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Mechanisms of oxidative removal of 1,4-dioxane via free chlorine rapidly mixing into monochloramine: Implications on water treatment and reuse

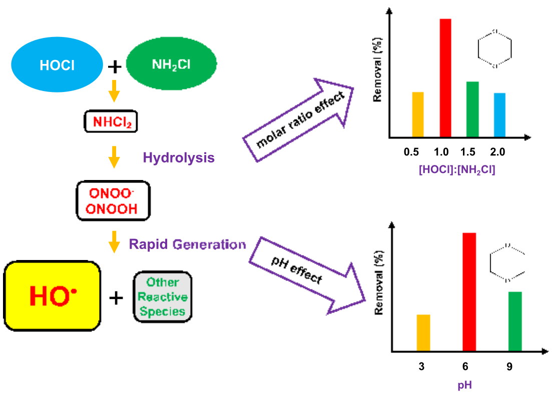
Liang Wu [a,b], Samuel D. Patton [a,b], Haizhou Liu [a,b,*]

[a] Environmental Toxicology Program, University of California, Riverside, CA 92521, USA
[b] Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, USA

HIGHLIGHTS

- The mixed $HOCl/NH_2Cl$ system removes 1,4-dioxane rapidly.
- Hydrolytic decay of $NHCl_2$ was a key step in the pathway to generate reactive radical species.
- Peroxynitrite was experimentally identified as the crucial precursor in the mixed $HOCl/NH_2Cl$.
- HO• was the primary contributor to 1,4-dioxane degradation.
- Optimum 1,4-dioxane removal was observed at pH 6 with the HOCl-to-NH_2Cl ratio of 1.

GRAPHICAL ABSTRACT



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ABSTRACT

Free chlorine (HOCl) and monochloramine (NH_2Cl) are two of the most commonly used water disinfectants in water treatment; however, the capability of rapid mixing of HOCl into NH_2Cl to induce oxidative reactions for efficient removal of contaminants remains largely unknown. In this study, 1,4-dioxane (1,4-D) removal was quantified during the rapid mixing of HOCl into NH_2Cl, to evaluate the effects of solution pH and HOCl-to-NH_2Cl ratio, and to identify mechanisms by which reactive species are generated in the system. Results showed that the highest 1,4-D removal was observed at the near-neutral pH of 6 with the HOCl-to-NH_2Cl molar ratio of 1. Hydroxyl radical ($HO^{\bullet}$) contributed to 60–70 % of 1,4-D degradation and its generation was initiated by the hydrolytic decay of NH_2Cl and $NHCl_2$ upon HOCl addition to NH_2Cl with rapid mixing, and subsequent transformation of peroxynitrite ($ONOO^-$) and peroxynitrous acid (ONOOH). The results also confirmed that the presence of dissolved oxygen was required to form $ONOO^-$/ONOOH, and $ONOO^-$ was a crucial precursor for reactive radical generation. These findings provide insight into the reaction mechanism associated with the system of rapidly mixed HOCl into NH_2Cl with the potential optimization and application for efficient trace organics removal in water treatment and reuse.

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* Corresponding author at: Department of Chemical and Environmental Engineering, University of California, Riverside, CA, 92521, USA.
E-mail address: haizhou@engr.ucr.edu (H. Liu).

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1. Introduction

Free chlorine (HOCl) is the most commonly used disinfectant in water treatment, due to its high oxidation potential and effectiveness as an antimicrobial agent (Keswick et al., 1985; Shin and Sobsey, 2008). More recently, chloramines, especially monochloramine (NH_2Cl), have also been applied as a disinfectant, due to benefits including reduced formation of disinfection byproducts and greater stability and longer efficacy in distribution systems (Simpson and Hayes, 1998; Hua and Reckhow, 2007; Bougeard et al., 2010). The co-existence of HOCl and NH_2Cl can occur during disinfection of conventional water treatment, where HOCl is added to ammonia-containing water as part of breakpoint chlorination (Pressley et al., 1972). Prior literature demonstrated that, compared to a single oxidant, the mixed oxidant system of HOCl and NH_2Cl more effectively inactivates *E. coli* in wastewater (Kouame and Haas, 1991). However, the underlying mechanism was unclear. Furthermore, in potable reuse treatment, NH_2Cl is commonly applied to prevent membrane biofouling, but easily passes through the membranes and into the reverse osmosis (RO) permeate due to its small size and neutral charge (Farhat et al., 2018; Ozaki and Li, 2002). Additionally, HOCl has been increasingly employed as a photo-oxidant for potable reuse and dosed into NH_2Cl-containing RO permeate for the UV-based advanced oxidation process (AOP) (Kwon et al., 2020; Yin et al., 2018). Therefore, the rapid mixing of HOCl into NH_2Cl inevitably occurs during water reuse treatment.

