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Degradation of *N*-Nitrosodimethylamine by UV-Based Advanced Oxidation Processes for Potable Reuse: a Short Review

Takahiro Fujioka[1] · **Shunya Masaki**[1] · **Hitoshi Kodamatani**[2] · **Keisuke Ikehata**[3]

Abstract The ultraviolet (UV)-based advanced oxidation process (AOP) is a powerful technology commonly utilised in recent potable water reuse (PR) schemes. The AOP involves the generation of highly reactive free radicals (e.g. hydroxyl, $HO^•$) and is primarily applied for the removal of two target trace organic chemicals—*N*-nitrosodimethylamine (NDMA) and 1,4-dioxane — in the PR schemes. Both of these organics are not well removed by the reverse osmosis (RO) process. NDMA is a probable carcinogen and is often present in reclaimed water at concentrations higher than the guidelines established for PR. This review aimed to provide an understanding of the current UV-based advanced oxidation technologies for NDMA removal in PR, their limitations and the future of advanced technologies for their removal. NDMA is readily photolysed by direct UV irradiation, while an AOP such as UV/H_2O_2 process is necessary for the destruction of 1,4-dioxane. Unfortunately, the generation of hydroxyl radicals through UV photolysis of H_2O_2 is largely inefficient with conversion on the order of 20% under normal plant operations and the addition of H_2O_2 (e.g. 3 mg/L) provides only a negligible improvement in NDMA destruction. However, AOP can also be achieved without continuous chemical addition through the application of UV irradiation to heterogeneous photocatalysts (e.g. TiO_2). The UV/TiO_2 process generates hydroxyl radicals and singlet oxygen molecules, both of which degrade NDMA into by-products (e.g. methylamine or dimethylamine). Recent studies revealed that modification of the surface morphology of TiO_2 can not only enhance NDMA destruction but also alter the composition of the degradation by-products.

Keywords *N*-nitrosodimethylamine (NDMA) · Hydroxyl radicals · Photocatalytic degradation · Potable reuse · Titanium oxide · 1,4-Dioxane

Introduction

The occurrence and fate of *N*-nitrosodimethylamine (NDMA; $C_2H_6N_2O$, molecular weight 74 g/mol) in potable water reuse (PR) have attracted significant attention in recent years [1, 2]. NDMA is an *N*-nitrosamine that has been classified as probable carcinogens by the US EPA [3]. Although reverse osmosis (RO) membrane treatment in water reclamation systems is a key barrier for the elimination of trace organic chemicals (TrOCs) in wastewater [4], NDMA readily permeates through RO due to its small size and non-ionic nature under treatment conditions. NDMA rejection by RO membranes has been reported at 10–70% [5–7]. The other challenging carcinogenic TrOC, 1,4-dioxane ($C_4H_8O_2$, molecular weight 88 g/mol), has an RO rejection similar to NDMA [8]. To comply with the regulatory guidelines and meet the PR notification levels of NDMA (10 ng/L) [9, 10] and 1,4-dioxane (1 μg/L) [11], most PR facilities in the USA and Australia are equipped with a post treatment–ultraviolet (UV)/hydrogen peroxide (H_2O_2) advanced oxidation process (AOP) [7, 12].

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The UV/H_2O_2 AOP involves the use of hydroxyl radicals that form through UV photolysis of H_2O_2 added to the reactor feedwater. Although NDMA is a photodegradable compound that can be readily destroyed by direct UV irradiation, 1,4-dioxane requires some form of radicals for its destruction. Inherent disadvantages of the UV/H_2O_2 AOP include the requirement of a continuous dose of chemical oxidant (e.g. H_2O_2). Moreover, only about 20% of H_2O_2 is consumed through the AOP [13, 14], meaning that the system requires a quenching step of residuals H_2O_2 using sodium thiosulphate (e.g. 2.5–3 mg dose to 1 mg-H_2O_2/L) [13], sodium hypochlorite [15] or granular activated carbon [16] in the following step. The occurrence of 1,4-dioxane in treated wastewater is more site specific because it is an industrial solvent and is often detected at concentrations lower than the regulated values [17]. As a result, recent research focus has been placed on NDMA removal by AOPs.

