Influence of Nitrate on UV-degradation of *N*-nitrosodimethylamine (NDMA)

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ABSTRACT

This study demonstrated degradation of NDMA by low or medium pressure UV at the concentration range of lower than 100 ng/l. In Milli-Q water, NDMA was degraded at the rate of 2.7 cm^2/J (low pressure UV), and 2.1 cm2/J (medium pressure UV). Its rate was reduced to 2.4 cm^2/J, 2.1 cm^2/J, 2.5 cm^2/J (low pressure UV) or 1.6 cm^2/J, 1.1 cm^2/J, 1.8 cm^2/J (medium pressure UV), in 10mgN/l or 100mgN/l of nitrate, and in tap water, respectively, possibly by UV absorption of dissolved matter.

Key words: Ultraviolet; Low pressure ultraviolet lamp; Medium pressure ultraviolet lamp; N-nitrosodimethylamine (NDMA);

INTRODUCTION

N-nitrosodimethylamine (NDMA) is a potentially carcinogenic compound to humans, and has been detected in various kinds of environmental waters (1, 2). It gives 10 -6 of risks at as low as 0.7 ng/l concentration (3). The tentative guideline value in drinking water is set at 9 ng/l in the Provence of Ontario, Canada (4), 3 ng/l in the State of California, USA (5) and 100 ng/l by WHO (6). In Japan, it was also nominated to the drinking water candidate list at the concentration of 100 ng/l (7). NDMA is known to produce chemically by nitrosation of dimethylamine (DMA), oxidation of unsymmetrical dimethyl hydrazine (UDMH) (8). In water treatment processes, it has been known to be produced during chlorination with ammonium nitrogen, or chloramination (9). Also, it was reported that NDMA can be produced during ozonation processes in water purification plant (1).

Several degradation methods had been tested for NDMA. Reverse osmosis (RO) membrane treatment (10), and ozonation (11) were tested, but not found much effective; its removal ratio was around 50 %. Biodegradation (12) or chemical degradation using a column of iron and nickel (13), was also studied, however, it would be difficult to apply such technologies into water treatment processes. Meanwhile, UV irradiation is expected to be effective for NDMA degradation, because it has an absorption peak at 227 nm and 332 nm in the UV region, and has a high quantum yield of 0.41 (14). There is some previous research investigating degradation of NDMA by UV, at the concentrations ranging from µg/l to mg/l. Stefan and Bolton have degraded NDMA by medium pressure (MP) UV lamp, whose initial concentration was 1mM. Degradation products had also been identified as DMA, nitrite, nitrate, formaldehyde, formic acid (15). Sharpless and Linden conducted NDMA degradation experiment by low pressure (LP) and MP UV lamp. They have used synthetic water containing dissolved organic carbon (DOC), nitrate, or other dissolved matter (16). Initial concentration of NDMA were 1 µM in their experiment and degradation rate was 2.3 cm^2/J (LP), and 2.4 cm^2/J (MP). Latest research also reported reduction of NDMA concentration after UV treatment, which imitated water purification plant (17). However, there still needs to be clarification on UV degradation kinetics at a lower concentration range, especially in relation to dissolved matter. In this study, we have tested degradation of NDMA by LP or MP UV at the initial concentration of 100 ng/l. We also tested various composition in water: Milli-Q water, 10 mgN/l or 100 mgN/l of sodium nitrate solution, and tap water. Finally, degradation rate in various water types was compared and the effect of dissolved matter was discussed in relation to UV transmittance.

MATERIALS AND METHODS

UV irradiation experiment

Monochromatic LP UV lamp (15W×2, GE/Hitachi) and polychromatic MP UV lamp (330W×1, B410MW, Ebara) was used for experiment. UV fluence was calculated using iodide/iodate actinometry (18), both for LP or MP UV. Briefly, 500ml of actinometry solution was added into the reactor, and irradiated by low or medium pressure UV lamp. A 500 ml glass beaker was used as a reactor, whose depth is

8.82 cm and diameter is 8.5 cm. After an appropriate irradiation period, absorbance of actinometry solution was measured. It was calculated to be 0.48 mW/cm^2 for LP UV, and 1.22 mW/cm^2 for MP UV.

