Impact of the Ultraviolet Photolysis of Monochloramine on 1,4-Dioxane Removal: New Insights into Potable Water Reuse

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Supporting Information

ABSTRACT: Although chloramines are ubiquitously present during ultraviolet-driven advanced oxidation processes (UV/AOP) that are becoming increasingly important for potable water reuse, the photochemistry of chloramines in treated wastewater, and the associated effects on trace chemical contaminant degradation, are unknown. This study investigated the fundamental radical chemistry involved in monochloramine (NH₂Cl) photolysis and its efficiency in degrading 1,4-dioxane using a low-pressure Hg lamp (λ = 254 nm). These results showed that the UV fluence-normalized rate of 1,4-dioxane degradation in UV/NH₂Cl ranged between 1.1 × 10⁻¹² and 2.9 × 10⁻¹⁴ cm³·m⁻¹·J⁻¹. The photolysis of NH₂Cl produced NH₂⁺ and Cl⁻, which further transformed to a series of reactive radical species. An optimal NH₂Cl dosage for 1,4-dioxane degradation was observed at a NH₂Cl/1,4-dioxane concentration ratio of 8.0, while excess NH₂Cl scavenged reactive radicals and decreased the treatment efficiency. Scavenging experiments and probe compound calculations showed that both Cl₂• and HO• contributed significantly to 1,4-dioxane removal, while the NH₂• radical reacted slowly with 1,4-dioxane. The presence of dissolved oxygen further decreased NH₂• reactivity. This study generated critical knowledge of the photochemistry of NH₂Cl and will allow for future optimization of the UV/AOP for more efficient water reuse treatments.

INTRODUCTION

Potable water reuse offers a sustainable approach to addressing water scarcity and mitigating the long-term impacts of climate change.¹,² The ultraviolet-based advanced oxidation processes (UV/AOP) that are integral to potable water reuse treatments. Typically, an oxidant, e.g., hydrogen peroxide (H₂O₂), persulfate (S₂O₈²⁻), or free chlorine (HOCl), is added and photolyzed to generate reactive radical species that degrade trace organic contaminants in the recycled water.³⁻¹³ However, membrane treatment processes, including microfiltration (MF) and reverse osmosis (RO), are employed prior to any UV/AOP. Chloramines, especially monochloramine (NH₂Cl), are deliberately generated in the feedwater to minimize membrane biological fouling.¹⁴,¹⁵ Because of their small molecular size and neutral charge, chloramines easily diffuse through RO membranes and subsequently will undergo photolysis in the UV/AOP.¹⁶ Neutral and low-molecular weight trace organic contaminants are also poorly removed by the RO membrane and carried over to the UV/AOP.¹⁷ For example, 1,4-dioxane (1,4-D), a solvent stabilizer used in many industrial and personal care products, is persistent in RO permeate.¹⁸ 1,4-D is classified as a probable Class 2B human carcinogen.¹⁹ It has served as a surrogate contaminant for the validation of AOPs as it is water-soluble, is not photolyzed at 254 nm, and requires oxidation to be removed from the recycled water.²⁰ Because of its significant implications on the quality of recycled water, regulatory standards in California require at least 0.5 log of removal for 1,4-D by the UV/AOP.²¹

As more water utilities adopt UV/AOPs as part of their wastewater treatment, the nature of chloramine photochemistry in recycled water of RO permeate needs to be better understood, as this can potentially provide additional removal of trace organic contaminants and enhance the UV/AOP performance for potable water reuse. Prior studies of chloramine photochemistry have mainly examined its reactivity as a disinfectant in swimming pools,²²,²³ formation of disinfection byproducts during drinking water treatment,²⁴,²⁵ solar irradiation in ballast water,²⁶ and its photolysis under organic-free conditions.²⁷,²⁸ The chemical condition of recycled water during the UV/AOP treatment step is characteristic of low natural organic matter content, acidic pH, and the presence of neutral and small trace organic contaminants. The nature of

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NH₂Cl photolysis after membrane treatment during the UV/AOP in recycled water has not been systematically explored. Currently, little is known about the nature and reactivity of NH₂Cl photochemistry with 1,4-dioxane in the unique water chemistry relevant to water reuse.

It was previously reported that the photolysis of NH₂Cl generates the amine radical (NH₂•) and the chlorine atom (Cl•).23,28,29 The Cl• atom can be converted to the hydroxyl radical (HO•) via its reaction with hydroxide, followed by the dissociation of ClO•⁻, or generate the chlorine dimer, Cl₂•−.30–33 The fate of NH₂• in water is largely unknown. Although its redox potential is estimated to be lower than that of HO•,34–37 prior studies have shown that NH₂• is capable of oxidizing antibiotics in wastewater and generating NH₃--adduct products.38–40 However, the equivalent monochloramine photochemistry with 1,4-dioxane and the associated radical reactivity have not yet been established.