Other AOPs that have been commercialised or extensively studied include UV/ozone [18] and ozone/H_2O_2 [19, 20]. UV/ozone AOP is based on the formation of hydroxyl radicals through UV photolysis of ozone at wavelengths of 200–280 nm. Ozone/H_2O_2 AOP generates hydroxyl radicals as a reaction product of the two oxidants (i.e. ozone and H_2O_2). Other emerging technologies include sulphate radical-based AOP [21, 22] and chlorine radical-based AOP [23, 24•]. However, all of the AOPs described earlier require continuous dosing of some chemical. AOPs that do not require any chemical dosing for NDMA removal include UV irradiation of heterogeneous photocatalysts (e.g. titanium oxide, TiO_2) [25••, 26]. In UV/TiO_2 AOP, hydroxyl radicals are formed at the surface of photocatalysts (i.e. TiO_2). Far less studies have been conducted for NDMA removal using UV/TiO_2 AOP. No large-scale UV/TiO_2 AOP system has been employed in any PR schemes to date.

In addition to the fate of NDMA in PR, the fate of NDMA precursors including dimethylamine (DMA) and tertiary amines has been extensively investigated [27•, 28–30]. A considerable increase in NDMA can occur from NDMA precursors and the presence of residual chloramine [31–33], both of which often remain in the source water at the end of the treatment process. Hydroxyl radicals formed by UV/TiO_2 AOP can transform NDMA into precursors that could reform NDMA through the reaction with chloramine [27•, 34]. The fate of NDMA precursors through UV/TiO_2 AOP is not very well understood. Therefore, a better understanding of the removal of NDMA and its precursors is a key factor to consider if UV/TiO_2 is to become a viable AOP.

This short review paper aimed to provide further understanding of the removal of NDMA and NDMA precursors through UV-based AOP with a particular focus on photocatalytic UV/TiO_2 AOP. The specific objectives are to clarify the effectiveness of UV-based AOP toward NDMA removal and to identify the degradation by-products. Thereafter, an assessment of the feasibility of utilising UV/TiO_2 AOP in PR applications will be discussed.

Occurrence and Fate of NDMA During Water Reclamation Processes

Municipal wastewater originates from a variety of domestic and industrial sources which contain a diverse range of constituents (e.g. dissolved and suspended solids, pathogens, organic and inorganic compounds). TrOCs are of great concern in PR, because they are difficult to remove by conventional water treatment technologies. These TrOCs include pharmaceuticals, personal care products, steroid hormones, pesticides, disinfection by-products and industrial chemicals. To ensure that safe and high-quality reclaimed wastewater is produced for the augmentation of drinking water supply, PR schemes are typically composed of a series of advanced water treatment processes that can remove a variety of constituents. These treatment processes include microfiltration (MF) or ultrafiltration (UF), RO and AOP [35–37]. MF/UF is employed as a pretreatment for RO to remove bacteria and suspended solids and minimise membrane fouling. RO treatment is a critical barrier against almost all constituents in water that include inorganics (ions and heavy metals) and most TrOCs. However, two specific TrOCs, NDMA (disinfection by-product) and 1,4-dioxane (solvent), readily permeate through RO membranes [38]. Both are uncharged and probably carcinogens [3, 39]. Among them, NDMA is often identified above the regulatory notification level (e.g. 10 ng/L in CA, USA) in the RO permeate at advanced water reclamation facilities [7]. To comply with the regulatory limits, an AOP (UV/H_2O_2) is typically applied following the RO treatment and therefore can successfully reduce NDMA concentrations to below its detection limit (i.e. 1–2 ng/L) [37, 40].

There are many sources of NDMA in treated wastewater. NDMA is typically present in primary wastewater effluent at the concentrations below 100 ng/L [41, 42]. In addition, NDMA forms through chloramination for mitigation of RO biofouling [5, 43], as well as during ozonation [44, 45]. DMA is widely reported as an NDMA precursor [31, 41], while others (e.g. amine-containing coagulation polymers, pharmaceuticals and personal care products, such as ranitidine—a component of antacids like Zantac®) have also been recognised to be its major sources [28, 43]. It should be noted that the molar conversion rate of DMA to NDMA is relatively low (<3% [46]) as compared with those of several tertiary amines that have DMA functional groups (e.g. ranitidine, 90% [28]). Most of the NDMA precursors are well removed by RO due to their large size, while some NDMA precursors can permeate through RO [47]. In addition, NDMA precursors can also be formed across the AOP through the degradation of NDMA and presence of residual chloramine in the effluent stream [27•, 34].

