

Degradation of *N*-nitrosodimethylamine (NDMA) in water by UV/O₃

Bingbing Xu, Zhonglin Chen, Fei Qi and Zhenzhen Xu

ABSTRACT

Experiments were carried out under various conditions to study the effects of ozone dosage, solution pH and initial concentration of *N*-nitrosodimethylamine (NDMA) and humic acid on degradation of NDMA by UV/O₃. Results indicated that NDMA could be completely decomposed to form intermediates within 20 minutes. The degradation of NDMA by UV/O₃ was found to follow pseudo-first-order kinetics. Reaction rates of NDMA degradation did not fluctuate with pH increasing from acid to neutral but dramatically decreased in basic aqueous solution. NDMA initial concentration did not have an obvious effect on NDMA degradation. However, the presence of humic acid inhibited NDMA degradation. Methylamine (MA), dimethylamine (DMA), NO₂⁻ and NO₃⁻ were focused on as NDMA degradation intermediates. Degradation of NDMA by UV/O₃ promoted the conversion from DMA to MA and from NO₂⁻ to NO₃⁻, respectively. With the help of tert-butanol and sodium azide, both ¹O₂ and ·OH were verified to be reactive species present in the process of NDMA degradation by UV/O₃. The mechanism of NDMA degradation by UV/O₃ was discussed based on the products detected in the present study and the previous literature. Several possible pathways of NDMA degradation were proposed.

Key words | dimethylamine, hydroxyl radical, kinetic, mechanism, *N*-nitrosodimethylamine, UV/O₃

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ABBREVIATIONS

DMA	dimethylamine
MA	methylamine
MMN	methylmethyleamine
NDMA	<i>N</i> -nitrosodimethylamine
NM	nitromethane
UDMH	1,1-dimethylhydrazine

INTRODUCTION

Nitrosamines are a class of compounds, many of which are carcinogenic, mutagenic and teratogenic (Andrzejewski *et al.* 2005). In particular, *N*-nitrosodimethylamine (NDMA) is a highly mutagenic compound that is suspected of carcinogenic activity in the human body (Stefan &

Bolton 2002; Liang *et al.* 2003). According to the US EPA, the maximum admissible concentration of NDMA in drinking water is 7 ng l⁻¹ with a risk estimation of 10⁻⁵. Previously, concerns about NDMA stemmed primarily from its presence in food, beverages, consumer products, contaminated groundwater and polluted air. In recent years, as NDMA was found to be a novel disinfection by-product of the chloramination process, NDMA contamination of drinking water and wastewater has been of increasing concern (Mitch *et al.* 2003; Richardson 2003). It has been known that NDMA is generated from both the reaction of dimethylamine (DMA) with monochloramine through a mechanism involving formation and oxidation of 1,1-dimethylhydrazine (UDMH) as an intermediate, and the nitrosation of dimethylamine with various nitric oxides including nitrite (Choi & Valentine 2002; Mitch & Sedlak 2002; Gerecke & Sedlak 2003). However, several studies

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found a novel pathway of NDMA formation (Schreiber & Mitch 2005, 2006). A reaction of dichloramine with DMA forms chlorinated UDMH which is subsequently transformed to NDMA by dissolved oxygen.

Treatment methods for removing NDMA from water are not well established. NDMA is semi-volatile, soluble in water, and is not likely to bioaccumulate, biodegrade, adsorb to particulate matter, or volatilize (Davie *et al.* 2006). To eliminate NDMA contamination in water, various water treatment technologies have been suggested. Reduction of aqueous NDMA using granular iron and nickel-catalysed granular iron has been reported by Odziemkowski *et al.* (2000) and Gui *et al.* (2002). However, the kinetic of this reduction was slow, and the reduction process exhibited catalytic poisoning. Photocatalytic degradation of NDMA with TiO₂ has been reported; the major products were methylamine (MA), DMA, nitrite, nitrate and ammonium (Lee & Choi 2005). There has also been a study using Fenton reagent to degrade NDMA, in which an important finding was that NDMA could be degraded by Fenton reagent (Hiramoto *et al.* 2002).

However, due to its photochemical lability, ultraviolet (UV) based processes have shown great promise for treating NDMA contaminated waters (Stefan & Bolton 2002; Sharpless & Linden 2003). The absorption spectrum of NDMA displays a strong band with a maximum at $\lambda = 228 \text{ nm}$ ($\epsilon = 7,378 \text{ M}^{-1} \text{ cm}^{-1}$) and a weak band with a smooth maximum at $\lambda = 332 \text{ nm}$ ($\epsilon = 109 \text{ M}^{-1} \text{ cm}^{-1}$) (Stefan & Bolton 2002). The first absorption band is regarded as a $\pi \rightarrow \pi^*$ intramolecular charge transfer, which was the absorption band of the N–N bond. The second absorption band is associated with an $n \rightarrow \pi^*$ transition band which was the absorption band of the N=O bond.

