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Use of Pulsed-UV Processes to Destroy NDMA

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emerging issues

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Bench-scale experiments were conducted to determine the effectiveness of using pulsed-ultraviolet (UV) irradiation and pulsed-UV/hydrogen peroxide (H_2O_2) processes to destroy N-nitrosodimethylamine (NDMA). The effects of various UV and H_2O_2 dosages and source waters, as well as nitrate (NO_3^-) and initial NDMA concentrations, were investigated as control parameters for both completely mixed batch reactor and continuously stirred tank reactor tests. The presence of compounds that interfere with UV light (e.g., NO_3^-) and the formation of total trihalomethanes after pulsed-UV treatment were also studied. Pulsed-UV technology was highly effective for destroying NDMA. The pseudo–first-order rate constants were calculated to be in the range of 1.4 to 12.2 min^{-1}. This technology offers other benefits (e.g., disinfection) and can be applied directly to drinking water treatment. However, potential concerns in pulsed-UV photolysis of NDMA include (1) the formation of undesirable chemicals as reaction intermediates and (2) possible reformation/regeneration of NDMA after chlorination of pulsed-UV–treated effluent. Pulsed-UV with a small amount of H_2O_2 could be used to control the reaction by-products and to inhibit the reformation of NDMA by using hydroxyl radicals generated during an advanced oxidation process. In contrast, pulsed-UV with a larger amount of H_2O_2 could inhibit NDMA decay by direct photolysis.

Use of pulsed-UV processes to destroy NDMA
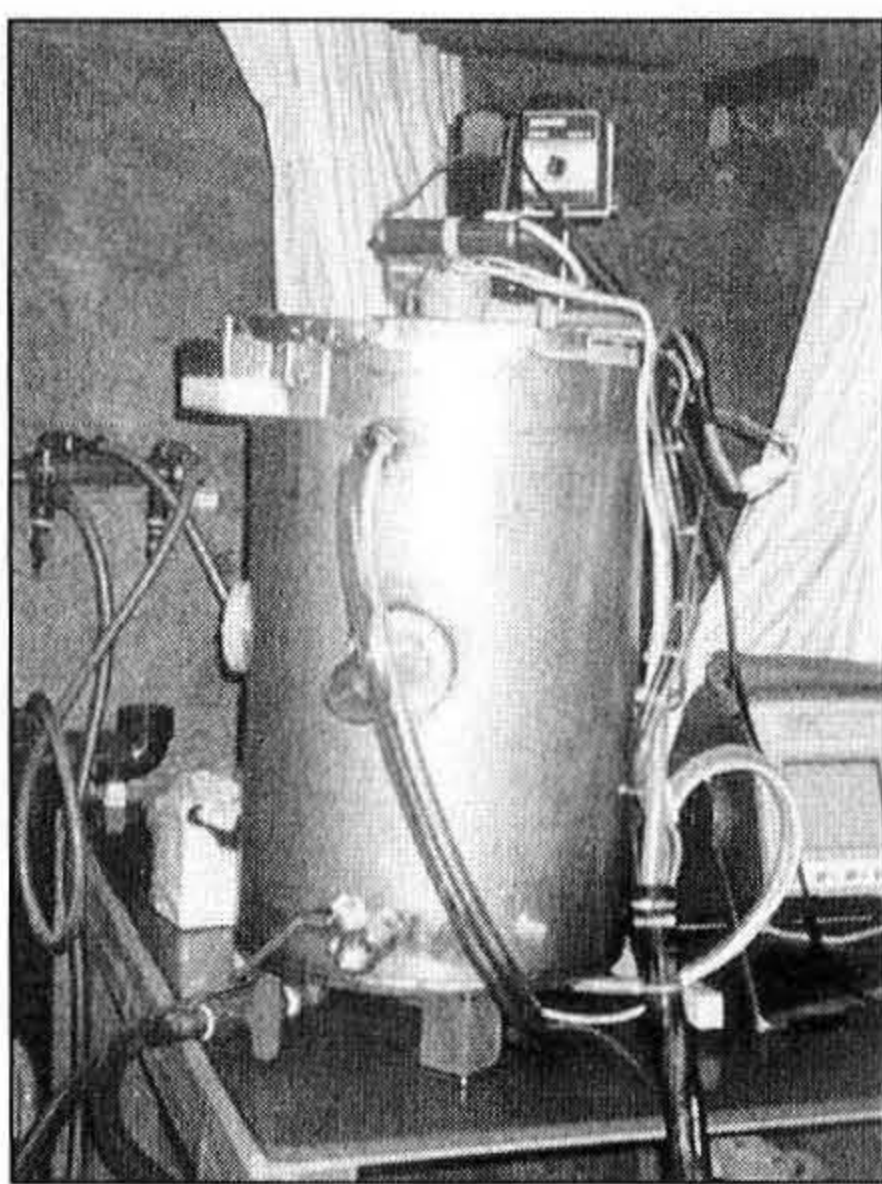
n February 1998, the presence of N-nitrosodimethylamine (NDMA) contamination in drinking water sources was detected at an aerospace facility in Northern California (CDHS, 2000). NDMA contamination was subsequently found in drinking water wells in Southern California (CDHS, 2000). NDMA is typically an oxidative degradation product of unsymmetrical dimethylhydrazine, a component of rocket fuel. However, NDMA is also formed during many kinds of manufacturing processes at industrial sites, as a by-product of reactions involving chemicals called alkylamines. Alkylamines include both natural and synthetic compounds that are found widely distributed throughout the environment.

The US Environmental Protection Agency has identified NDMA as a probable human carcinogen. Because NDMA has not historically been considered a common drinking water contaminant, no federal or state drinking water standards exist for it. In April 1998, the California Department of Health Services (CDHS) announced an action level of 2 ng/L for NDMA (CDHS, 2000). The level of NDMA found in a Northern California drinking water well in eastern Sacramento County was approximately 150 ng/L (CDHS, 2000). In Southern California, NDMA in the range of 70 to 3,000 ng/L (CDHS, 2000) was found in three drink-

FIGURE 1   Characteristics of various types of UV lamps and NDMA absorption spectrum

NDMA—N-nitrosodimethylamine, UV—ultraviolet
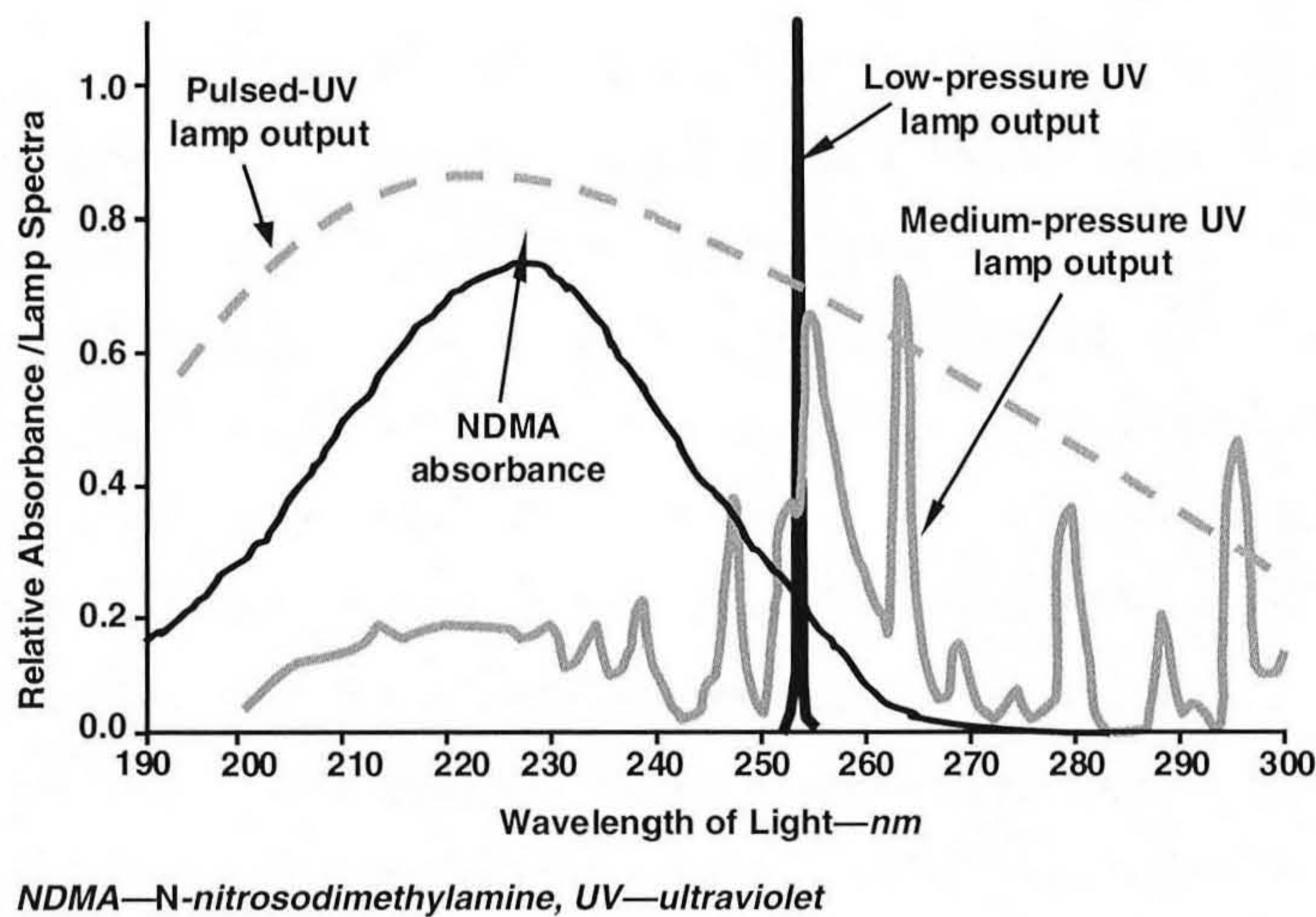
ing water wells in the San Gabriel Basin. It has recently been suggested that NDMA may be present in (1) sewage and reclaimed water after chlorination (Brennan & Robbins, 2000) and (2) surface water processed by conventional drinking water treatment methods (Choi et al, 2001; Davis et al, 2000). Although the exact mechanisms of NDMA formation are unknown, they appear to be associated with the chlorination process. In December 1999, the CDHS established a "temporary" action level of 20 ng/L for NDMA so that more utilities could participate in the initial screening effort. In March 2002, the CDHS revised its temporary action level to 10 ng/L (CDHS, 2003).