Degradation of NDMA by Direct UV

NDMA is readily degraded by direct photolysis at wavelengths <260 nm. It has a maximum absorbance at a wavelength of 227 nm, which originates from a $\pi \rightarrow \pi^*$ transition, and absorbs UV light strongly at 254 nm (ε = 1974 M^{-1} cm^{-1}), which commercial low-pressure mercury-vapour UV lamps emit [48, 49]. NDMA also has a weak UV absorption at 332 nm due to an $n \rightarrow \pi^*$ transition (ε = 109 M^{-1} cm^{-1}) [50]. Quantum yield of NDMA photolysis in a buffered solution with neutral pH (e.g. 7–8) and sufficient oxygen concentrations is >0.3 [48, 51]. A 1-log removal of NDMA can be achieved with 1000 mJ/cm^2 UV dose [49].

A previous study conducted by Lee et al. [48] has suggested that UV degradation of NDMA in aqueous solution at pH <8.5 fundamentally undergoes three pathways: (1) homolytic cleavage of N–NO bonds, (2) heterolytic cleavage of N–NO bonds and (3) photooxidation. All the pathways start with the protonation of NDMA into an excited NDMA (NDMA*–H$^+$) following UV irradiation. In the first pathway, the excited NDMA decays to two species—aminium radical $\left((CH_3)_2NH^+\right)$ and nitric oxide $\left({}^{\bullet}N\,O\right)$ (Eq. 1). They decay further to hyponitrous acid (HNO) and protonated *N*-methylidenemethylamine ($CH_2 = N^+HCH_3$) [52]. The protonated *N*-methylidenemethylamine undergoes hydrolysis, producing methylamine ($CH_3NH_3^+$, MA) and formaldehyde (HCOH) (Eq. 2). In a neutral pH (e.g. pH >5.5) environment, the reaction between aminium radical $\left((CH_3)_2NH^+\right)$ and ${}^{\bullet}N\,O$ leads to the formation of amidoxime ($CH_3NHC = NOH$) (Eq. 3). The reaction between $CH_3NHC = NOH$ and nitrite ion $\left(NO_2^-\right)$ forms *N*-methylformamide (CH_3NCOH) and N_2O.

Pathway 1

$$NDMA^* \rightarrow (CH_3)_2\dot{N}H^+ + {}^{\bullet}N\,O \tag{1}$$

$$(CH_3)_2\dot{N}H^+ + {}^{\bullet}N\,O \underset{-HNO}{\rightarrow} CH_2 = N^+HCH_3 \overset{\text{hydrolysis}}{\rightarrow} CH_3NH_3{}^+ + HCOH \tag{2}$$

$$(CH_3)_2\dot{N}H^+ + {}^{\bullet}N\,O \rightarrow CH_3NHC = NOH \xrightarrow{+NO_2^-} CH_3NCOH + N_2O \tag{3}$$

In the second pathway, the excited NDMA reacts with a water molecule or NO_2^- that leads to heterolytic cleavage of N–NO bonds and the formation of DMA ($(CH_3)_2NH_2^+$) and nitrite (Eq. 4) [51].

Pathway 2

$$NDMA^* \xrightarrow[H^+/H_2O \text{ or } NO_2^-]{} (CH_3)_2NH_2^+ + HNO_2 \tag{4}$$

In the third pathway, a one-electron transfer occurs from the excited NDMA and reacts with oxygen to yield protonated *N*-methylidenemethylamine ($CH_2 = N^+HCH_3$), ${}^{\bullet}N\,O$ and superoxide radical $\left(O_2^{\bullet -}\right)$ (Eq. 5). The protonated *N*-methylidenemethylamine ($CH_2 = N^+HCH_3$) decays to MA and HCOH by hydrolysis (Eq. 2) [48]. The reaction between ${}^{\bullet}N\,O$ and $O_2^{\bullet -}$ leads to the formation of peroxynitrite ($ONOO^-$), which transforms into nitrate ion (NO_3^-) (Eq. 6).