Although it is well known that direct UV photolysis can reduce NDMA in water, there are still some concerns. If the water is turbid, coloured or contains chemicals that can interfere with the short wavelength (<270 nm) light, the effectiveness of UV photolysis can be obviously reduced. And there is also a possibility of NDMA reformation, which would make drinking water hazardous again.

To overcome these difficulties, advanced oxidation technologies are employed for NDMA degradation. One study utilizing low- and medium-pressure Hg lamps for the direct and H₂O₂ assisted UV photodegradation of

NDMA in simulated drinking water was performed (Sharpless & Linden 2003). The results have shown that H₂O₂ slightly enhanced the time-based rate constant in the low-pressure system but definitely hindered the medium-pressure system, which suggested that H₂O₂ is of little or no economic benefit for NDMA removal by UV. It has also been recently shown that pulsed-UV with a small amount of H₂O₂ could be used to control the reaction by-products and to inhibit the reformation of NDMA. In contrast, pulsed-UV with a large amount of H₂O₂ could inhibit NDMA decay by direct photolysis (Liang *et al.* 2003). Although the H₂O₂ assisted UV process was efficient for NDMA degradation, the residual H₂O₂ remains a problem.

Ozonation combined with UV radiation is deemed a more effective process for removing organics. The purpose of introducing UV irradiation in the ozonation process is to enhance the ozone decomposition, yielding more free radicals, such as hydroxyl radicals, which react with most organic compounds with rate constants within the range of $10^6 \sim 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (Staelin & Hoigné 1982). The degradation of less reactive compounds may be accelerated with the presence of free radicals.

The aims of the research presented here are to assess the potential of UV/O₃ for degradation of NDMA, and deduce the pathways of NDMA degradation by UV/O₃.

METHODS

Reagents

NDMA was synthesized in our own lab by the method described by Hu & Ma (1980). The purity of synthesized NDMA was above 95% confirmed by HPLC. Other chemicals (MA, DMA, benzenesulfonyl chloride, dichloromethane, NaNO₂, NaNO₃, NaHCO₃, Na₂SO₄, Na₂SO₃, NaOH and H₂SO₄) used were of reagent grade and were used without further purification. All stock solutions were prepared in distilled water. The NDMA solution used in UV/O₃ degradation was prepared by directly diluting stock solutions of NDMA (13.5 mmol l^{-1}) with distilled water to a suitable concentration. The concentration of NDMA solution was confirmed with HPLC.

Experimental procedure

UV/O₃ degradation of NDMA experiments were performed in a cylindrical glass reactor (shown in Figure 1), exposing the solution to the UV irradiation with an 8 W low-pressure Hg lamp (8 W, emission at 253.7 nm, Tianjin Xinjing Co. China). Ozone was produced by a laboratory ozonizer (DHX-SS-1G, Harbin Jiujiu Electrochemistry Engineering Ltd, China), with a maximum ozone production of 9 g h⁻¹, using pure oxygen as feed gas. Varying the oxygen flux, voltage of the ozone producing canal and ozone introduction time, the dissolved ozone concentration in the reactor could be controlled.

After the ozone was introduced into 700 ml distilled water, the calculated aliquot of NDMA stock solution and other reagents were added to the reactor immediately. For investigation of the reactive oxygen species in the irradiation system, tert-butanol (for ·OH) or sodium azide (for ¹O₂) was also introduced into the reaction system. Then the circulation pump and the low-pressure Hg lamp were turned on, and samples were withdrawn at predetermined time intervals and rapidly analysed after the sampling. The ozone oxidation reaction was quenched by addition of an aliquot of 0.1 mol l⁻¹ Na₂SO₃ solution (1 ml). The solution pH was adjusted with 0.1 mol l⁻¹ H₂SO₄ and NaOH solution.

Analysis

NDMA was analysed by HPLC (LC-10A, Shimadzu, Japan) with a Venusil Mp-C₁₈ column (150 mm × 4.6 mm, 5 μm,

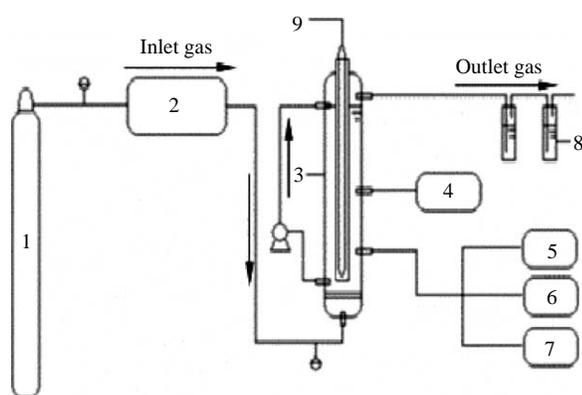


Figure 1 | Schematic diagram of UV/O₃ system: 1, oxygen bottle; 2, ozone generator; 3, reactor; 4, dissolved ozone analysis; 5, HPLC; 6, GC-MS; 7, IC; 8, KI solution; 9, UV lamp.