FIGURE 2   Schematic of pulsed-UV batch reactor—completely mixed batch reactor (A) and continuously stirred tank reactor (B)

The current widespread detection of NDMA and its changing regulatory status point to the need for a technology that can remediate drinking water sources contaminated by this compound. It is well known that NDMA can be reduced by ultraviolet (UV) technologies (Sharpless et al, 2001; Bolton et al, 2001; Calgon Carbon, 1996). Pulsed-UV has the potential to provide much more complete oxidation of NDMA because of its ability to deliver much higher UV light intensities than other continuous-wave UV technologies. In addition, pulsed-UV/hydrogen peroxide (H_2O_2), which uses the generation of hydroxyl radicals, is expected to react with NDMA and further break down intermediate NDMA degradation by-products to avoid the reformation of NDMA after chlorination. Therefore, there is a growing interest in pulsed-UV and pulsed-UV/H_2O_2 treatment processes for removing NDMA from drinking water.

BACKGROUND

Physical/chemical properties of NDMA. NDMA is the simplest dialkylnitrosamine, with a molecular formula of $C_2H_6N_2O$. It is a volatile, combustible, yellow, oily liquid (MOE, 1991). NDMA has a high water solubility (Table 1) and a low octanol–water-partitioning coefficient (log K_{ow} = –0.51) and can readily leach into groundwater. In addition, NDMA is not likely to bioaccumulate, adsorb to particulate, or volatilize (because of a low Henry's law constant, 2.63×10^{-7} atm-m^3/mol), which enhances its potential to move through soil and sediment into groundwater.

Pulsed-UV irradiation. Pulsed-UV irradiation uses high-intensity UV flash lamps. Flash lamps operate in the pulsed mode with peak intensities much greater than those that occur with continuous sources of the same average power. The pulse duration is typically in the microsecond time scale, whereas the interval between pulses is on the order of milliseconds. The electrical discharge quickly heats the fill gas to a high enough temperature (~15,000 K) to create a plasma that emits blackbody light characteristic of its temperature. Unique features of pulsed lamps include the ability to come to full power immediately (without a warmup period) and the ability
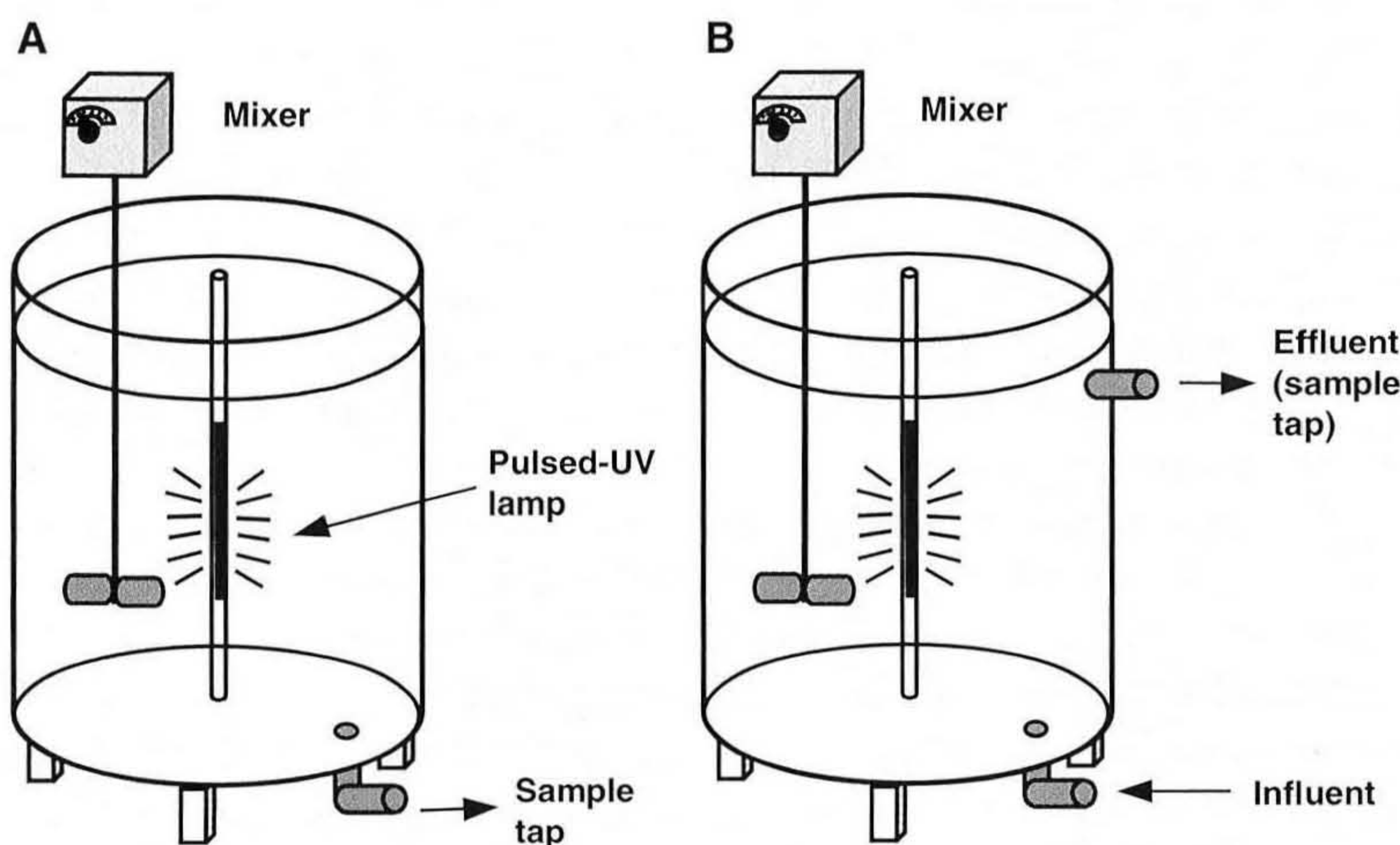
to shift the spectrum of a single lamp by simply changing the peak pulse power. Unlike low- or medium-pressure mercury-based lamps, commonly used fill gases for pulsed-UV lamps include xenon, argon, and other inert gases or mixtures. Thus, lamp breakage does not pose any significant challenges compared with those from the mercury-based lamps. Xenon plasmas generally have the greatest efficiency for photon production.

Pulsed-UV treatment systems are polychromatic in nature, providing continuous spectra between the wavelengths of 185 and 1,000 nm. With high plasma temperature occurring during pulsing, the low-wavelength emission reaches maximum energy level. A typical xenon flash lamp is maximized at 230 nm and has significant output at wavelengths below 200 nm (Figure 1). However, excessively high pulse energies increase thermal stresses and may shorten the life of a lamp. Pulsed-UV flash lamp intensities of several hundred to 1,000 W/in. (discharge length) contrast with a few hundred watts per inch for low- and medium-pressure mercury lamps. The greater power density may allow the use of a shorter contact time or a smaller contactor.