Pathway 3

$$NDMA^* \underset{O_2}{\rightarrow} CH_2 = N^+HCH_3 + {}^{\bullet}N\,O + O_2^{\bullet -} \tag{5}$$

$${}^{\bullet}N\,O + O_2^{\bullet -} \rightarrow ONOO^- \rightarrow NO_3{}^- \tag{6}$$

DMA and MA are breakdown products associated with the degradation of NDMA by UV irradiation. Prolonged exposure to UV photolysis does not lead to a reduction in the concentration of DMA and MA [50, 53]. The major pathway of photolytic degradation is determined by the solution pH. At low pH (e.g. 3–4), pathway 2 is dominant with DMA and NO_2^- as major degradation products. DMA formation decreases with increasing pH, while MA formation increases. At water treatment pH 7–8, the pathways 1–3 concurrently occur leading to similar formation levels of DMA and MA. Overall, UV photolysis at higher pH can minimise the formation of DMA, which is advantageous because DMA is a major NDMA precursor. Nevertheless, NDMA photolysis at pH higher than approximately 8 could be negatively impacted by very low quantum yield [48, 51] due to the light scavenging effects of carbonate ions (CO_3^{2-}), bicarbonate ions (HCO_3^-) and dissolved organic matter (DOM) [53–55].

Selection of the UV lamp is an important factor for the destruction of NDMA [56]. Low-pressure (LP) mercury lamp emits monochromatic light at 254 nm, while the medium-pressure (MP) mercury lamp emits a broader spectrum of UV–visible light at wavelengths between 200 and 500 nm. Although the wide range of wavelengths of MP lamps covers the absorbance of many substances in the source water, it could lead to a lower energy efficiency for compounds with narrow absorbance spectrum. Sharpless et al. [49] reported that the photonic efficiencies (UV fluence-based rate constants, cm^2/mJ at wavelengths 200–300 nm) of LP and MP UV lamps were similar, with the MP lamp having an average light emission of approximately 256 nm between 200 and 300 nm. UV lamps with light emission ranges lower than LP and MP UV lamps (e.g. excimer UV lamps [57]) could be more suitable for NDMA removal due to the 227 nm absorbance maximum of NDMA. Sakai et al. [58] used a KrCl excimer lamp that emits monochromatic light at 222 nm and reported reaction rate constants in pure water at 11 and 2.6 cm^2/J for the KrCl excimer lamp and a LP lamp, respectively. The high efficiency of the KrCl excimer lamp was attributed to the high absorptivity and high quantum yield of NDMA at 222 nm [58]. KrCl excimer lamps have a significantly shorter lifetime (<4000 h) than LP and MP UV lamps (e.g. >10,000 h) [59].

Degradation of NDMA by UV/H_2O_2 AOP

AOP is a water treatment process that utilises strong oxidising agents (e.g. hydroxyl radical, $HO^\bullet$) to oxidise and degrade contaminants of public health concern [24•]. UV/H_2O_2 AOP generates hydroxyl radicals through irradiation of H_2O_2 at wavelengths <270 nm with a quantum yield of 1.11 [60]. UV irradiation photolyses H_2O_2 ($\varepsilon_{245\ nm} = 19.6\ M^{-1}\ cm^{-1}$) and generates hydroxyl radicals as follows:

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \tag{7}$$

Molar absorption coefficient of H_2O_2 increases with decreasing UV wavelength. Because the molar absorption coefficient of H_2O_2 is generally low at the wavelengths of typical UV lamp (e.g. 254 nm for LP mercury lamp), the production rate of hydroxyl radicals also remains low [13]. Accordingly, a high concentration of H_2O_2 (3–5 mg/L) is required for H_2O_2 to absorb more UV light [61].

Hydroxyl radical reactions include four basic pathways: (a) abstraction of a hydrogen atom usually for aliphatic hydrocarbon groups, (b) radical addition for unsaturated or aromatic hydrocarbon groups, (c) electron transfer for inorganics and (d) radical–radical reaction [61]. The degradation of NDMA by UV/H_2O_2 AOP occurs by hydrogen atom abstraction from the methyl groups in NDMA as follows [49, 62]:

$$NDMA + HO^\bullet \rightarrow {}^\bullet CH_2(CH_3)N{-}N = O + H_2O \tag{8}$$

The hydroxyl radical rate constant for NDMA is $4.3 \times 10^8\ M^{-1}\ s^{-1}$ [62], and 1-log removal of NDMA by UV/H_2O_2 AOP can typically be achieved with a UV dose of ≥1000 mJ/cm^2 and 3 mg/L of H_2O_2. To the best of our knowledge, further degradation pathways of NDMA by UV/H_2O_2 AOP have not well been established, while Lee et al. [19] have described the degradation mechanisms by hydroxyl radicals formed through ozone/H_2O_2 AOP. In pathway 1, the carbon-centred NDMA radical self-decomposes to protonated *N*-methylidenemethylamine ($CH_2 = N^+HCH_3$) (Eq. 9). The pathway 1 is a major pathway of NDMA degradation by hydroxyl radicals.