Agela Technologies Inc.) employing UV detection at 230 nm. The mobile phase consisted of water and methanol, the ratio was 95/5 (v/v) and the flow rate was 1.0 ml min⁻¹. The detection limit of NDMA was approximately 0.04 nmol l⁻¹.

DMA and MA were derived with benzenesulfonyl chloride (Sacher *et al.* 1997) and then were analysed by GC-MS (Agilent 6890-5973N, USA). The water sample (20 ml) in a 250-ml round-bottomed flask was diluted to 200 ml, and then 8 ml NaOH (10 mol l⁻¹) and 2 ml benzenesulfonyl chloride were added. The flask was closed and stirred for 10 minutes at room temperature. Then another 10 ml of 10 mol l⁻¹ NaOH were added and the mixture was agitated again for 10 minutes at 80°C in order to hydrolyse the excess of derivatization reagent. Subsequently the solution was cooled down with ice water and acidified under steady cooling with 18.5% HCl to pH 5.5. The mixture was extracted twice with 10 ml dichloromethane. The aqueous solution was discarded, while the organic phase was washed once with 15 ml 0.05 mol l⁻¹ NaHCO₃ and dried with Na₂SO₄. Then the solvent was injected into GC-MS. All GC-MS data were obtained with an Agilent 6890/5973N instrument equipped with a column (DB-1MS, 30 m × 0.25 mm i.d. × 0.25 μm). An over temperature gradient was carried out. The initial over temperature was 80°C (hold for 5 minutes), increased to 150°C (hold for 10 minutes) at 10°C min⁻¹, and then increased to 300°C (hold for 1 minutes) at 50°C min⁻¹. The temperature of injection was 290°C in splitless mode. High purity He gas was used as carrier gas, and the column flow rate was 0.5 ml min⁻¹ at constant flow mode. The ion source of mass spectra was operated in the electron impact mode (EI; electron energy 70 eV, 230°C). Full-scan mass (*m/z* 40–500) were recorded for identification of analytes at high concentration. Confirmation of trace chemicals was achieved by use of three characteristic MS ions and by matching GC retention times to those of known standard compounds. The ions selected in this study were *m/z* 77 for quantification, *m/z* 44 and 185 for qualitative of DMA derivative product, *m/z* 77 for quantification, *m/z* 141 and 171 for qualitative of MA derivative product.

NO₂⁻ and NO₃⁻ were analysed with ion chromatography (ICS-3000, Dionex, USA) equipped with an Ion Pac ASII-HC (Dionex, USA) ion-exchange column;

30.0 mmol l⁻¹ KOH solution was used as eluant, and the flow rate was 1.2 ml min⁻¹.

The aqueous ozone concentration was measured with the indigo method (Bader & Hoigné 1981).

RESULTS AND DISCUSSION

Effect of O₃ dosage on the degradation of NDMA by UV/O₃

Before the UV/O₃ process, NDMA degradation by UV alone was examined. As shown in Figure 2, NDMA was strongly photolabile (Stefan & Bolton 2002). It degraded almost completely with 20 minutes of UV irradiation. The removal efficiency of NDMA degradation by UV alone was above 99%. Then a range of O₃ concentrations from 2.64 mg l⁻¹ to 6.64 mg l⁻¹ were introduced into the UV irradiation process. The decay of NDMA degradation by UV/O₃ displayed the same trend as UV alone. NDMA was well degraded under the three O₃ dosage conditions. The removal efficiency of NDMA was above 99% in all cases. But it was noticeable that introducing O₃ into the UV irradiation process did not enhance NDMA degradation significantly, which suggested that UV irradiation was more important for NDMA degradation in the UV/O₃ process. The reaction rate of NDMA degradation by UV/O₃ with low O₃ dosage was a little faster than that by UV alone.

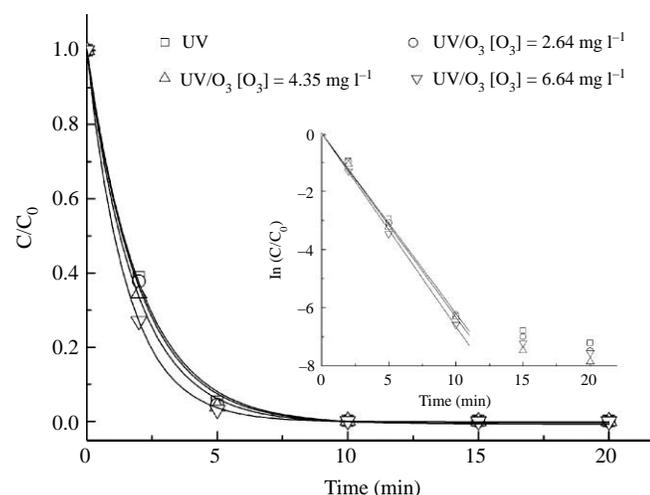


Figure 2 | Effect of O₃ dosage on NDMA degradation by UV/O₃: [NDMA] = 0.1 mmol l⁻¹; pH = 6.0; irradiation 1,000 μW cm⁻².