Photolysis and oxidation of NDMA. NDMA absorbs UV light in a strong band centered at 228 nm (Figure 1) and a weak band centered at 332 nm, resulting in breakdown of the nitrogen–nitrogen bond in the molecule—the primary mechanism of NDMA removal (Bircher et al, 1999). Because the absorption band is strong, direct photolysis of NDMA by UV technologies alone is a promising treatment process. Pulsed xenon lamps are even more capable of direct photolysis of NDMA than low-pressure mercury lamps because of the greater polychromatic wavelength produced between 200 and 300 nm (Figure 1).
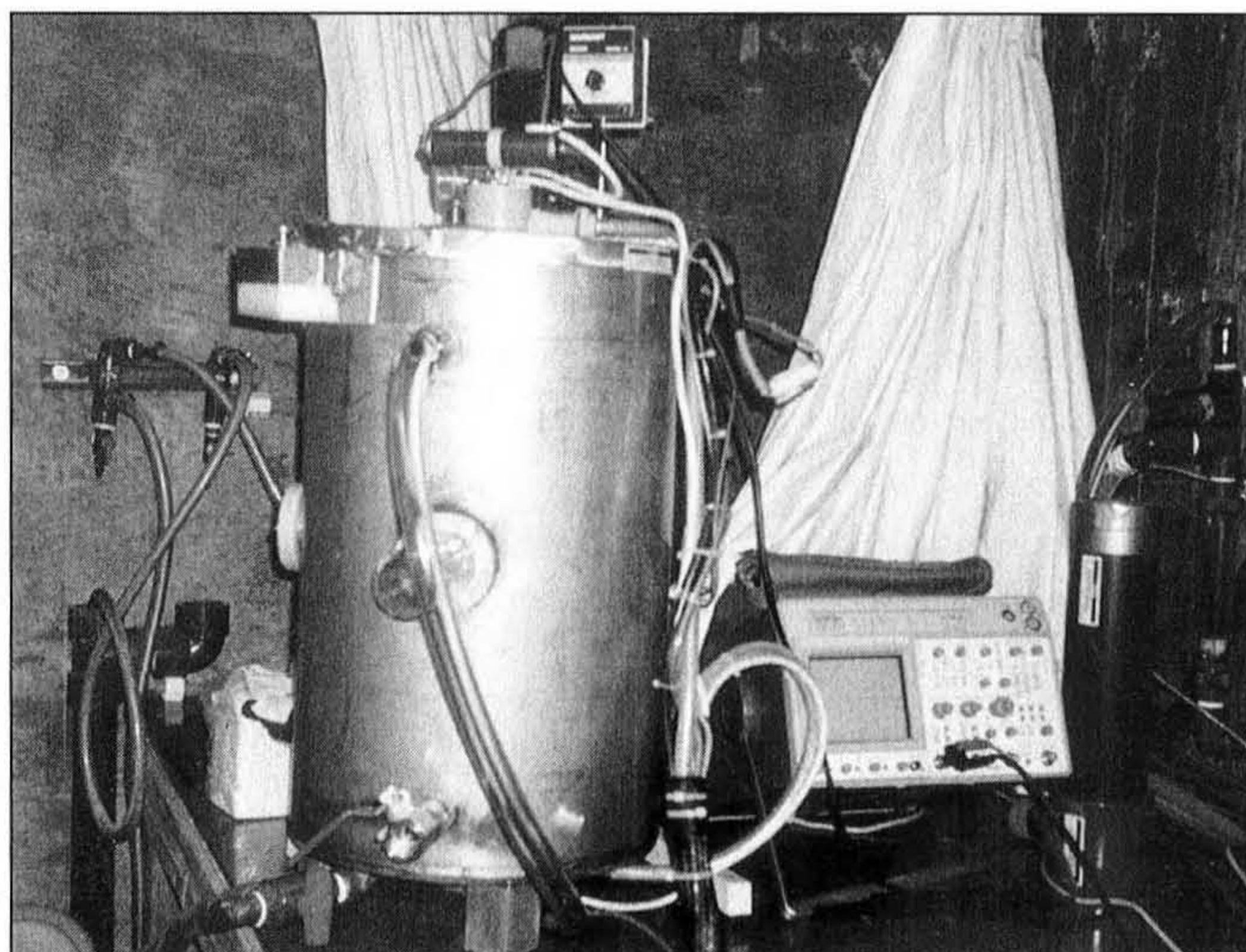
A pulsed-ultraviolet (UV) system can effectively treat water contaminated by *N*-nitrosodimethylamine with the use of a non–mercury-based lamp. Applied UV dosage for a pulsed-UV system can be adjusted easily by changing the lamp's pulse frequency.

When H_2O_2 is present during the UV process, hydroxyl radicals ($\cdot OH$) can be produced by the photolysis of H_2O_2, as shown in Eq 1.

$$H_2O_2 \xrightarrow{h\nu} 2 \cdot OH \qquad (1)$$

The hydroxyl radicals attack organic compounds nonselectively, with rate constants ranging from 10^7 to 10^9 L $\times$ mol^{-1} $\times$ s^{-1}. The rate constant of NDMA oxidation by hydroxyl radicals is 3.3×10^8 L $\times$ mol^{-1} $\times$ s^{-1} (Buxton et al, 1988), and this may serve as a secondary NDMA removal mechanism.

LITERATURE REVIEW

Treatment technologies. Because of NDMA's highly water-soluble, polar nature, it cannot be effectively removed from water using air-stripping, reverse osmosis membranes, or granular activated carbon (Jobb et al, 1994; Jobb et al, 1992). Jobb et al (1994, 1992) showed that low-pressure mercury UV lamp irradiation could reduce NDMA from 89 to 5 ng/L at a UV dosage of approximately 2.6 kW·h/m^3 (or 10 kW·h/1,000 gal) in the laboratory-scale test. Furthermore, pilot-scale studies (Jobb et al, 1994; Jobb et al, 1992) found that a UV dose of 1.26 kW·h/m^3 (or 4.85 kW·h/1,000 gal) was effective in reducing NDMA to <5 ng/L. Bircher et al (1999) reported that NDMA was reduced from 53 to 2 ng/L in groundwater with a UV dose of 0.39 kW·h/m^3 (1.5 kW·h/1,000 gal) produced through a medium-pressure lamp.

Potential destruction pathway for NDMA. When NDMA strongly absorbs UV light in a band centered around 228 nm, an unstable dimethylamino radical and a nitric oxide (NO) radical are initially formed. Bircher et al (1999) proposed that the dimethylamino and NO radi-

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FIGURE 3 Correlation between hydraulic retention time and UV dose for the pulsed-UV system used
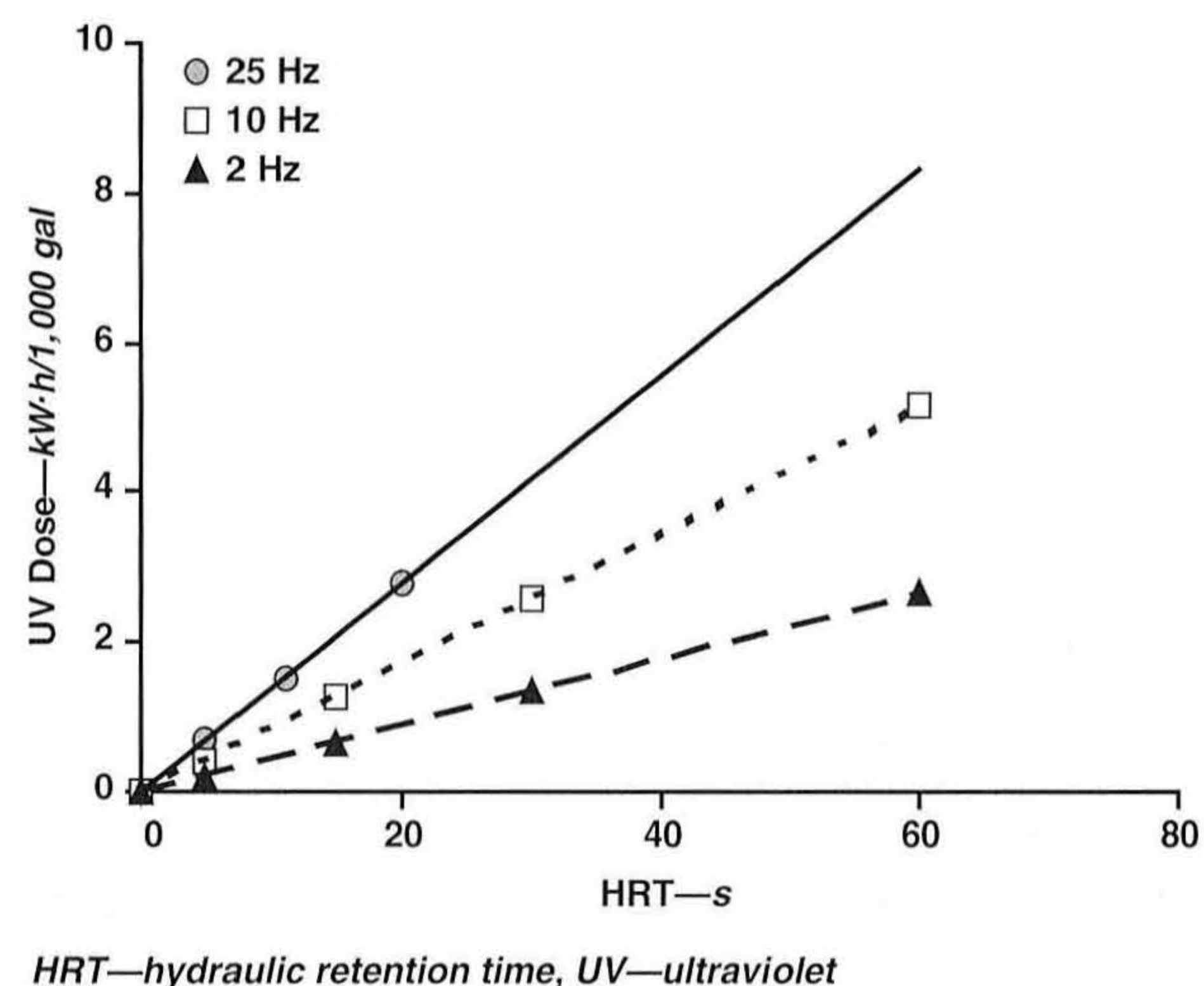

HRT—hydraulic retention time, UV—ultraviolet

TABLE 1   Chemical properties of *N*-nitrosodimethylamine

Chemical Property	Measurement
Molecular weight	74.08 g/mol
Boiling point at 760 mmHg	151–154 °C
Melting point	–50°C (estimated)
Vapor pressure @ 20°C	2.7 mmHg
Vapor density at 25°C	2.56 g/L
Density at 20°C	1.0048
Solubility	Miscible, 3,978 mg/L
Henry's law at 25°C	2.63×10^{-7} atm-m³/mol (estimated)
Log K_{oc}	1.41
Log K_{ow}	–0.57

TABLE 2   Raw water quality characteristics

Parameters	Deionized Water*	Southern California Groundwater	Colorado River Water
Total organic carbon—*mg/L*	0.11	0.17	3.04
Electrical conductivity—*µmhos*	1.08	389	919
Nitrate—*mg/L*	ND†	1.98	1.1
Alkalinity—*mg/L*	NA‡	166	131
Turbidity—*ntu*	NA	0.07	0.88
pH—*unit*	5.4	7.76	8.29
Ultraviolet absorbance at 254 nm—*abs/cm*	ND	ND	0.1