For the NDMA degradation experiment, 500 ml of NDMA solution at an initial concentration of 100 ng/l was prepared. The prepared solution was poured into the reactor (500 ml glass beaker) and exposed to LP or MP UV lamp. UV irradiation was conducted to achieve 580 mJ/cm^2, 1150 mJ/cm^2, 1740 mJ/cm^2 by LP UV, 700 mJ/cm^2, 1390 mJ/cm^2, 2090 mJ/cm^2 by MP UV. NDMA was dissolved into (i) Milli-Q water, (ii) 10 mgN/l of sodium nitrate solution, (iii) 100 mgN/l of sodium nitrate solution, or (iv) tap water. Tap water was taken from the tap in the engineering 14th building of the University of Tokyo, Japan.

NDMA measurement

After exposure to LP or MP UV light, 1g of sodium bicarbonate and 5 ng of NDMA d_6 (Cambridge Isotope laboratories) was added into 500ml of sample solution. The water sample was passed through the Resprep cartridge under EPA 521 method for concentration at a flow rate of 5ml/min. The cartridge had been preconditioned by 10 ml of dichloromethane (DCM), 10ml of methanol, 20 ml of Milli-Q water. After drying by nitrogen purging, NDMA was eluted from the cartridge by 10 ml of DCM, then concentrated to 200 µl under a gentle nitrogen gas, and then analyzed by UPLC-MS/MS (Waters, Acquity UPLC/TQD) operated in the electrospray/ chemical positive ionization mode. A gradient mobile phase of 0.1% formic acid and acetonitrile was used. NDMA concentration was corrected by the recovery ratio of NDMA d_6. The detection limit of this method is 0.4 ng/l. Details of UPLC-MS/MS analyses are described elsewhere (1, 2).

Spectrum measurement

The UV emission spectrum and absorption spectrum of each water was investigated. Emission spectra of LP and MP UV lamp were measured using multi channel photo detector (MCPD 2000, Ohtsuka electronics). The absorption spectrum of each water was measured by spectrophotometer (Hitachi, U-2010).

RESULTS AND DISCUSSIONS

Degradation of NDMA at the concentration range of lower than 100 ng/l

NDMA was dissolved into various types of water at the initial concentration of 100 ng/l. Those water samples were exposed to LP or MP UV light. The degradation of NDMA is compared in **Table 1**. NDMA degradation in those waters is expressed in **Figure 1**. The horizontal axis shows UV fluence, while the vertical axis shows NDMA concentration in a logarithmic scale. The NDMA concentration was reduced with a straight line in a logarithmic scale under both LP and MP UV exposure experiments. The degradation rate is calculated in **Table I**, assuming a first order reaction.

In Milli-Q water, degradation rate was 2.7 cm^2/J for LP UV, and 2.1 cm^2/J for MP UV. The value was a little bit lower in MP UV degradation. The value obtained in this research slightly different from the values obtained in the previous study by Sharpless and Linden; they had demonstrated 2.3 cm^2/J for LP UV and 2.4 cm^2/J for MP UV (15). However, if we take into account experimental setup details, these two results could be considered to be not so different. It can be said that degradation efficiency would show little difference between 100 ng/l and 1 µM of initial concentration.

TABLE I UV DEGRADATION RATE OF NDMA (cm^2/J)

Type of UV lamp	Water composition			
	Milli-Q	10 mgN/l sodium nitrate	100 mgN/l sodium nitrate	Tap water
LP	2.7	2.4	2.1	2.5
MP	2.1	1.6	1.1	1.8

There was a little difference between LP and MP UV results in this study. It could be speculated that some wavelength range between 200 to 300 nm contributed less to UV degradation of NDMA, compared with 254 nm.