However, the reaction rate increased with the increase of O₃ dosage. NDMA degradation by UV/O₃ was the fastest when O₃ dosage was 6.64 mg l⁻¹.

The degradation of NDMA by UV/O₃ was found to follow pseudo-first-order kinetics at various O₃ dosages and the kinetic behaviour is illustrated in Figure 2. The kinetic parameters of NDMA degradation by UV/O₃ are listed in Table 1.

Ozonation is an effective way to reduce the chemical oxygen demand (COD) and total organic carbons (TOCs) by oxidizing the stream solutions with ozone. When UV irradiation was combined with ozonation, the decomposition of ozone was enhanced to yield more free radicals resulting in a higher oxidation rate:



The hydroxyl radical ($\cdot\text{OH}$) is non-selective and vigorous, and reacts with most organic compounds with rate constants within the range of 10⁶ ~ 10⁹ l mol⁻¹ s⁻¹ (Staehelin & Hoigné 1982). NDMA in water at room temperature had been determined using electron pulse radiolysis and transient absorption spectroscopy ($\cdot\text{OH}$ and e_{aq}^-) and EPR free induction decay attenuation ($\cdot\text{H}$) measurements (Mezyk *et al.* 2004). Specific

Table 1 | Kinetic parameters of NDMA degradation by UV/O₃

Reaction conditions		K (min ⁻¹)	R ²
O ₃ dosage (mg l ⁻¹)	0	0.6168	0.9948
	2.64	0.6191	0.9968
	4.35	0.6319	0.9982
	6.64	0.6642	0.9991
Solution pH	3.2	0.6472	0.9952
	6.0	0.6168	0.9948
	7.1	0.6215	0.997
	11.0	0.5354	0.9606
[NDMA] (mmol l ⁻¹)	0.04	0.6265	0.9986
	0.1	0.6168	0.9948
	0.2	0.6314	0.9975
[HA] (mg l ⁻¹)	0	0.6168	0.9948
	2.9	0.4974	0.9989
	5.7	0.3816	0.9997
	11.4	0.2166	0.9996

values of $(4.30 \pm 0.12) \times 10^8$, $(1.41 \pm 0.02) \times 10^{10}$ and $(2.01 \pm 0.03) \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ were measured, respectively. Accordingly, $\cdot\text{OH}$ played the role of increasing the reaction rates during NDMA degradation by UV/O₃. However, the discrepancy with the removal of NDMA was not so clear, which suggested that UV irradiation played a more important role for NDMA degradation by UV/O₃ than $\cdot\text{OH}$.

Effect of solution pH on the degradation of NDMA by UV/O₃

It is widely known that solution pH is one of the most important factors influencing the degradation of contaminants and the formation of products in wastewater treatment processes. Hence the effect of solution pH on NDMA degradation by UV/O₃ was tested under different solution pH conditions (pH = 3.2, 6.0, 7.1, 11.0). As shown in Figure 3, NDMA was almost completely degraded with 20 minutes of UV irradiation at all four solution pH values. Removal efficiency of NDMA degradation was above 99%. NDMA degradation by UV/O₃ at different pH followed pseudo-first-order kinetics. The kinetic parameters are listed in Table 1. The reaction rates of NDMA degradation did not fluctuate with pH increasing from acid to neutral but dramatically decreased in basic aqueous solution.

In the UV/O₃ process, UV irradiation interacts with ozone to decompose organic compounds. The effect of solution pH on NDMA degradation in the UV/O₃ process was, therefore, complicated. Ozone may attack

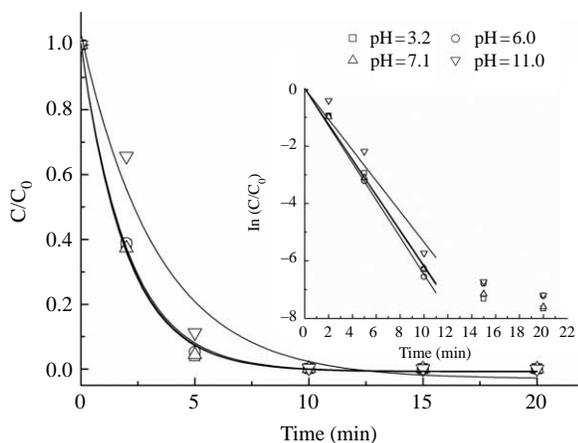


Figure 3 | Effect of pH on NDMA degradation by UV/O₃: [NDMA] = 0.1 mmol l⁻¹; [O₃] = 6.64 mg l⁻¹; irradiation 1,000 μW cm⁻².