*Super-Q,© Millipore Corp., Bedford, Mass.
†ND—not detected
‡NA—not applicable

FIGURE 4   Effects of pulsed-UV dosages on NDMA reduction in deionized water
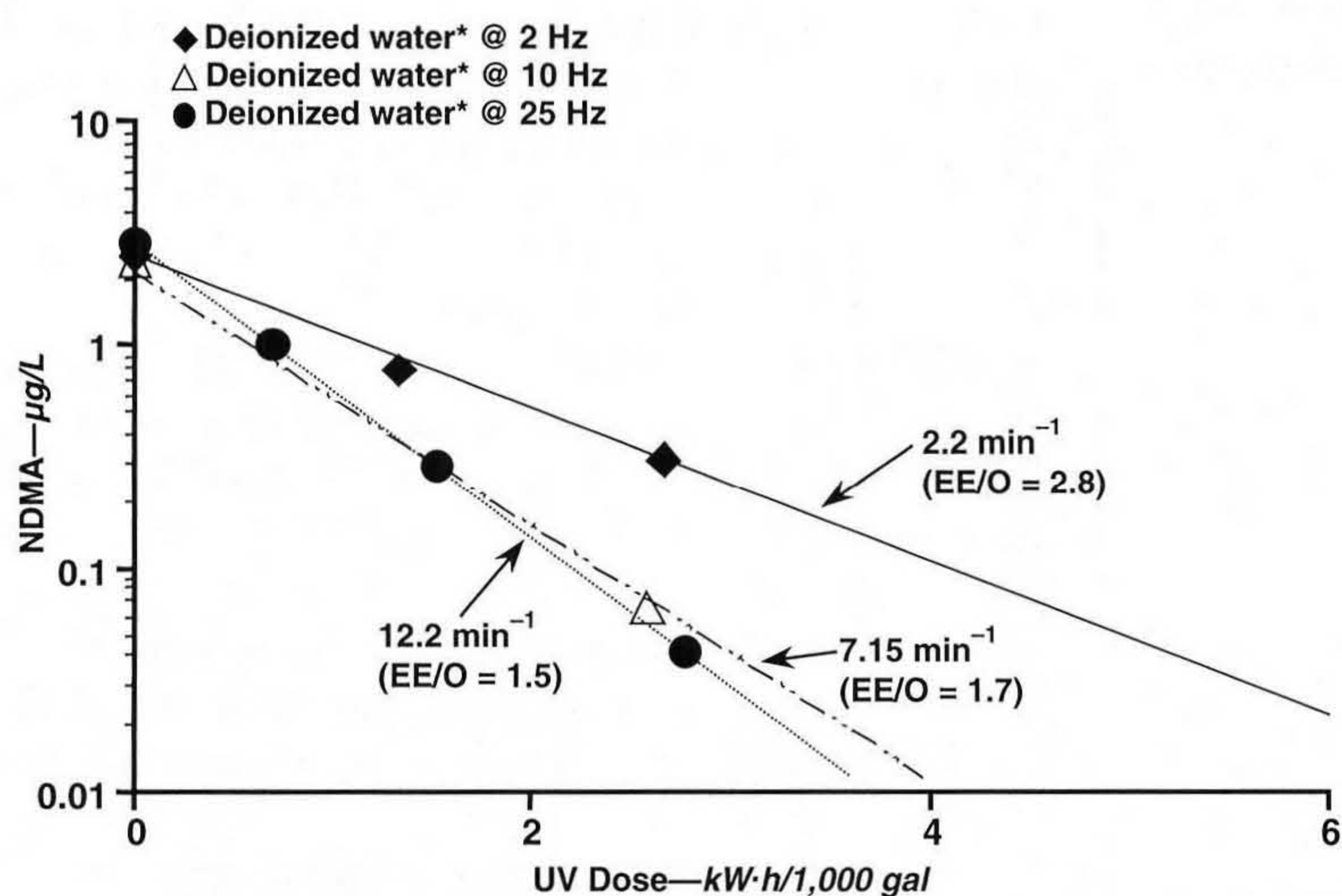
Super-Q©, Millipore Corp., Bedford, Mass.
EE/O—electrical energy per order, NDMA—N-nitrosodimethylamine, UV—ultraviolet

cals could react with a hydroxyl radical and oxygen to become bicarbonate and nitrate (NO_3^-), respectively. The dimethylamino radical has the potential to combine readily with a hydroxyl radical abstracted from a water molecule to form dimethylamine (Challis et al, 1978). Dimethylamine may combine with nitrite to reform NDMA under certain conditions. This might explain the reformation/regeneration of NDMA following chlorination of UV-irradiated water.

OBJECTIVES

The main objective of this study was to evaluate the effectiveness of pulsed-UV and pulsed-UV/ H_2O_2 processes for NDMA removal. The following goals were pursued during the course of the study:

• investigate the effects of pulsed-UV dosage on NDMA destruction,

• determine the effects of pulsed-UV and H_2O_2 dosages in pulsed-UV/H_2O_2 processes for NDMA removal,

• evaluate the effects on NDMA destruction exerted by other pulsed-UV–absorbing compounds that compete for pulsed-UV light,

• using flowthrough tests, evaluate the effects of pulsed-UV and pulsed-UV/H_2O_2 dosages on various levels of NDMA, and

• investigate the possible reformation/regeneration of NDMA in water treated with pulsed-UV.

EXPERIMENTAL DESIGN

Batch reactor description. The pulsed-UV system[1] consisted of a 316-grade stainless-steel batch reactor that included a mixer, a 5-kW power source, and a 15-cm xenon-filled, tungsten-electrode lamp[2] inside a quartz jacket—a conduit for deionized (DI) cooling water. For benchtop experiments, this lamp arrangement was housed inside a treatment chamber that could be operated as either a completely mixed batch reactor (CMBR) or a continuously stirred tank reactor (CSTR) system (Figure 2). With power applied to the lamp,

a standby "simmer mode" of steady-state partial ionization of the xenon gas was maintained with a low-current arc between the electrodes (Smith, 1986). Pulses were generated by an electrical discharge that quickly heated the xenon gas and created a plasma of ionized gas, which reached a temperature high enough (near 15,000 K) to emit blackbody light radiation from 185 to 400 nm and above. The electrical hardware allowed the bulb to operate up to 30 flashes/s.

In the CMBR experiments, the pulsed-UV reaction volume was 10 or 12 gal (0.038 or 0.045 m³), and samples were taken from the reactor after various exposure times. In the CSTR experiments, the pulsed-UV reaction volume was 13 gal (0.049 m³) with a flow rate of 7.4 gpm (0.028 m³/min). The samples were collected after approximately four retention times. Both US pharmaceutical-grade H_2O_2 (at 3% by weight) and NDMA[3] (at 5,000 µg/mL) were prespiked to a desired concentration, when appropriate, into 5 gal (0.019 m³) carboys in the fume hood. The NDMA-spiked carboys were covered in black plastic bags to avoid any exposure to sunlight during transfer to the reactor.

Bench-scale tests. The pulsed-UV irradiation and pulsed-UV/H_2O_2 tests for NDMA reduction were conducted in two phases. The study tested three types of water: organic-free DI water,[4] Colorado River water (CRW), and a Southern California groundwater. The first phase of testing was performed in a CMBR to determine (1) the required pulsed-UV dosage and H_2O_2-to-NDMA ratios for NDMA oxidation and (2) the optimum retention time for NDMA destruction. The effects of other compounds (e.g., NO_3^-) on NDMA destruction and the possible reformation of NDMA were also investigated in the CMBR setup. The second-phase tests were conducted in a CSTR to investigate the effects of two influent NDMA concentrations (100 and 3,000 ng/L) on NDMA removal and to validate the optimized conditions for NDMA removal with a pulse frequency of 25 Hz and a hydraulic retention time (HRT) of 1.75 min.

Sampling. DI water, CRW, and groundwater pumped from the Southern California region were analyzed for turbidity, pH, alkalinity, conductivity, bromide, NO_3^-, UV light absorbance at 254 nm (UV_{254}), sulfate, and total organic carbon (TOC). Kinetic samples were also taken from the CMBR and CSTR at various time intervals. Analyses for H_2O_2 residual, NDMA, and NO_3^-, when appropriate, were conducted for the kinetic samples.