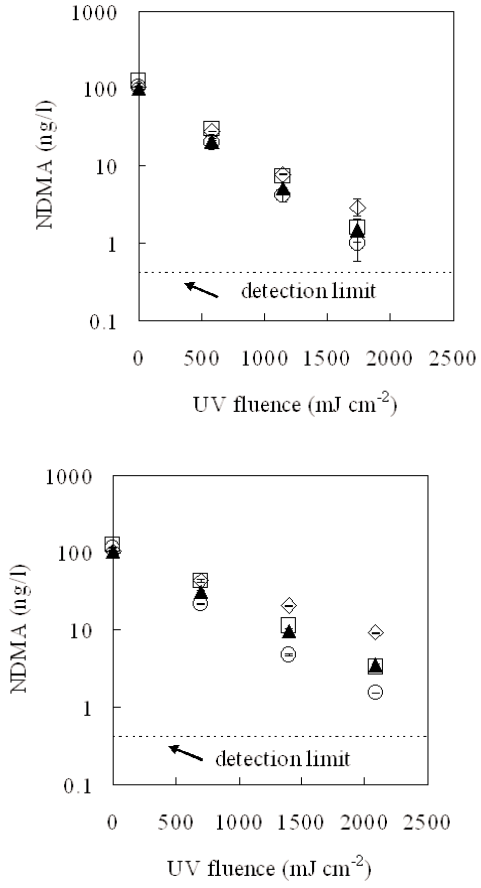

Figure1: NDMA concentration after LP (left) or MP (right) UV irradiation.

NDMA was dissolved into Milli-Q water (○), 10 mgN/l of sodium nitrite (▲), 100 mgN/l of sodium nitrite ( ), or tap water (□). Data, except tap water, are the geometric mean of three identical experiments. Error bar indicates maximum and minimum of each data set.

Effect of dissolved matter on UV degradation

NDMA degradation in various composition of water was tested and the results are compared in in **Figure 1** and **Table I**. When sodium nitrate was added, the degradation rate got slower, compared with Milli-Q water. This was more noticeable in MP UV than in LP UV testing. In the case of LP UV, the degradation rate was reduced by about 10% by the addition of 10 mgN/l of sodium nitrate. It was reduced by another 10%, when sodium nitrate concentration was increased to 100 mgN/l. In the case of MP UV, degradation rate was reduced by about 25%, by the addition of 10 mgN/l of sodium nitrate. It was reduced by another 25%, when sodium nitrate concentration was increased to 100 mgN/l. In tap water, degradation rate was also reduced. It was reduced by about less than 10 % by LP UV, and about 15% by MP UV.

The cause of slower degradation in sodium nitrate solution and tap water could be absorption of UV light by the water. In **Figure 2**, the emission spectrum of LP and MP UV are shown. In **Figure 3**, absorption spectrum of each water is shown as well. It could be clear that dissolved matter in sodium nitrate solution and in tap water had absorbed UV light, especially at the wavelength range of shorter than 254 nm. NDMA has an absorption peak at 227 nm and 332 nm (15). Poly chromatic MP UV lamp emits wavelength around 227 nm, therefore degradation rate would have been more affected by water composition in MP UV than in LP UV.