The objectives of this study were to investigate the photochemistry of NH₂Cl under RO permeate chemical conditions, to examine the distribution and reactivity of the radical species generated, and to elucidate the mechanisms associated with the oxidation of 1,4-dioxane in a water reuse scenario.

■ MATERIALS AND METHODS

All chemicals used in this study were reagent grade or higher. Solutions were prepared using deionized (DI) water (resistivity of >18.2 MΩ, Millipore System) purged with ambient air to achieve air-saturated conditions. In some experiments, the DI water was purged with N₂ for 30 min prior to use to remove the dissolved O₂. A 50 mM NH₂Cl working solution was prepared daily by adding a HOCl stock solution to (NH₄)₂SO₄ with a N:Cl molar ratio of 1.2:1 buffered at pH 5.8 and 11.42 The ionic strength was controlled with a diode array detector (details provided as Text S1 in the Supporting Information). Dissolved O₂ was measured using a dissolved O₂ probe (Mettler Toledo). Nitrobenzene (20 μM) and benzoic acid (10 μM) were added simultaneously as probe compounds to quantify the steady-state concentrations of reactive radicals in the UV/NH₂Cl experiments using competition kinetics. tert-Butanol (TBA) was employed as a radical scavenger in some experiments. The second-order rate constants of reactive chlorine species (Cl• and Cl₂•−) reacting with 1,4-D were determined by electron pulse radiolysis experiments conducted at Notre Dame Radiation Laboratory in Notre Dame, IN. In short, the electron pulse radiolysis of water in the presence of chloride and persulfate was conducted and the production of Cl₂•− that absorbed strongly at 340 nm was monitored to measure the rate constants. Details about the radiolysis experiments and data analysis are provided as Text S2 and Figures S2 and S3 in the Supporting Information.

■ RESULTS AND DISCUSSION

1,4-Dioxane Degradation in UV/NH₂Cl. 1,4-D degradation took place in UV/NH₂Cl under RO permeate chemical conditions (Figure 1A). The UV fluence-normalized pseudo-first-order rate constant of 1,4-D degradation (k₁,4-dioxane)
NH₃Cl consumption exhibited bell-shaped behavior (Figure S4 and S5). The incipient increase in NH₃Cl dosage enhanced the generation of NH₂* and Cl* (reaction 1 in Scheme 1; all subsequent reactions refer to Scheme 1). On the basis of the rate constants of radical reactions, Cl* was transformed to HO* mainly via the Cl₂•− and ClOHO•− pathways (reactions 2–6). Detailed calculations on the rate of Cl*, Cl₂•−, and HO* are provided in Texts S3–S5. Essentially, the increase in NH₃Cl dosage promoted HO* and Cl₂•− formation and enhanced 1,4-D degradation. The subsequent decrease in the 1,4-D degradation rate at NH₃Cl concentrations of >2 mM was due to the scavenging of HO* and Cl₂•− by NH₃Cl (reactions 7 and 8). The scavenging reactions produced NHCl• that did not significantly contribute to the oxidation of 1,4-D. The correlation between the rates of 1,4-D degradation and NH₃Cl consumption exhibited bell-shaped behavior (Figure 1B). Lower NH₃Cl consumption rates corresponded to the desirable conditions under which HO* and Cl₂•− generated from NH₃Cl photolysis effectively reacted with 1,4-D. Higher NH₃Cl consumption rates were dominated by scavenging reactions that decreased the yields of Cl*, OH*, and Cl₂•−. In addition, higher concentrations of NHCl• were associated with higher Cl₂•− concentrations, contributing to higher steady-state concentrations of Cl₂•− and a larger contribution of Cl₂•− to 1,4-D oxidation.

Nature of Reactive Amine Radicals in UV/NH₃Cl. To understand the reactivities of radical species with 1,4-D in UV/NH₃Cl, especially reactive amine radicals, including NH₃*, additional UV/H₂O₂ experiments were conducted in the presence of varying concentrations of NH₃ at different levels of pH and dissolved O₂. The generation of NH₃* was controlled via the addition of NH₃, which scavenged HO* during H₂O₂ photolysis (reaction 9). Experiments showed that in N₂-purged solutions and at pH 11, as the branching ratio of HO* reacting with NH₃ increased from 0 to 90% (i.e., the percentage of HO* reacting with NH₃ over HO* reacting with NH₃ and 1,4-D combined, which is indicative of the extent of NH₃* formation via HO*), the rate of 1,4-D degradation decreased by 80% (Figure 2). NH₂* was reported not to react significantly with primary amines (<10⁵ M⁻¹ s⁻¹) and phenolate (10⁶ M⁻¹ s⁻¹). The NH₃ scavenging trend also suggested NH₂* had very limited reactivity with 1,4-D. When the pH of the N₂-purged solution was decreased to 5.8, the rate of 1,4-D degradation remained high and stable at varying NH₃ branching ratios (Figure 2). This indicated that the NH₂* was not generated via HO* at the acidic pH when NH₄+ was the predominant ammonium species (pK = 9.6).