the pollutants via two different reaction pathways: (1) direct ozonation by the ozone molecule, which happens at low pH; and (2) radical ozonation by the highly oxidative free radicals such as hydroxyl free radicals, which are formed by the decomposition of ozone in aqueous solution at high pH (Stahelin & Hoigné 1985). Ozone oxidation is more selective and predominates under acidic condition, while radical oxidation is less selective and predominates under basic condition. Thus the yields of free radicals at high pH are higher than at low pH in the UV/O₃ process. For UV irradiation, NDMA degradation depends on the quantum yield (Lee *et al.* 2005a). According to our previous study (data not shown here), the quantum yield in acidic solution was higher than that in neutral and alkaline solution, which is in accordance with reports by Lee *et al.* (2005a). In addition, protonation of NDMA was likely to take place in acidic and neutral solution depending on its pK_a. The protonated form of excited-state NDMA was assumed to be more photolabile than its unprotonated analogue (Lee *et al.* 2005a). Consequently, the reaction rate of NDMA photolysis in acidic solution would be faster than that in neutral and alkaline solution. According to the results shown in Figure 3, UV irradiation played a more important role than free radicals which were derived from ozone decomposition in the UV/O₃ process.

Effect of NDMA initial concentration on degradation of NDMA by UV/O₃

Degradation of NDMA by UV/O₃ was investigated over a range of NDMA initial concentrations from 0.04 mmol l⁻¹ to 0.2 mmol l⁻¹. Figure 4 shows the effect of initial concentration of NDMA on its conversion and the kinetic behaviour. NDMA was almost completely degraded in 20 minutes. Removal efficiency of NDMA with different initial concentrations was above 99% in all cases. The conversion decreased with the increase in initial concentration of NDMA. NDMA degradation by UV/O₃ followed pseudo-first-order kinetics with various NDMA initial concentrations. As listed in Table 1, there were no obvious differences in reaction rates with initial concentrations of NDMA of 0.04 mmol l⁻¹, 0.10 mmol l⁻¹ and 0.2 mmol l⁻¹, which shows that UV/O₃ was effective for NDMA degradation.

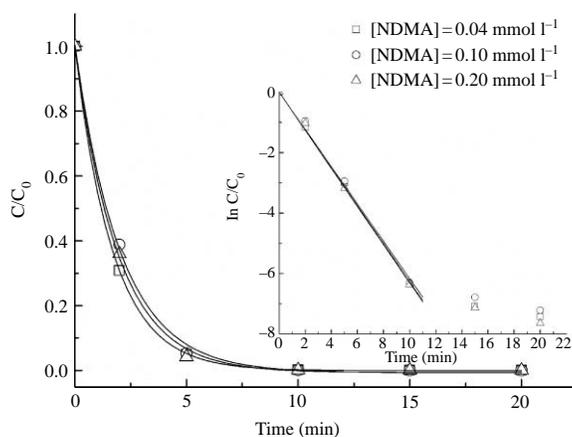


Figure 4 | Effect of initial NDMA concentration on NDMA degradation by UV/O₃: [O₃] = 6.64 mg l⁻¹; pH = 6.0; irradiation 1,000 μW cm⁻².

Effect of humic acid on the degradation of NDMA by UV/O₃

Natural organic matter (NOM) is known to be complex in nature with varying structural and functional characteristics (Chen *et al.* 2002). Humic substances are one of the components of NOM, consisting of humic acid and fulvic acid. Due to its photoactive nature, humic substances could induce photodegradation of organic compounds with solar radiation (Zepp *et al.* 1985; Brezonik & Fulkerson-Brekken 1998; Gerecke *et al.* 2001; Lam *et al.* 2003). Humic acid was taken as an example to investigate the effect of NOM on NDMA degradation by UV/O₃. The results are shown in Figure 5, which suggests that humic acid would inhibit NDMA degradation and that the degradation of NDMA by UV/O₃ followed pseudo-first-order kinetics. Though NDMA was almost completely degraded in 20 minutes, reaction rate clearly decreased with the increase of humic acid concentration (also see Table 1).

Effect of O₃ dosage on products of NDMA degradation by UV/O₃

Mechanistic studies on the photolysis of NDMA indicated that the principal products were MA, DMA, NO₂⁻ and NO₃⁻ (Lee *et al.* 2005b). Small amounts of N₂O, N₂, HCHO and HCOOH could also be formed, but their concentration levels were strongly dependent on the chemical reaction environment. Figure 6 shows the yields of products

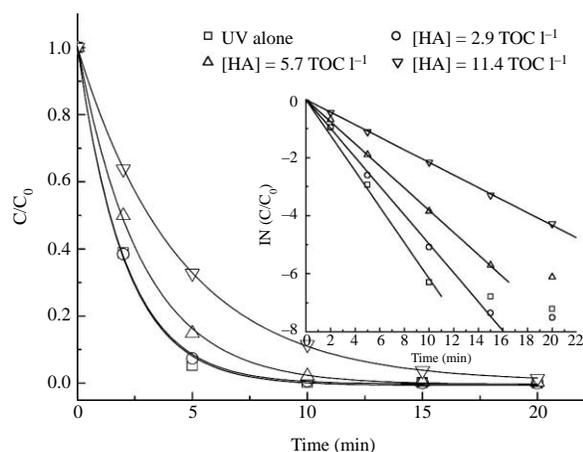


Figure 5 | Effect of humic acid on NDMA degradation by UV/O₃: [NDMA] = 0.1 mmol l⁻¹; pH = 6.0; irradiation 1,000 μW cm⁻².

including MA, DMA, NO₂⁻ and NO₃⁻ which we focused on in the UV/O₃ process.