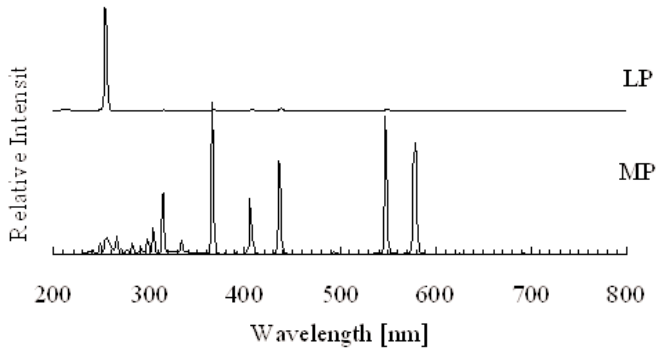

Figure 2: Emission spectrum of LP & MP UV

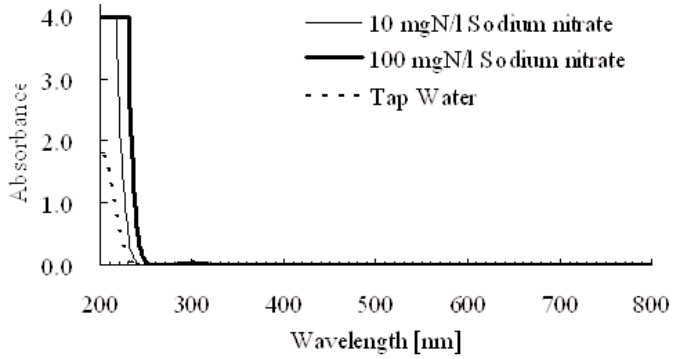

Figure 3: Absorption spectrum of each water .

In order to clearly discuss the effect of absorption, relations between irradiated energy and degradation rate were shown in Figure 4. In this figure, both vertical and horizontal axis shows relative value, standardized by the result of Milli-Q water. The original absolute value in horizontal axis is the irradiated UV energy, corrected by UV absorption of the water. This was calculated by each 1 nm between 200 to 300 nm. For MP UV analysis, UV energy between 200 to 300 nm was employed, while single 254 nm was used for LP UV analysis. The vertical axis shows the relative degradation rate, calculated from Table I. In case of LP UV, analyzed results are shown on the diagonal line with results corrected by absorption explain the experimental results very well. In the case of MP UV, tap water results were almost on the diagonal line. Result of sodium nitrate was situated a little bit away from the line.

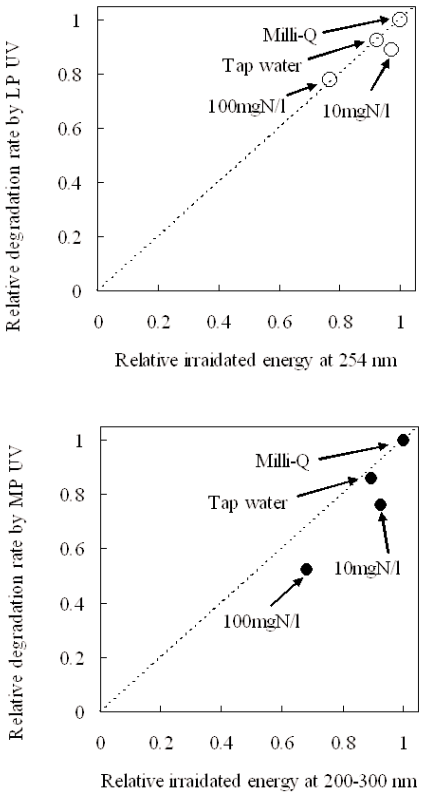

Figure 4: Relations between relative irradiated energy and relative degradation ratio (LP UV: left, MP UV: right)

Influence of nitrate on UV-degradation of NDMA

In this study, NDMA degradation was studied in various water and the effect of dissolved matter was examined. Especially in the case of sodium nitrate solution, the degradation rate slowed. Degradation by medium pressure UV lamp was more severely affected by the absorption of UV light by dissolved matter. This reduction is somewhat explained by either 254 nm absorption for LP UV or 200-300 nm absorption for MP UV. Further study should aim at seeking a more practical indicator, instead of calculated absorption at 200-300 nm for MP UV.

CONCLUSIONS

This study experimentally investigated the degradation of NDMA by LP or MP UV irradiation, with the following conclusions:

(i) LP or MP UV could degrade NDMA at lower than 100 ng/l, with almost the same efficiency around 1 μM.

(ii) UV degradation of NDMA was affected by UV absorption, caused by sodium nitrate or dissolved matter in tap water.

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