Pathway 1

$${}^\bullet CH_2\ (CH_3)N{-}N = O + H^+ \rightarrow CH_2 = N^+HCH_3 + {}^\bullet N\ O \tag{9}$$

In pathway 2, the carbon-centred NDMA radical reacts with dissolved oxygen to form a peroxyl radical $\left({}^\bullet O_2CH_2(CH_3)N{-}N = O\right)$ (Eq. 10), which decomposes to protonated *N*-methylidenemethylamine ($CH_2 = N^+HCH_3$) (Eq. 11). Both pathways 1 and 2 generate MA as the primary product from a reaction between NDMA and hydroxyl radicals (Eq. 12). The formed MA can be further degraded by hydroxyl radicals (rate constant $k_{HO^\bullet} = 1.8\text{–}5.7 \times 10^9\ M^{-1}\ s^{-1}$ [63]). Lee et al. [19] found no formation of DMA during the reaction, suggesting that DMA is not a degradation by-product of NDMA by hydroxyl radicals.

Pathway 2

$${}^\bullet CH_2(CH_3)N{-}N = O + O_2 \rightarrow {}^\bullet O_2CH_2(CH_3)N{-}N = O \tag{10}$$

$${}^\bullet O_2CH_2(CH_3)N{-}N = O \rightarrow CH_2 = N^+HCH_3 + HNO_2 + O_2^{\bullet -} \tag{11}$$

$$CH_2 = N^+HCH_3 \xrightarrow{hydrolysis} CH_3NH_3{}^+ + HCOH \tag{12}$$

Dosing H_2O_2 (~3 mg/L) has shown to have a negligible effect on the degradation of NDMA [27•, 49]. A previous study [16] reported that H_2O_2 addition prior to UV irradiation enhanced NDMA degradation by only 10%, while another pilot-scale study [56] reported a negligible impact of H_2O_2 addition (0–10 mg/L) on NDMA degradation. Inefficient degradation of NDMA by the powerful $HO^\bullet$ oxidant may stem from a slow reaction of the methylene carbon-centred radical with dissolved oxygen to form a peroxyl radical (Eq. 10) [62–64].

High concentrations of H_2O_2 can lead to a reduction in the rate of NDMA degradation due to the scavenging of hydroxyl radicals ($k_{HO^\bullet} = 2.7 \times 10^7\ M^{-1}\ s^{-1}$) [65, 66]:

$$H_2O_2 + HO^\bullet \rightarrow H_2O + {}^\bullet HO_2 \tag{13}$$

Hydroxyl radicals can also react with natural organic matter in the source waters, which reduces the availability of hydroxyl radicals for reaction with NDMA [64]. Other inorganic and organic compounds in water can also scavenge hydroxyl radicals and reduce the rate of NDMA degradation. The hydroxyl radical scavengers include carbonate, bicarbonate, nitrite and bromide [65, 67]. Other parameters that influence NDMA degradation include NDMA concentrations, UV intensity, solution pH and anion concentrations [54].

UV lamps with lower wavelengths are preferable due to the larger molar adsorption coefficient of H_2O_2 at shorter wavelength. Nevertheless, the effects of UV lamp selection on the destruction of NDMA are not conclusive. For example, Sharpless et al. [49] reported a 30% increase in the fluence-based rate constant with the addition of 100 mg/L of H_2O_2 under LP UV irradiation, while effect from a MP UV lamp was negligible. In contrast, a pilot-scale UV lamp study [56] revealed that the addition of 5 and 10 mg/L H_2O_2 had a negligible impact, but the results from a MP UV lamp slightly enhanced NDMA degradation.

Degradation of NDMA by UV/TiO_2 AOP

Photocatalysts typically used for water treatment include TiO_2 [68, 69]. UV irradiation of heterogeneous TiO_2 generates hydroxyl radicals ($HO^{\bullet}$) and singlet oxygen (${}^1O_2$) at the surface through multiple pathways [70]. The photocatalytic reaction is initiated by UV irradiation of TiO_2. The semiconductor has two energy bands: an energy band occupied by free electrons (valence band (VB)) and an energy band that is generally empty (conduction band (CB)). The VB is lower in energy than the CB. The energy difference between the VB and the CB is called the bandgap. When electrons in the VB absorb UV that has a sufficient photon energy (hv) greater than the energy of the bandgap (e.g. $\lambda = <390$ nm for anatase TiO_2), the electrons are excited and jump to the CB forming electron-hole pairs—positive holes in the VB ($h^+_{TiO_2}$) and negative electrons in the CB ($e^-_{TiO_2}$) (Eq. 14). Water molecules that come in contact with the positive holes react to form hydroxyl radicals and protons (H^+) (Eq. 15), while dissolved oxygen reacts with electrons to form superoxide ions ($O_2^{\bullet -}$) (Eq. 16). The dissolved oxygen concentration is a key parameter in the photocatalytic degradation of chemical contaminants in UV/TiO_2 AOP [71].