As seen from Figure 6, DMA and NO₂⁻ were the principal products of NDMA degradation by UV alone. However, some differences emerged when ozone was added into the UV irradiation process. DMA decreased with increasing O₃ dosage, whereas MA increased under the same conditions. MA was almost equal to DMA when the concentration of ozone was 6.64 mg l⁻¹. Conversion of NO₂⁻ followed the same trend as DMA, decreasing with increasing O₃ dosage. And the yields of NO₃⁻ were increased in the UV/O₃ process. NDMA degradation by UV/O₃ promoted conversion from DMA to MA and from NO₂⁻ to NO₃⁻.

It is well known that DMA is the principal precursor of NDMA during chlorination (Mitch & Sedlak 2002). The formation of NDMA may involve the slow formation of 1,1-dimethylhydrazine by the reaction of monochloramine and DMA followed by its rapid oxidation to NDMA. Other pathways also lead to NDMA formation during chlorination such as the reaction of sodium hypochlorite with DMA. DMA derived from NDMA was decreased in the UV/O₃ process compared with UV alone, which resulted from the reactions with ozone and ·OH. Both ozone and ·OH reactions with DMA were fast, and the precursor of NDMA was effectively removed from water. As a result, the risk of NDMA formation was eliminated (Von Gunten 2003).

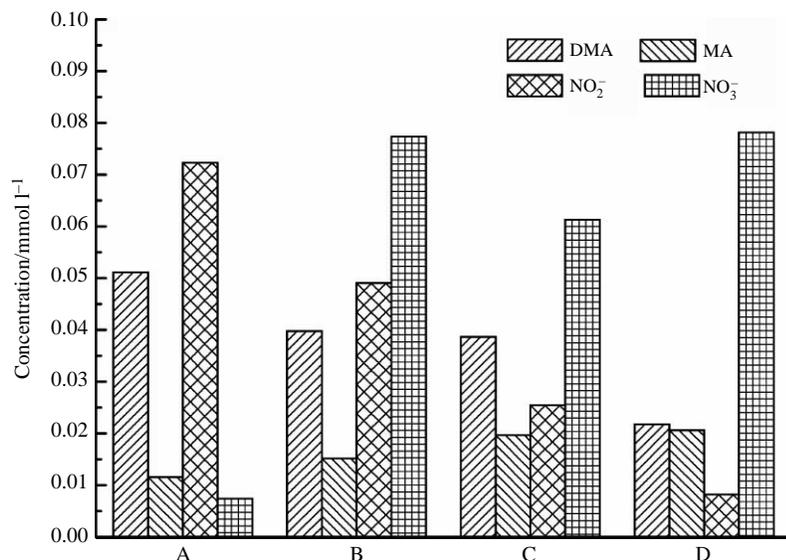


Figure 6 | Effect of O₃ dosage on products of NDMA degradation by UV/O₃: A, UV; B, UV/O₃ [O₃]₀ = 2.64 mg l⁻¹; C, UV/O₃ [O₃]₀ = 4.35 mg l⁻¹; D, UV/O₃ [O₃]₀ = 6.64 mg l⁻¹; [NDMA] = 0.1 mmol l⁻¹; pH = 6.0; irradiation 1,000 μW cm⁻².

Effect of solution pH on the products of NDMA degradation by UV/O₃

The four main products of NDMA degradation were analysed over the pH range of 3.2–11.0. Figure 7 shows the concentration of the products obtained from the complete degradation (>99%) of 0.1 mmol l⁻¹ NDMA. In Figure 7, MA and NO₃⁻ were the principal products of

NDMA degradation by UV/O₃ at pH 3.2 and 11.0. The yields of NO₂⁻ increased with solution pH, but were lower than NO₃⁻ at all pH ranges tested. The formation of DMA increased with pH increasing from acid to neutral but dramatically decreased in basic aqueous solution. The reason for this dramatic decrease at pH 11.0 was a property of ozone which existed in the UV/O₃ process.

