.* 39 (2005) 7065–7076.
- [37] C. Lee, C. Schmidt, J. Yoon, U. Von Gunten, Oxidation of *N*-nitrosodimethylamine (NDMA) precursors with ozone and chlorine dioxide: kinetics and effect on NDMA formation potential, *Environ. Sci. Technol.* 41 (2007) 2056–2063.
- [38] Y.H. Heur, A.J. Streeter, R.W. Nims, L.K. Keefer, The Fenton degradation as a nonenzymatic model for microsomal denitrosation of *N*-nitrosodimethylamine, *Chem. Res. Toxicol.* 2 (1989) 247–253.
- [39] S.P. Mezyk, W.J. Cooper, K.P. Madden, D.M. Bartels, Free radical destruction of *N*-nitrosodimethylamine in water, *Environ. Sci. Technol.* 38 (2004) 3136–3167.
- [40] N.A. Landsman, K.L. Swancutt, C.N. Branford, C.R. Cox, J.J. Kidle, S.P. Mezyk, Free radical chemistry of advanced oxidation process removal of nitrosamines in water, *Environ. Sci. Technol.* 41 (2007) 5818–5823.