$$TiO_2 + hv \rightarrow h^+_{TiO_2} + e^-_{TiO_2} \tag{14}$$

$$h^+_{TiO_2} + H_2O \rightarrow HO^{\bullet} + H^+ \tag{15}$$

$$e^-_{TiO_2} + O_2 \rightarrow O_2^{\bullet -} \tag{16}$$

${}^1O_2$ is formed through the oxidation of $O_2^{\bullet -}$ on $h^+_{TiO_2}$ in the VB (Eq. 17). ${}^1O_2$ can also be formed through the reaction of $O_2^{\bullet -}$ with another $O_2^{\bullet -}$ (Eq. 18), H_2O_2 (Eqs. 19 and 20) and $HO^{\bullet}$ (Eq. 21) [72, 73].

$$O_2^{\bullet -} + h^+_{TiO_2} \rightarrow {}^1O_2 \tag{17}$$

$$O_2^{\bullet -} + O_2^{\bullet -} + 2H^+ \rightarrow {}^1O_2 + H_2O_2 \tag{18}$$

$$O_2 + 2e^-_{TiO_2} + 2H^+ \rightarrow H_2O_2 \tag{19}$$

$$O_2^{\bullet -} + H_2O_2 \rightarrow {}^1O_2 + OH^- + HO^{\bullet} \tag{20}$$

$$O_2^{\bullet -} + HO^{\bullet} \rightarrow {}^1O_2 + OH^- \tag{21}$$

Photocatalytic degradation of NDMA by hydroxyl radicals is initiated with the attack at one of three positions: methyl group, amine nitrogen or nitrosyl nitrogen, as proposed by Lee et al. [74]. Attack of the methyl group (pathway A) leads to the formation of a carbon-centred NDMA radical (${}^{\bullet}CH_2(CH_3)N{-}N=O$), which reacts with oxygen molecule and forms peroxyl radical (${}^{\bullet}O_2CH_2(CH_3)N{-}N=O$) (Eq. 22). The peroxyl radical degrades to alkoxyl radical intermediates (Eq. 23) and eventually forms MA (Eq. 24) [75, 76]. This is the major pathway under oxygen-rich conditions.

Pathway A

$${}^{\bullet}CH_2(CH_3)N{-}N=O + O_2 \rightarrow {}^{\bullet}O_2CH_2(CH_3)N{-}N=O \tag{22}$$

$$2\left({}^{\bullet}O_2CH_2(CH_3)N{-}N=O\right) \rightarrow {}^{\bullet}OCH_2(CH_3)N{-}N=O + O_2 \tag{23}$$

$${}^{\bullet}OCH_2(CH_3)N{-}N=O \xrightarrow[-HCOH]{} CH_3\dot{N}{-}N = O \xrightarrow[-NO,+2e^-/2H^+]{} CH_3NH_2 \tag{24}$$

With the attack of amine nitrogen (pathway B), protonated *N*-methylidenemethylamine ($CH_2{=}N^+HCH_3$) is generated, which decays to MA and HCOH by hydrolysis (Eq. 25). A recent study conducted by Guo et al. [77•] suggested another pathway for NDMA degradation that is initiated with the attack of the same amine nitrogen but formation of DMA (Eq. 26).

Pathway B

$$(CH_3)_2\dot{N}^+{-}N=O \xrightarrow[-NO]{} CH_2 = N^+HCH_3 \xrightarrow[hydrolysis]{} CH_3NH_2 + HCOH \tag{25}$$

$$(CH_3)_2\dot{N}^+{-}N=O + HNO_2 \rightarrow (CH_3)_2NH_2^+ + N_2O_3 \tag{26}$$

With the attack of nitrosyl nitrogen (pathway C), NDMA is converted into dimethylaminyl radical ($(CH_3)_2N^{\bullet}$) and nitric acid (Eq. 27) [74]. The dimethylaminyl radical, which is unreactive with oxygen but reactive with H-atom-donating compounds, decays to DMA through e^-/H^+ or an H-atom abstraction from NDMA (Eq. 28) [50, 78].