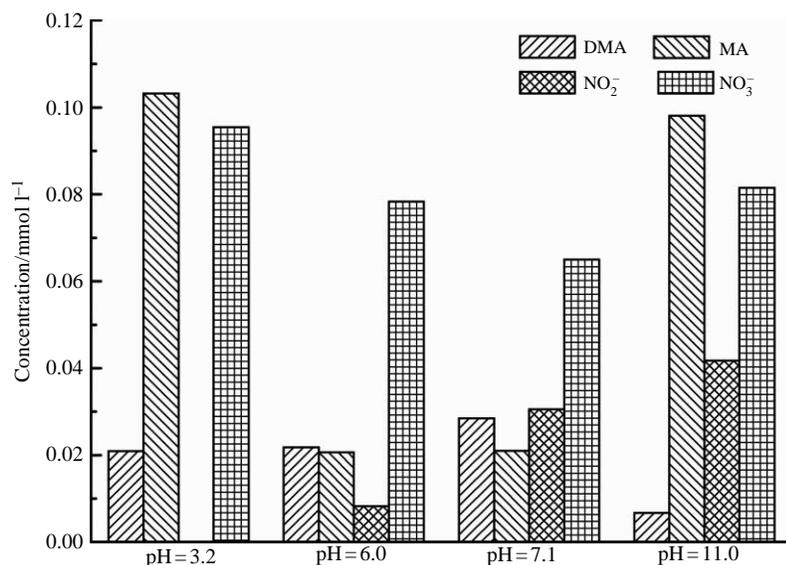


Figure 7 | Effect of pH on products of NDMA degradation by UV/O₃: [NDMA]₀ = 0.1 mmol l⁻¹; [O₃]₀ = 6.64 mg l⁻¹; irradiation 1,000 μW cm⁻².

In basic aqueous solution, ozone decomposition is catalysed by hydroxide ions and proceeds more rapidly with increasing pH, which eventually produces free radicals, especially hydroxyl radicals (Lau *et al.* 2007):



The lowest formation of DMA in the UV/O₃ process was obtained at pH 11.0, where excessive hydroxide ions were present for generating $\cdot\text{OH}$ from the decomposition of ozone. As mentioned above, DMA reacted with ozone and $\cdot\text{OH}$ and the risk of NDMA formation was eliminated.

Reactive oxygen species in the UV/O₃ process

In order to investigate the reactive oxygen species in the irradiation system, typical inhibitors were introduced into the reaction system. The inhibitors reacted with the reactive oxygen species competitively, and then the degradation of contamination would be inhibited. Hereby, we could confirm which reactive oxygen species existed in the reaction system (Brezonik & Fulkerson-Brekken 1998). In the current investigation, two inhibitors were introduced into the solution. One was tert-butanol which was an inhibitor for $\cdot\text{OH}$ and the other was sodium azide, an inhibitor for $^1\text{O}_2$. The reaction rate constant of tert-butanol reacting with $\cdot\text{OH}$ was $5 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ (Pi *et al.* 2003)

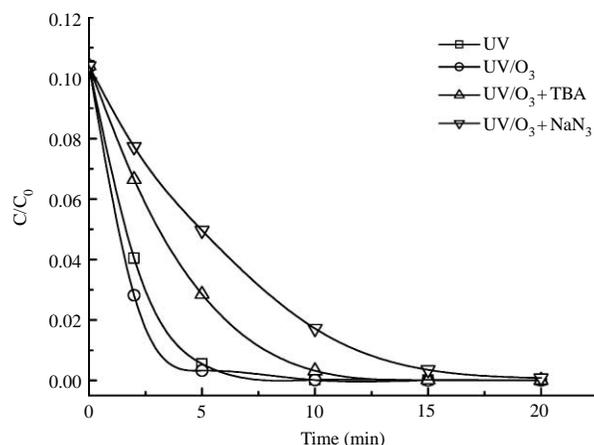


Figure 8 | Effect of tert-butanol and sodium azide on NDMA degradation by UV/O₃: [NDMA]₀ = 0.1 mmol l⁻¹; [O₃]₀ = 6.64 mg l⁻¹; [TBA] = 50 mmol l⁻¹; [NaN₃] = 50 mmol l⁻¹; irradiation 1,000 μW cm⁻².

and the reaction rate of sodium azide reacting with $^1\text{O}_2$ was $7.9 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ (Buxton *et al.* 1988).

The inhibitory effect of tert-butanol and sodium azide on NDMA degradation by UV/O₃ is shown in Figure 8. Though NDMA was almost completely degraded in 20 minutes, the reaction rate clearly decreased with tert-butanol and sodium azide addition. As Figure 8 shows, the inhibitory effect of sodium azide on NDMA degradation by UV/O₃ was much stronger than that of tert-butanol. Accordingly, we conclude that, while $\cdot\text{OH}$ played an important role in the process of NDMA degradation by UV/O₃, $^1\text{O}_2$ played a more important role in the degradation process. So both $\cdot\text{OH}$ and $^1\text{O}_2$ were the reactive oxygen species in the reaction of UV/O₃ degradation of NDMA in water.