Analytical methods. All inorganic and organic analyses were performed at the Metropolitan Water District of Southern California's Water Quality Laboratory. Each
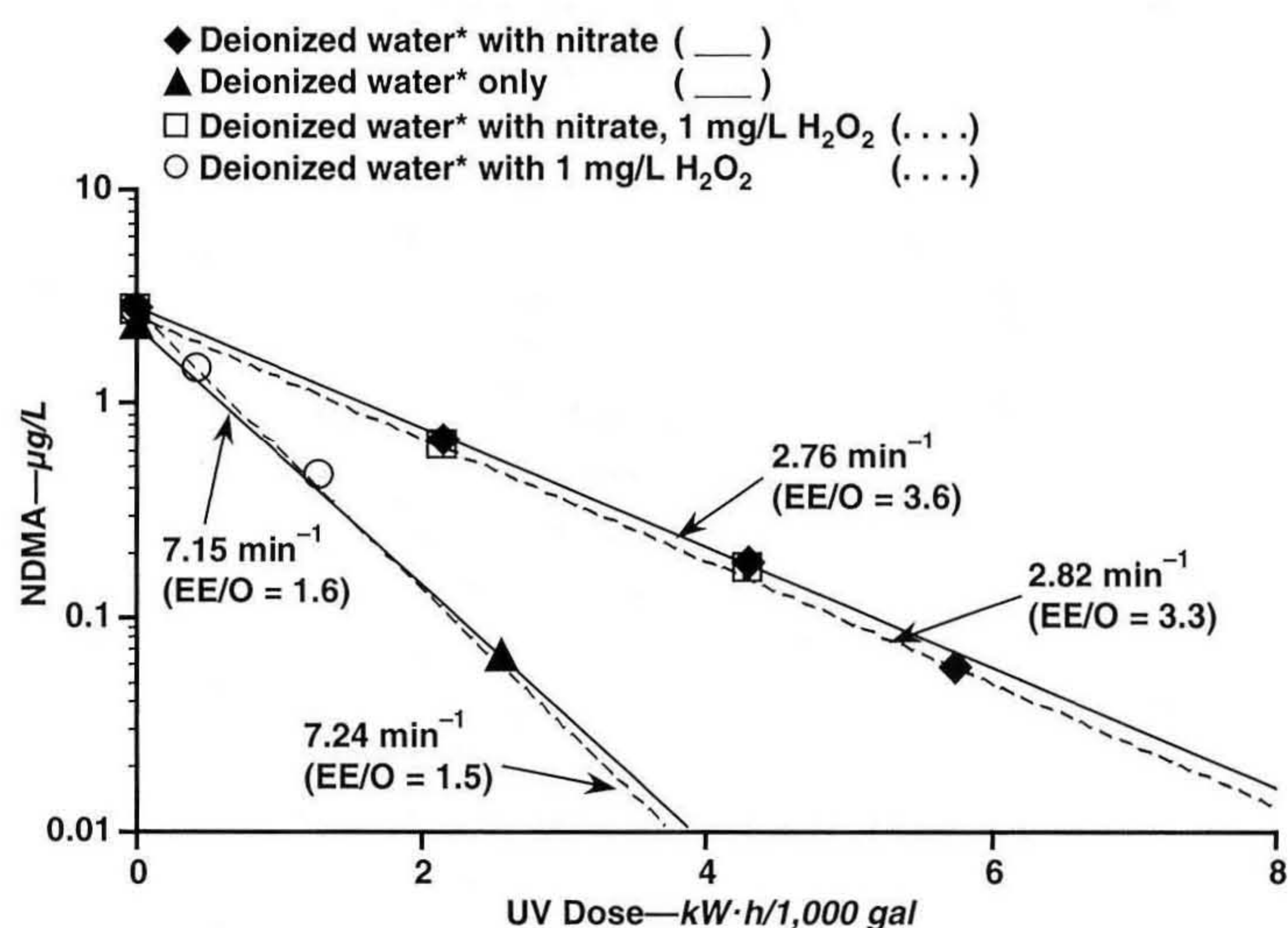

FIGURE 5   Effects of source water on NDMA reduction at 10 Hz
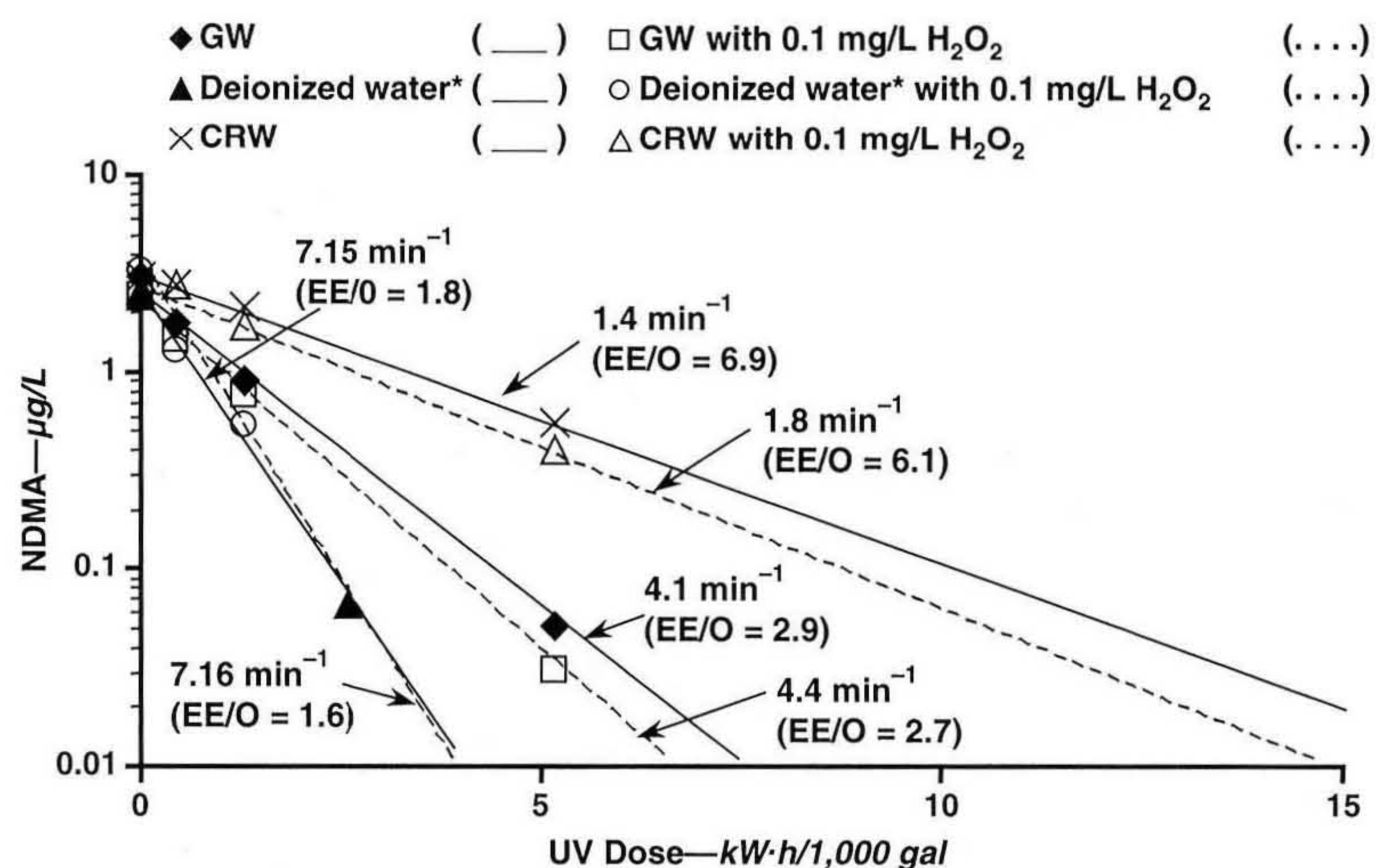
Super-Q©, Millipore Corp., Bedford, Mass.
CRW—Colorado River water, EE/O—electrical energy per order, GW—groundwater, H_2O_2—hydrogen peroxide, NDMA—N-nitrosodimethylamine, UV—ultraviolet
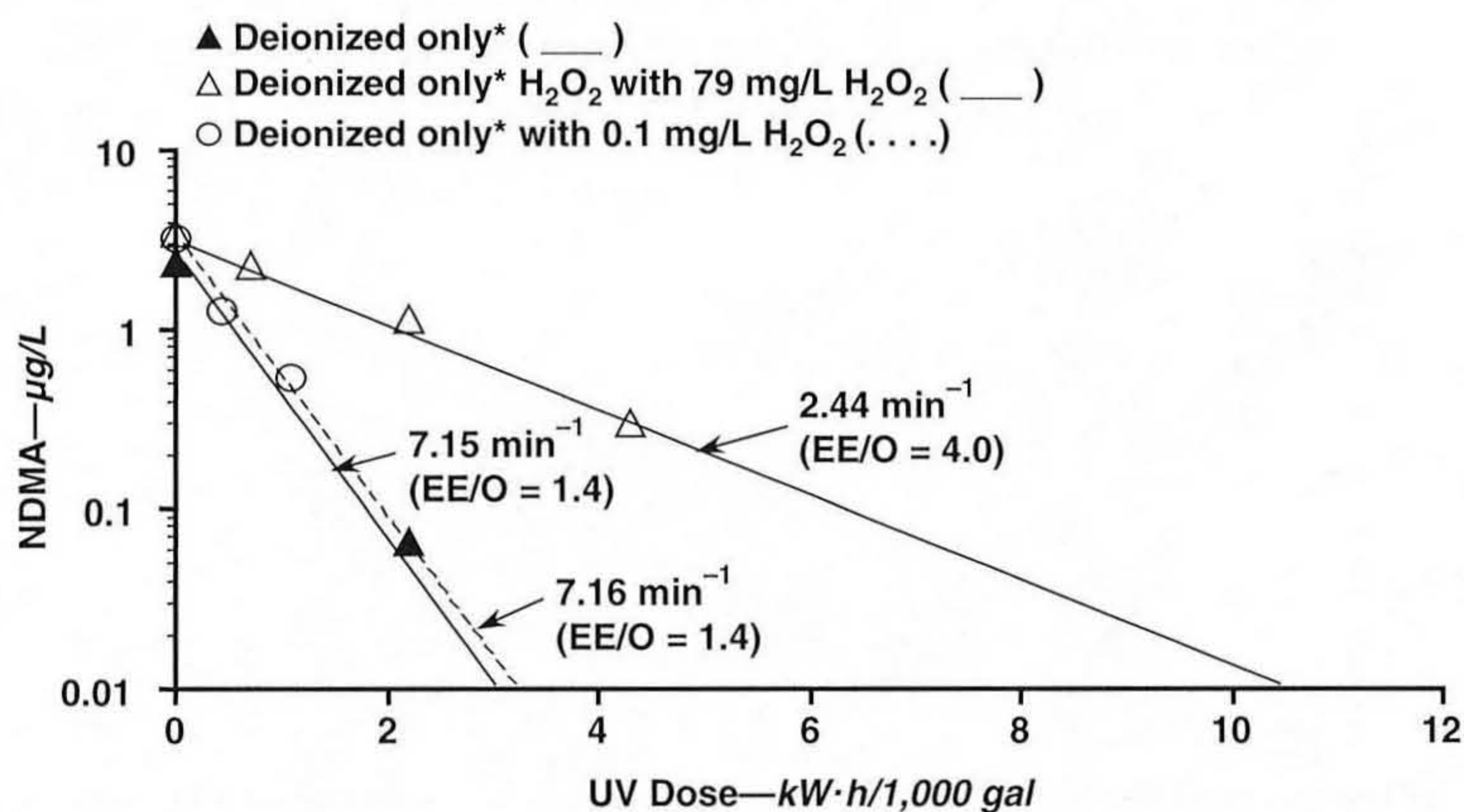

FIGURE 6   Effects of nitrate on NDMA reduction in deionized water* at 10 Hz

Super-Q©, Millipore Corp., Bedford, Mass.
EE/O—electrical energy per order, H_2O_2-hydrogen peroxide, NDMA—N-nitroso-dimethylamine, UV-ultraviolet

FIGURE 7   Effects of H_2O_2 on NDMA reduction in deionized water* at 10 Hz

▲ Deionized only* (___)
△ Deionized only* H_2O_2 with 79 mg/L H_2O_2 (___)
○ Deionized only* with 0.1 mg/L H_2O_2 (. . . .)