Pathway C

$$(CH_3)_2N{-}N\dot{O}OH \rightarrow (CH_3)_2N^{\bullet} + HNO_2 \tag{27}$$

$$(CH_3)_2N^{\bullet} \xrightarrow[\text{H−abstraction from NDMA}]{+e^-/H^+ \text{ or}} (CH_3)_2NH \tag{28}$$

The resultant MA and DMA can be adsorbed onto TiO_2 where DMA can be degraded into MA, ammonium (NH_4^+) and NO_3^-, while MA further degraded into NH_4^+ and NO_3^- [79].

In addition to the formation of hydroxyl radicals, ${}^1O_2$ generated through UV/TiO_2 AOP [80, 81] can play an important role in the photocatalytic degradation of NDMA. NDMA reacts with ${}^1O_2$ and favourably degrades to DMA through the pathway described in Eq. 29 [25••]. The specific location of ${}^1O_2$ attack among three positions (i.e. methyl group, amine nitrogen or nitrosyl nitrogen) has not been clarified.

Pathway D

$$NDMA + {}^1O_2 \rightarrow DMA + NO_3^- \tag{29}$$

Pathways of photocatalytic degradation of NDMA are summarised in Fig. 1. The proportion of formed MA and DMA varies depending on the solution matrix (e.g. pH) and the characteristics of photocatalysts [25••]. For example, the concentration of formed MA can be two to four times greater than that of formed DMA with pure TiO_2, while with surface-coated TiO_2 DMA can be formed at concentrations higher than MA [74]. In

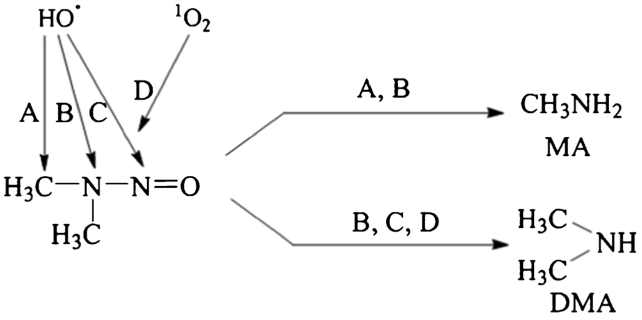

Fig. 1 Pathways of NDMA destruction by UV/TiO_2 AOP

addition to DMA and MA, the photocatalytic destruction of NDMA leads to the formation of NO_2^- and NO_3^-, whose concentrations can be as much as formed DMA and MA [77•]. The photocatalytic destruction of NDMA in a high pH solution (e.g. pH = >10) can also form ammonium ions [74].

Recent advances in materials science have allowed the use of TiO_2 with a different morphology for NDMA removal. A notable example is a study conducted by Guo et al. [25••] where TiO_2 was prepared in the form of TiO_2 nanotubes (diameter = 5–6 nm) from anatase TiO_2 to attain surface area larger than commercial TiO_2 powders and particles (e.g. Degussa P25 [48, 51] and Aeroxide P25 [26]). Their study revealed that $^1O_2$ formed with the TiO_2 nanotubes contributed to NDMA degradation greater than typical TiO_2 particles. Guo et al. [25••] speculated that the enhanced photocatalytic degradation of NDMA with smaller TiO_2 particles could be attributed to small pores where NDMA molecules could enter. This could also be attributed to greater formation of $^1O_2$ due to the increased number of adsorbed oxygen molecules with a larger surface [80].

Photocatalytic degradation of chemicals by UV/TiO_2 AOP could be improved with surface modifications or doping of the TiO_2 heterogeneous photocatalyst [82]. For example, a previous study [74] reported that silica-loaded TiO_2 with UV irradiation can enhance NDMA destruction by 30% as compared to unmodified TiO_2. Another study by Guo et al. [77•] modified the surface of TiO_2 nanotubes with gold nanoparticles. Interestingly, NDMA destruction with these TiO_2 nanotubes led to the formation of DMA as a major by-product. This indicates that the selection of additives could alter the major pathways of NDMA degradation (pathways A–D) and alter the formation of major by-products. Doping TiO_2 with different materials is an effective strategy to modify the optical properties of TiO_2 that leads to an increase in the absorption of the visible (Vis) light ($\lambda > 380$ nm). TiO_2 particles doped with metals or non-metal dopants attain new energy levels between their VB and CB, which reduce the bandgap and allow Vis light to be absorbed [83]. Many previous studies have demonstrated the effects of Vis light on the photocatalytic degradation of contaminants such as endocrine-disrupting compounds and pharmaceuticals [70, 84]. Nevertheless, no attempts have been reported in regard to NDMA destruction by UV-Vis/TiO_2 AOP.