When similar experiments were conducted in air-saturated solutions, the rate of 1,4-D degradation also decreased with increasing NH₄+ branching ratios at pH 11; however, these rates were nearly 40% lower in the air-saturated solution than under N₂-purged conditions for a NH₄+ branching ratio of >50% (Figure 2). It has been reported that NH₄+ reacts with dissolved O₂ to yield NH₂O₂* (reaction 10). It is likely that NH₂O₂* further decayed to less oxidative species that negligibly impacted 1,4-D degradation (Text S6). In addition, when the pH of the air-saturated solution decreased to 5.8, the rate of 1,4-D degradation also remained stably high regardless of the NH₃ branching ratio (Figure 2). It is noticeable that there was only a trace level of carbonate species in the solution, and the generation of carbonate radical CO₃•− was negligible (Text S7).

Nature of Reactive Chlorine Radicals in UV/NH₃Cl. Cl₂•− was the predominant chlorine radical species that contributed to 1,4-dioxane degradation in UV/NH₃Cl. On the basis of the decay of radical probe compounds (calculations provided in Text S8), the steady-state concentrations of Cl₂•−, HO*, and NH₂* were calculated as 4.9 × 10⁻¹ⁱ, 1.6 × 10⁻¹³, and 8.7 × 10⁻⁹ M, respectively, in UV/NH₃Cl with 2 mM NH₃Cl and 250 μM 1,4-dioxane. Because of the low reactivity of NH₂*...
with 1,4-D. HO* and Cl\textsuperscript{−} contributed 76 and 24\%, respectively, to 1,4-D degradation (reactions 11 and 12, respectively).

Additional TBA scavenging experiments were performed to further confirm the importance of Cl\textsuperscript{−}. 1,4-D degradation was suppressed by approximately 30\% with 5 mM TBA (Figure 3).

Figure 3. Impacts of tert-butanol (TBA) on 1,4-dioxane degradation in UV/NH\textsubscript{2}Cl with a N\textsubscript{2}-purged solution. Initial [1,4-D] = 250 μM, initial [NH\textsubscript{2}Cl] = 2 mM, pH 5.8, and ionic strength = 35 mM.

This decrease in reaction rate resulted from the TBA scavenging of Cl\textsuperscript{*}, Cl\textsubscript{2}\textsuperscript{−}, and HO*. TBA reacted quickly with HO* and Cl\textsuperscript{*} yet quite slowly with Cl\textsubscript{2}\textsuperscript{−} (Table S1). The scavenging of Cl\textsuperscript{*} by 5 mM TBA decreased the steady-state concentrations of Cl\textsubscript{2}\textsuperscript{−} and HO* by 8 and 34\%, respectively (detailed calculations in Text S9). The combined predicted scavenging effects on Cl\textsubscript{2}\textsuperscript{−} and HO* by 5 mM TBA decreased the degradation rate of 1,4-D by approximately 30\% (Text S9), which was consistent with the experimental observation (Figure 3). The consistency between the calculated steady-state radical concentrations and the experimental data strongly suggested that both Cl\textsubscript{2}\textsuperscript{−} and HO* significantly contributed to 1,4-D degradation in UV/NH\textsubscript{2}Cl. Furthermore, an increase of TBA concentration from 5 to 50 mM increased the decay rate of 1,4-D (Figure 3). This was likely contributed by a significant generation of intermediate reactive TBA oxidation products. Previous studies showed that an intermediate radical from TBA oxidation, \textsuperscript{·}CH\textsubscript{2}C(CH\textsubscript{3})\textsubscript{2}OH, also possibly reacted with 1,4-dioxane.\textsuperscript{44,48,49}

**Environmental Implications.** The presence of chloramines in the UV/AOP as carryover chemical residuals from membrane treatment processes can also be harnessed as an oxidant beneficial to water reuse. To maximize the efficiency of UV/NH\textsubscript{2}Cl in trace organic contaminant removal, an optimal chloramine dosage is required, as higher NH\textsubscript{2}Cl concentrations act as self-scavengers to decrease the yields of reactive radicals, i.e., HO* and Cl\textsuperscript{*}. It should be noted that the NH\textsubscript{2}Cl dose in our experiments promoted the production of Cl\textsubscript{2}\textsuperscript{−}, which would have a yield lower than that of Cl\textsuperscript{*} under applied RO permeate conditions. Considering the long-term impacts of climate change and drought, an efficient utilization of chloramine photolysis will lead to more sustainable water management. The generation of amine and halide radicals in UV/NH\textsubscript{2}Cl may affect the formation of nitorgenous disinfection byproducts (N-DBPs) and will be investigated in the future.

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