2.44 min⁻¹ → $2.44\ min^{-1}$ (EE/O = 4.0)

$7.15\ min^{-1}$ (EE/O = 1.4)

$7.16\ min^{-1}$ (EE/O = 1.4)

NDMA—µg/L

UV Dose—kW·h/1,000 gal

*Super-Q©, Millipore Corp., Bedford, Mass.
EE/O—electrical energy per order, H_2O_2—hydrogen peroxide, NDMA—N-nitroso-
dimethylamine, UV—ultraviolet

analysis was conducted in accordance with the procedures described in *Standard Methods* (1995), except as noted in the following paragraphs.

Residual H_2O_2. The analyses for H_2O_2 residual involved the reactions of H_2O_2 with *p*-hydroxy-phenylacetic acid and horseradish peroxidase, followed by detection of the fluorescent product by a fluorescence spectrophotometer,[5] as described by Kok et al (1986).

NDMA. Prior to June 1999, NDMA samples were analyzed by a contract laboratory,[6] which extracted NDMA samples by continuous liquid–liquid extraction and analyzed the extract by gas chromatography/mass spectrometry (GC/MS), using a selected ion-monitoring mode to determine NDMA. This method has a detection limit of 20 ng/L. NDMA samples taken after June 1999 were analyzed at the Canadian Ministry of the Environment, Etobicoke, Ont. NDMA was analyzed by a solid-phase extraction method combined with low-resolution GC/MS, as described by Taguchi et al (1994). This method has a detection limit of 1 ng/L. Before the NDMA samples were submitted for analysis, catalase was spiked into the samples to quench the residual H_2O_2 and prevent any further NDMA reaction.

Simulated distribution system (SDS) tests. The water samples were dosed with chlorine at 1.5 mg/L in the laboratory and incubated at 25°C for one day. The chlorine dosage of 1.5 mg/L was chosen because preliminary chlorine demand tests indicated that this was the dosage needed to maintain a residual of at least 0.2 mg/L after 24 h. Analyses were conducted on SDS samples to evaluate the formation of pentane-extractable disinfection by-products (DBPs)—such as total trihalomethanes (TTHMs), haloacetonitriles (HANs), haloketones (HKs), and chloropicrin—that used modi-

fied THM liquid–liquid extraction as described by Koch et al (1988).

RESULTS AND DISCUSSION

Raw water quality. The pertinent raw water quality parameters of the water tested in this study are listed in Table 2. In general, DI water contains low TOC concentrations, low conductivity, and nondetectable levels of NO_3^- and UV_{254} absorbing organic compounds. CRW typically contains high concentrations of TOC, conductivity, turbidity, and UV_{254}-absorbing organic compounds. The groundwater selected for this study contained high concentrations of total alkalinity, low concentrations of TOC and turbidity, and NO_3^- at approximately 2 mg/L.

The characteristics of the water can play an important role in UV treatment. For example, high turbidity lowers the transmittance of the source water, thus lowering the penetration of the UV for effective photolysis. Also, water with constituents that strongly absorb UV light (such as NO_3^-) can compete for UV light with NDMA, thus reducing removal efficiency.

NDMA removal. The following discussion of NDMA removal examines the effects of pulsed-UV dosage, source water, H_2O_2, and NO_3^-, as well as the effects of initial NDMA concentration. Overall, effective reduction of NDMA was observed for most of the test conditions used. A pseudo–first-order kinetic model can fit NDMA removal data as described in Eq 2.

$$\ln (C/C_0) = -kt \qquad (2)$$

in which C is the NDMA concentration (µg/L), C_0 is the initial NDMA concentration (µg/L), k is the pseudo–first-order rate constant (min⁻¹), and t is time (min).

The calculated pseudo–first-order rates for the conditions used are shown in Figures 3–7 for the conditions used. Rates for each water matrix with H_2O_2 are also shown in the figures. For comparison purposes, electrical energy per order (EE/O) values are also included for the pseudo–first-order rates in these figures.

Effects of UV dosage. UV dosage is commonly derived from the product of average UV irradiance and theoretical contact time (or HRT) (Figure 3). For conventional low-pressure UV, UV irradiance is usually measured by collimated beam test equipment (e.g., a joulemeter or radiometer) at bench scale, and residence time distribution is determined by tracer studies. However, reliable determination of UV dosages for CMBR and CSTR systems is much more difficult. This is especially true for polychromatic UV light, such as pulsed UV, because determination

of the synergistic effect of multiple peaks on the compounds used in dose measurement is more challenging than for the case with single-wavelength, low-pressure UV. As a result, pulsed-UV dosage cannot be accurately provided in millijoules per square centimetre. Alternatively, UV dosage can be represented by a measure of total lamp electrical energy applied (power [kW] × time [h]) to a fixed volume of water (1,000 gal [3.785 m³]) to reflect parameters such as flow rate (or HRT) and lamp energy into a combined number. Therefore, UV dosage in kilowatt hours per 1,000 gal, as described in Eq 3, was used throughout this study.

$$UV\ dose = average\ power\ input\ (kW)$$
$$\times \frac{residence\ time\ (h)}{reactor\ volume\ (gal)}$$
$$\times \frac{1,000\ gal}{1,000\ gal} \quad (3)$$

The energy input to the system was calculated by using the HRT and power requirement from the pulsed-UV system (lamp and system) used for this study at 1.6, 3.1, and 5 kW at 2, 10, and 25 Hz, respectively. Approximately 1 kW was a system power requirement, and the remaining energy input was for the lamp.

UV dosage can also be provided in EE/O of NDMA destruction. EE/O is the UV dosage required for 90% (1-log) reduction from the initial concentration. EE/O values are also provided in this article, when appropriate, to be used in comparing the efficacy of NDMA destruction with that of the more commonly used mercury lamps.

NDMA-spiked DI water was irradiated in the absence of H_2O_2 at pulsed-UV frequency inputs of 25, 10, and 2 Hz in a CMBR system. Because DI water contains an insufficient amount of background precursor to generate hydroxyl radicals, the process of NDMA removal is likely to be dominated by direct photolysis of NDMA. It is apparent that the NDMA level decreases with increasing UV dosage (irradiation time) at the same pulse input (frequency), as shown in Figure 4. For example, NDMA removals of 69 and 88% in DI water were achieved with applied UV doses of 1.3 and 2.6 kW·h/1,000 gal, respectively, at a pulse input of 2 Hz. According to Eq 1, the kinetic rates of NDMA decay are 12.2,

TABLE 3 Effects of NO₃⁻* on NDMA† reduction in deionized water‡ at 10 Hz in a completely mixed batch reactor system

Irradiation Time s	UV Dose kW·h/1,000 gal	Pulsed-UV§ Alone		Pulsed-UV + 1.0 mg/L H₂O₂**		
		NDMA ng/L	NO₃⁻ mg/L	NDMA μg/L	NO₃⁻ mg/L	H₂O₂ Residual μg/L
0	0	2,800	38.4	2,700	NA††	870
30	2.2	690	NA	640	NA	900
60	4.3	180	NA	170	NA	870
80	5.7	58	34.1	NA	NA	NA
120	8.6	NA	NA	19	NA	800
Percent removal		97.9%	NA	99.2%	NA	NA

*NO₃⁻—nitrate
†NDMA—N-nitrosodimethylamine
‡Super-Q,© Millipore Corp., Bedford, Mass.
§UV—ultraviolet
**H₂O₂—hydrogen peroxide
††NA—not applicable

TABLE 4 Effects of NO₃⁻ on NDMA reduction in Southern California groundwater at 25 Hz in a continuously stirred tank reactor system*

Sampling Location	UV Dose kW·h/1,000 gal	Pulsed-UV† Alone		Pulsed-UV + 1.0 mg/L H₂O₂‡		
		NDMA ng/L	NO₃⁻ mg/L	NDMA μg/L	NO₃⁻ mg/L	H₂O₂ Residual μg/L
Influent	NA§	2,300	41.6	2,400	39.9	NA§
Effluent	11.2	140	37	110	37.2	NA
Percent removal		93.9%	NA	95.4%	NA	NA

*NO₃⁻—nitrate, NDMA—N-nitrosodimethylamine
†UV—ultraviolet
‡H₂O₂—hydrogen peroxide
§NA—not applicable