Summaries and Future Roadmap

The UV photolysis and UV-based AOPs discussed in this review are summarised in Table 1. This review focused on a fundamental UV technology (i.e. direct UV), a commercialised AOP (i.e. UV/H_2O_2) and a potential AOP without continuous chemical addition (i.e. UV/TiO_2). UV photolysis is very effective for NDMA degradation, but a log reduction of NDMA typically requires a UV dose ≥1000 mJ/cm^2. In addition, UV alone is ineffective for 1,4-dioxane removal, which requires an AOP with radical generation (e.g. hydroxyl) for effective destruction. Therefore, UV/H_2O_2 AOP has been employed at most of the recent potable water facilities. However, this AOP requires continuous dosing of H_2O_2 and often requires quenching to remove the residual. The UV/TiO_2 AOP technology can be a good alternative to direct photolysis and UV/H_2O_2 AOP as recent studies have shown promising performance for NDMA degradation, and it does not require continuous chemical dosing. The technology relies solely on UV irradiation of the TiO_2 heterogeneous photocatalyst for the formation of hydroxyl radicals and singlet oxygen.

One of the uncertainties of the UV/TiO_2 AOP technology includes the frequency of TiO_2 surface cleaning. Although hydroxyl radicals can essentially destroy most organic compounds, the adsorption of impurities—both organics and inorganics—onto TiO_2 could occur over long-term operations screening the surface of the photocatalyst from UV light. Moreover, the lifetime of the catalyst is of great interest as it contributes to the operational costs. Short catalyst lifetime renders the feasibility of UV/TiO_2 AOP questionable. To scale up the technology, further investigation is necessary for photocatalytic reactor design. Most UV/TiO_2 AOP systems used for laboratory- and pilot-scale studies apply immobilised TiO_2 beds or TiO_2 fine particles in a slurry form [68]. Immobilised TiO_2 beds must be in direct contact with UV irradiation, and much of the surface area remains inaccessible and inactive. A slurry system can utilise large

Table 1 Comparison of UV (photolysis) and UV-based advanced oxidation technologies for NDMA removal

	Advantages	Disadvantages	Technology level [61]
UV	Well established	Not effective for 1,4-dioxane	Commercial
UV/H_2O_2	Well established	Requirement of continuous chemical addition	Commercial
UV/TiO_2	No continuous chemical addition	Not sufficiently established	Research to commercial

surface active sites, while it has operational difficulties in a separation system to avoid the loss of TiO_2 fine particles for reconditioning/recycling and reuse. Overall, a feasibility study focusing on the continuous use of TiO_2 and photocatalytic reactor design is required to consider UV/TiO_2 AOP as an alternative to the most commonly used AOP in PR—UV/H_2O_2 AOP.

Conclusions

This paper comprehensively reviewed UV-based advanced oxidation technologies currently used and available for NDMA removal. Direct photolysis at wavelengths below 270 nm is a very effective way of NDMA removal. However, depending on pH, direct photolysis produces DMA as a major by-product. Since DMA is a major NDMA precursor, regeneration of NDMA can occur if chloramine is used after the UV treatment. UV/H_2O_2 AOP—the most common approach that is based on UV irradiation in combination with H_2O_2 dosing—does not provide a significant improvement in NDMA removal in comparison with the direct photolysis. UV/TiO_2 AOP is an alternative approach that does not involve continuous dosing of H_2O_2 (or other oxidants) and subsequent quenching step. Hydroxyl radicals and singlet oxygen are formed by UV/TiO_2 AOP, both of which are generated at the catalytic surface through UV irradiation. NDMA destruction by UV/TiO_2 AOP forms both DMA and MA, at ratios that vary depending on the reaction conditions and surface properties of TiO_2. Further improvement of NDMA degradation can be expected by developing the surface morphology modification and doping methods of TiO_2. In addition, further research on other uncertainties (e.g. the lifetime of TiO_2, cleaning methods and photocatalytic reactor design) is also needed to scale up the technology in PR applications.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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- • Of importance,
- •• Of major importance

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