Mechanism of NDMA degradation by UV/O₃

In the UV/O₃ process, a dosage of 6.64 mg l⁻¹ O₃ depleted NDMA completely within 20 minutes' UV irradiation (data not listed here). The products of NDMA degradation were analysed after 20 min irradiation, and included MA, DMA, NO₃⁻ and NO₂⁻. The mechanism of NDMA degradation in the UV/O₃ process was complicated by the presence of UV, ozone and $\cdot\text{OH}$. According to the yields of products as a result of complete NDMA degradation under various conditions and from previous literature, the possible pathways of NDMA degradation by UV/O₃ are illustrated in Figure 9.

$\cdot\text{OH}$ generated as the result of UV irradiation combined with ozonation was non-selective and vigorous. Second-order rate constants for the reaction of $\cdot\text{OH}$ and NDMA were determined as $(4.30 \pm 0.11) \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$

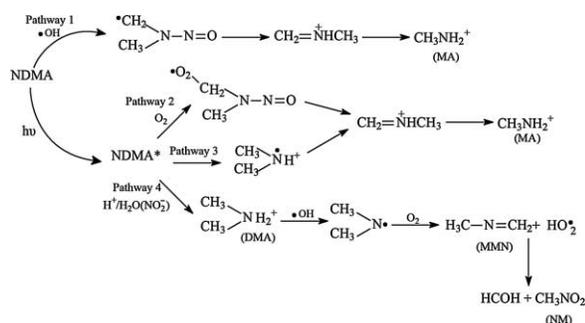


Figure 9 | Possible pathways of NDMA degradation by UV/O₃.

(Landsman *et al.* 2007) and $(4.50 \pm 0.21) \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ (Lee *et al.* 2007) by current research. The mechanism of the reaction of $\cdot\text{OH}$ with NDMA is proposed to occur by hydrogen atom abstraction from one of its methyl groups (Mezyk *et al.* 2004). Then NDMA can be oxidized to MA through the self-decomposition of the carbon-centred NDMA radical. The results that yields of MA increased with increasing O₃ dosage in this study were consistent. Lee *et al.* (2007) found MA and ammonium were produced as oxidation products of NDMA by conventional ozonation and advanced oxidation process (O₃/H₂O₂); no formation of DMA was observed in all conditions. DMA was still detected to be one of the products of NDMA degradation in the UV/O₃ process but the amount was much lower than that formed in the UV process alone. With the UV irradiation, the N-N bond fission of NDMA perhaps took place to produce products such as MA, DMA, NO₃⁻ and NO₂⁻. The homolytic cleavage of N-NO bonds produced the corresponding aminium radical and nitric oxide, and the heterolytic cleavage of N-NO bonds produced parent secondary amines and nitrite. The reaction between DMA and $\cdot\text{OH}$ was proposed to produce methylmethyleamine (MMN) and nitromethane (NM) as the intermediate products (Siddiqui & Atasi 2004). Another possible pathway of NDMA degradation by UV/O₃ involves the reaction with dissolved oxygen. As described by Lee *et al.* (2007), the carbon-centred NDMA radical reacted with oxygen to produce the corresponding peroxy radical, which was decomposed to an iminium ion.

CONCLUSION

Ozone combined with UV irradiation was employed as an effective method for the removal of NDMA in water. Introducing O₃ into the UV irradiation process did not enhance NDMA degradation significantly compared with UV alone, suggesting that UV irradiation was more important for NDMA degradation in the UV/O₃ process, but O₃ did change the degradation pathway to produce different products. The degradation of NDMA by UV/O₃ was found to follow pseudo-first-order kinetics. Solution pH had little effect on NDMA degradation in the UV/O₃ process. The reaction rate of NDMA degradation did not

fluctuate with pH increasing from acid to neutral but dramatically decreased in basic aqueous solution. Initial NDMA concentration did not have an obvious effect on NDMA degradation by UV/O₃; however, humic acid did inhibit NDMA degradation.

The products of NDMA degradation by UV/O₃ were substantially different. DMA and NO₂⁻ decreased with increasing O₃ dosage, suggesting that the risk of NDMA formation was reduced. Solution pH also had an effect on formation of the degradation intermediates. MA and NO₃⁻ were the principal products of NDMA degradation by UV/O₃ at pH 3.2 and 11.0. DMA increased with pH increasing from acid to neutral but dramatically decreased in basic aqueous solution.

With the help of tert-butanol and sodium azide, both ¹O₂ and $\cdot\text{OH}$ were verified to be the reactive oxygen species present in the process of NDMA degradation by UV/O₃.

Based on the results obtained in this study and previous literature, the mechanism of NDMA degradation by UV/O₃ was suggested. In the UV/O₃ process, NDMA may be oxidized by both $\cdot\text{OH}$ and dissolved oxygen to form MA, or even decomposed as a result of homolytic cleavage and heterolytic cleavage of N-NO bonds to form MA and DMA. Then DMA would react with $\cdot\text{OH}$ to produce MMN and NM as the intermediate products undetected in the UV/O₃ process.

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