TABLE 5 Effects of initial NDMA* concentration on NDMA reduction in Southern California groundwater at 25 Hz in a continuously stirred tank reactor system

Sampling Location	UV Dose kW·h/1,000 gal	Pulsed-UV† Alone			Pulsed-UV + 1.0 mg/L H₂O₂‡	
		Test 1 NDMA ng/L	Test 2 NDMA ng/L	Test 3 NDMA ng/L	NDMA⁻ ng/L	H₂O₂ Residual μg/L
Influent	NA§	2,800	100	100	92	NA
Effluent	11.2	30	19	1.6	1.5	NA
Percent removal		98.9%	98.1%	98.4%	98.3%	NA

*N-nitrosodimethylamine
†UV—ultraviolet
‡H₂O₂—hydrogen peroxide
§NA—not applicable

TABLE 6   Effects of H_2O_2 on NDMA reformation in a continuously stirred tank reactor system*

NDMA in Southern California Groundwater				NDMA in Deionized Water†				
UV‡ Dose kW·h/1,000 gal	Pulsed- UV Alone ng/L	Pulsed-UV + 1 mg/L H_2O_2 ng/L	H_2O_2 Residual μg/L	UV Dose kW·h/1,000 gal	Pulsed- UV Alone ng/L	UV Dose kW·h/1,000 gal	Pulsed-UV + 1 mg/L H_2O_2 ng/L	H_2O_2 Residual μg/L
11.2	1.6	1.5	NA§	5.7	58	8.6	19	800
1 mg/L Cl_2** for five days	3.9	1.5	NA§	1 mg/L Cl_2 for five days	99	1 mg/L Cl_2 for five days	35	NA

*H_2O_2—hydrogen peroxide, NDMA—N-nitrosodimethylamine
†Super-Q,© Millipore Corp., Bedford, Mass.
‡UV—ultraviolet
§NA—not applicable
**Cl_2—chlorine

7.15, and 2.2 min^{-1} for pulsed-light inputs of 25, 10, and 2 Hz, respectively. A comparison of the kinetic rates of NDMA decay at pulsed-light inputs of 25, 10, and 2 Hz suggests that strong pulsed-UV intensity is produced at the high pulsed-light input of 25 Hz, resulting in more effective reduction of NDMA. However, optimization of the energy input (frequency) may be needed in the design of a pulsed-UV system.

Effects of source water. Different source water supplies, such as Southern California groundwater and CRW spiked with NDMA, were irradiated at the pulsed-light input of 10 Hz (Figure 5). Over the duration of the experiments (<5 min), the pH of the water did not change significantly. NDMA removals of 98% in Southern California groundwater and 82% in CRW were achieved with an applied pulsed-UV dose of 5.2 kW·h/1,000 gal. The kinetic rates of NDMA decay were 4.1 min^{-1} in Southern California groundwater and 1.4 min^{-1} in CRW. The results might suggest a strong competition for the pulsed-light absorption between NDMA and background organic compounds (e.g., TOC or a UV-absorbing organic) in Southern California groundwater and CRW. It appeared that pulsed-UV alone was more effective in destroying NDMA in the Southern California groundwater than in CRW, because CRW contained higher levels of both background organic compounds (which may compete for pulsed UV) and turbidity (which reduces the applied UV as a result of the lower transmittance) than did the Southern California groundwater.

Effects of UV/H_2O_2. The rate of NDMA dissociation by UV is much faster than the rate of NDMA oxidation by hydroxyl radicals; thus, the addition of H_2O_2 does not necessarily increase the NDMA removal efficiency. Furthermore, H_2O_2 only weakly absorbs pulsed-UV light at a peak wavelength of 200 nm compared with NDMA. NDMA-spiked DI water was irradiated in the presence of H_2O_2. The effects of H_2O_2 on NDMA removal with 0.1 and 1.0 mg/L H_2O_2 (at molar H_2O_2-to-NDMA ratios of 68 and 784) were investigated at a pulsed-UV input of 10

Hz (Figures 5 and 6). With the addition of H_2O_2, the kinetic rates of NDMA decay were 7.16 and 7.24 min^{-1} for 0.1 and 1.0 mg/L H_2O_2, respectively. Compared with the use of pulsed-UV alone at 10 Hz, the addition of H_2O_2 did not significantly increase the kinetic rate of NDMA decay. These results showed that pulsed-UV alone and pulsed-UV with a low concentration of H_2O_2 were equally effective in reducing NDMA.

Because NDMA removal is primarily accomplished by direct photolysis, rather than by hydroxyl radicals, the presence of a small amount of H_2O_2 had no major effect on the efficiency of NDMA removal. Similar results were observed in NDMA-spiked Southern California groundwater and CRW (Figure 5). However, the presence of a high concentration of H_2O_2 (79 mg/L) significantly hindered NDMA reduction because of the strong competition for UV light by the high concentration of H_2O_2 (Figure 7). The kinetic rate decreased from 7.15 min^{-1} in the absence of the H_2O_2 spike to 2.44 min^{-1} with the addition of 79 mg/L H_2O_2. The production of hydroxyl radicals from H_2O_2 did not improve NDMA reduction, because the oxidation of NDMA by hydroxyl radicals is much slower compared with direct photolysis of NDMA. In fact, the addition of a high concentration of H_2O_2 resulted in a decreased NDMA decay rate because of the strong competition for UV light in the presence of a high concentration of H_2O_2. Thus, H_2O_2 dosage should be optimized if it must be added to inhibit reformation of NDMA upon chlorination of UV-treated effluent.

Effects of NO_3^-. The UV absorption spectrum of aqueous NO_3^- solution features two bands in the ranges of 230–240 nm and 300–310 nm, which are close to the absorption bands of the aqueous NDMA solution (Calgon Carbon, 1996). For the direct photolysis process, a strong competition for UV light absorption between NO_3^- ions and NDMA can reduce the effectiveness of NDMA removal. In addition to direct photolysis of NO_3^- ions, the irradiation of NO_3^- in its long-wavelength absorption at the maximum of 302 nm results in two primary photo-

chemical pathways (Warneck & Würzinger, 1988; Zepp et al, 1987), as shown in Eq 4.

$$NO_3^- \xrightarrow{h\nu} NO_3^{-*} \begin{cases} \rightarrow NO_2^- + O\ (^3P) \\ \rightarrow NO_2^- + \cdot O^- \end{cases}$$ (4)
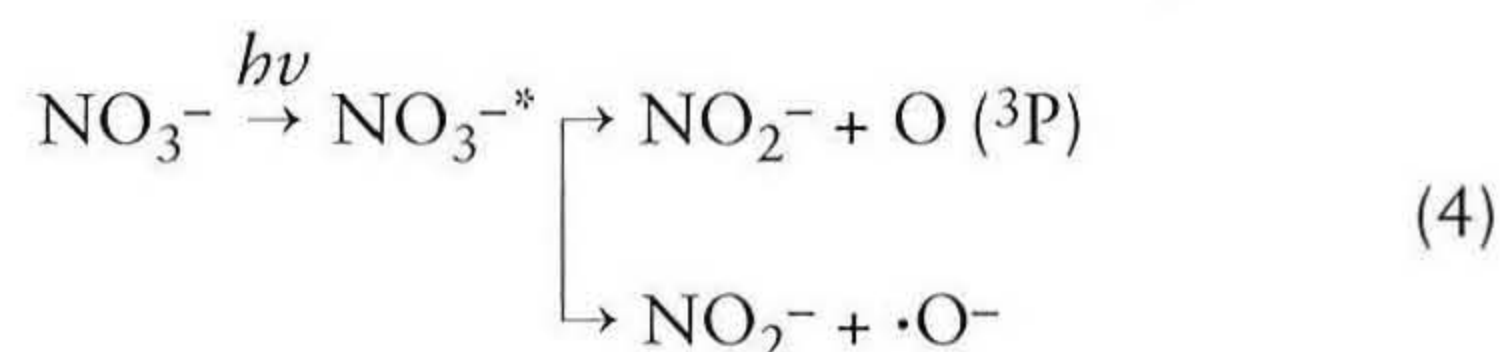
The $\cdot O^-$ radical ion generated by the reaction pathway shown in Eq 4 subsequently combines with a proton to form a hydroxyl radical. It is suggested that photochemically induced hydroxyl radicals from NO_3^- may oxidize organic chemicals such as NDMA. However, in some cases, the net effect may be small or even negative, because NO_3^- competes for UV light, which is the dominant source of the NDMA removal mechanism.

NDMA-spiked DI water was irradiated in the presence of NO_3^- at a pulsed-light input of 10 Hz in the CMBR (Table 3). The kinetic rate of NDMA decay decreased from 7.15 min^{-1} in the absence of NO_3^- to 2.76 min^{-1} in the presence of 38 mg/L NO_3^- (Figure 6). It is apparent that NO_3^- competed with NDMA for UV light, consequently limiting the effectiveness of direct photolysis in breaking down NDMA. As discussed earlier, the results did not show any nitrate-induced, photooxidation–enhanced NDMA reduction, because hydroxyl radical–mediated NDMA oxidation is a slower process than direct photolysis of NDMA by UV.

With the addition of 1.0 mg/L H_2O_2, the kinetic rate of NDMA decay changed only insignificantly (from 2.76 to 2.82 min^{-1}) in the presence of NO_3^-, as previously shown. Similarly, in a CSTR system, no significant difference in NDMA removal was shown between the use of pulsed-UV alone (93.9%) and pulsed-UV with 1.0 mg/L H_2O_2 (95.4%) in the presence of approximately 40 mg/L NO_3^- in Southern California groundwater at the pulsed-UV input of 25 Hz. Under all tested conditions, NO_3^- was reduced only up to 11%, in contrast with the NDMA removal of >90% (Table 4).

Effects of initial NDMA concentration in a CSTR system. Southern California groundwater, spiked at two concentrations (2,800 and 100 ng/L) of NDMA, was irradiated at the applied pulsed frequency of 25 Hz in a CSTR system (Table 5). Pulsed UV alone achieved NDMA removals of 98% at these conditions when applied at a UV dose of 11.2 kW·h/1,000 gal. The retention time of 1.75 min provided a sufficient UV dosage for the test using a low NDMA concentration (<2,800 ng/L) to yield <2 ng/L effluent NDMA concentration. However, a longer retention time at an applied UV dose of 11.2 kW·h/1,000 gal would be needed for the testing using a higher NDMA spike (>2,800 ng/L), when the effluent concentration was 30 ng/L—exceeding the proposed action level set by the CDHS.

Reformation/regeneration of NDMA. The reformation/regeneration of NDMA is of concern because the degradation products from the photolytic destruction of NDMA

TABLE 7   Effects of NDMA* destruction on disinfection by-product formation in a Southern California groundwater

Compound	No NDMA Spiking			NDMA Spiking With a Concentration of 3,000 ng/L		
	No Pulsed-UV† Treatment	Pulsed-UV Alone	Pulsed-UV + 1 mg/L H$_2$O$_2$‡	No Pulsed-UV Treatment	Pulsed-UV Alone	Pulsed-UV + 1 mg/L H$_2$O$_2$
Trihalomethanes—µg/L						
Chloroform	0.27	0.23	0.3	0.17	<0.1	1.28
Dichlorobromomethane	0.42	0.52	0.44	0.26	0.11	1.31
Dibromochloromethane	0.45	0.55	0.49	0.25	0.21	0.96
Bromoform	<0.1	0.13	0.12	<0.1	0.36	0.19
Total	1.14	1.43	1.35	0.68	0.68	3.74
Haloacetic nitriles—µg/L						
Dibromoacetonitrile	0.26	NA§	NA	NA	NA	NA
Bromochloroacetonitrile	0.17	0.22	0.19	0.13	0.13	NA
Dichloroacetonitrile	<0.1	NA	NA	NA	<0.1	0.14
Trichloroacetonitrile	NA	NA	NA	NA	NA	NA
Haloketones—µg/L						
1,1-Dichloropropanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,1,1-Trichloropropanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chloropicrin—µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	0.15

*NDMA—N-nitrosodimethylamine
†UV—ultraviolet
‡H$_2$O$_2$—hydrogen peroxide
§NA—not applicable

could recombine to form NDMA after chlorinating the UV-treated effluent. Samples taken for the NDMA reformation study were dosed with 1 mg/L Cl_2 for five days at 4 to 8°C. For the test with Southern California groundwater, NDMA concentrations increased from 1.6 (after the UV dose of 11.2 kW·h/1,000 gal) to 3.9 ng/L, whereas NDMA concentrations did not change for the sample in which NDMA was treated with UV combined with 1.0 mg/L H_2O_2 (Table 6). In addition, reformation/regeneration of NDMA was also observed in DI water spiked with 3,000 ng/L NDMA and 40 mg/L NO_3^-. After chlorination, NDMA concentrations increased from 58 ng/L (for pulsed-UV alone after a UV dose of 5.7 kW·h/1,000 gal) to 99 ng/L and from 19 ng/L (after a UV dose of 8.6 kW·h/1,000 gal combined with 1.0 mg/L H_2O_2) to 35 ng/L. It is apparent that the pulsed-UV/H_2O_2 process was more effective than pulsed-UV alone in inhibiting NDMA reformation. However, the development of an exact mechanism for such behavior will need further investigation.

DBPs. The SDS test was used to estimate the amounts of DBPs that would form in the distribution systems (Table 7). The DBPs analyzed included THMs (chloroform, dichlorobromomethane, dibromochloromethane, bromoform); HANs (dibromoacetonitrile, bromochloroacetonitrile, dichloroacetonitrile, trichloroacetonitrile); HKs (1,1-dichloropropanone and 1,1,1-trichloropropanone); and chloropicrin. For the control samples without NDMA addition, no significant change in THMs, HANs, HKs, or chloropicrin was observed among SDS test samples taken from different treatment processes (e.g., without pulsed-UV, with pulsed-UV, and with pulsed-UV combined with 1 mg/L H_2O_2). With an NDMA spike of 3,000 ng/L, TTHMs were formed in concentrations of 0.68 and 3.74 μg/L after treatment by pulsed-UV alone and by pulsed UV combined with 1 mg/L H_2O_2, respectively. Higher concentrations of chlorinated THMs were formed after the advanced oxidation process (pulsed-UV/H_2O_2), whereas higher concentrations of brominated THMs were formed after photolysis (pulsed-UV alone). In the presence of NDMA, the DBPs (e.g., HANs, HKs, and chloropicrin) did not change significantly among SDS test samples taken from different experiments.

Residual H_2O_2. As mentioned previously, H_2O_2 is a weaker absorber of pulsed-UV light at a peak wavelength of 200 nm than is NDMA. In general, addition of H_2O_2 in the pulsed-UV/H_2O_2 process resulted in only a small reduction of H_2O_2. According to the analyses done for H_2O_2 residuals, only up to 20% of H_2O_2 was reduced in the tests. The addition of H_2O_2 did not necessarily enhance destruction of NDMA by the hydroxyl radicals produced from H_2O_2, but the presence of H_2O_2 seemed to inhibit reformation of NDMA and production of DBPs.

SUMMARY AND CONCLUSIONS

On the basis of the tests performed, the following conclusions can be drawn regarding the effectiveness of pulsed-UV irradiation and pulsed-UV/H_2O_2 processes for the destruction of NDMA:

• The results generated from bench-scale testing in both the CMBR and CSTR systems indicated that pulsed-UV alone was effective in removing NDMA. For example, pulsed-UV alone achieved NDMA removals of 98% at initial concentrations of 2,800 and 100 ng/L NDMA in Southern California groundwater with an applied UV dose of 11.2 kW·h/1,000 gal in both the CMBR and CSTR modes.

• Although the addition of low concentrations of H_2O_2 does not significantly enhance removal of NDMA or increase the kinetic rate of NDMA decay, the pulsed-UV/H_2O_2 process was more effective in oxidizing NDMA by-products than was pulsed-UV alone and resulted in less reformation of NDMA after chlorination. The addition of a high concentration of H_2O_2 slowed down the reduction of NDMA.

• Applied pulsed-UV dosage was the most significant parameter affecting the percentage of NDMA reduction. In a CMBR system, NDMA reduction increased with increasing UV dosage at a constant pulse input (frequency). For example, NDMA removals of 69 and 88% in DI water were achieved with applied UV doses of 1.3 and 2.6 kW·h/1,000 gal, respectively, at a pulse input of 2 Hz.

• The kinetic rates of NDMA decay at pulse rates of 25, 10, and 2 Hz suggest that a strong UV intensity produced at the pulse rate of 25 Hz resulted in more effective reduction of NDMA.

• A strong competition between NDMA and background organics (e.g., TOC and UV_{254}–absorbing organic compounds) for pulsed-light absorption affected NDMA removal. Pulsed-UV alone was more effective in destroying NDMA in Southern California groundwater than in CRW, possibly because higher levels of background organic compounds are present in CRW than in the Southern California groundwater used for this study.

• NO_3^- competed with NDMA for UV light and consequently limited the effectiveness of direct photolysis of NDMA. The test results did not indicate that the nitrate-induced photooxidation enhanced NDMA reduction.

• Pulsed-UV/H_2O_2 produced higher TTHMs than pulsed-UV alone. With an NDMA spike of 3,000 ng/L, TTHMs were formed in concentrations of 0.68 and 3.74 μg/L, respectively, after treatment by pulsed-UV alone and by pulsed-UV combined with 1 mg/L H_2O_2.

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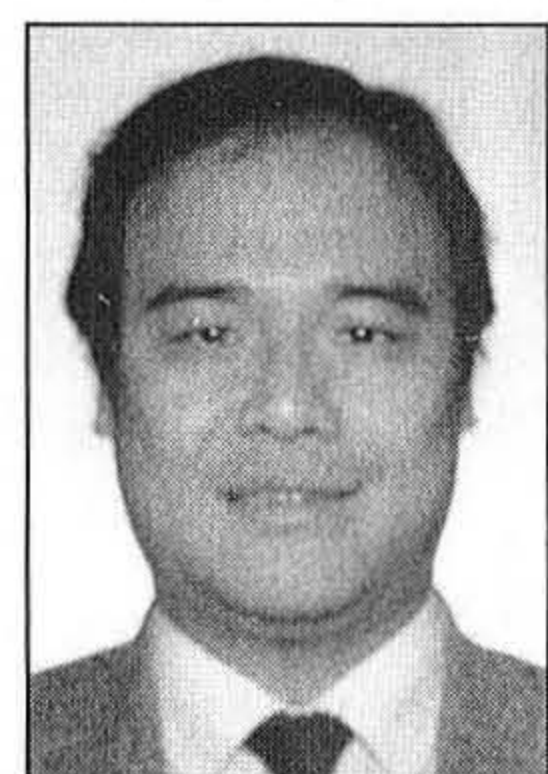
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FOOTNOTES

[1]Innovatech Inc., El Cajon, Calif.
[2]ILC Technology, Sunnyvale, Calif.
[3]Supelco, Inc., Bellefonte, Pa.
[4]Super-Q,© Millipore Corp., Bedford, Mass.
[5]Lambda-3B model, PerkinElmer Corp., Norwalk, Conn.
[6]DataChem Labs Inc., Salt Lake City, Utah
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