When HOCl is mixed into NH_2Cl, a series of redox reactions take place. HOCl first reacts with NH_2Cl to form dichloramine ($NHCl_2$) and trichloramine (NCl_3), depending on the HOCl-to-NH_2Cl molar ratio and solution pH: (Valentine and Jafvert, 1992)

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \tag{R1}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \tag{R2}$$

A series of intermediate species are subsequently generated as chloramines undergo hydrolytic decay and further reacts with HOCl, which ultimately produces reactive radical species (Phillip and Diyamandoglu, 2011; Driss and Bouhelassa, 2014). Prior studies examined breakpoint chlorination in consideration of the elimination of carbamazepine and formation of disinfection byproducts (DBPs), (Yang et al., 2005; Stefan et al., 2019; Wang et al., 2018), but the mechanisms and pathways on the generation of reactive species in the system where HOCl is rapidly mixed into NH_2Cl remains insufficiently understood. Furthermore, the potential application of the reactive species to degrade trace organic contaminants in water treatment and reuse has not been explored.

Peroxynitrite ($ONOO^-$) and peroxynitrous acid (ONOOH) were postulated as intermediates generated in systems where $NHCl_2$ is present (Schreiber and Mitch, 2007). NH_2Cl can undergo hydrolytic decay to form hydroxylamine (NH_2OH) and further produces nitroxyl (HNO) upon reaction with oxidants (e.g., HOCl and NH_2Cl) which then forms $ONOO^-$ (Anear and Yagil, 1962; Johnson et al., 2002; Shafirovich and Lymar, 2002; Pham et al., 2021). It has been reported that ONOOH decays into reactive species including hydroxyl radical ($HO^\bullet$) and nitrogen dioxide radical ($NO_2^\bullet$), while $ONOO^-$ forms nitric oxide radical ($NO^\bullet$) and superoxide radical ($O_2^{\bullet-}$) (Merenyi and Lind, 1998; Patton et al., 2022). Prior studies attempted to understand the reactive species generated in the mixed system, but mostly focused on the breakpoint chlorination reaction between chlorine and ammonia (NH_3), not chlorine with chloramines (Pressley et al., 1972; Valentine and Jafvert, 1992; Patton et al., 2022; Aghdam et al., 2021). Compared to the NH_3-initiated breakpoint chlorination reactions, mixing of HOCl into NH_2Cl provides a more direct pathway to promote the formation of $NHCl_2$ and subsequent reactive species. In water treatments, including water reuse and desalination, pre-formed NH_2Cl widely occurs (Patton et al., 2022; Kim et al., 2015). The HOCl addition to the NH_2Cl-containing water can be critical to create a highly oxidative system to degrade organic contaminants. Therefore, it is important to systematically investigate the reaction mechanisms of HOCl and NH_2Cl.

Currently the effects of major water chemical parameters on the generation of reactive species and associated degradation of contaminants in the mixed HOCl and NH_2Cl system are worth further investigation. For example, solution pH strongly affects the stability and decay of $NHCl_2$ and NH_2Cl, which can initiate subsequent chain reactions to generate reactive species that promotes organic contaminant degradation (Anear and Yagil, 1962; Saunier and Selleck, 1979). Solution pH also affects the speciation of HOCl/OCl^-, $ONOO^-$/ONOOH, as well as the formation of reactive chlorine species (Matthew and Anastasio, 2006; Koppenol et al., 1992; Goldstein et al., 2005). In addition, the HOCl-to-NH_2Cl molar ratio in the mixed HOCl/NH_2Cl system affects the speciation of chlor(am)ine species and the yield of reactive species.

One ubiquitously present trace organic contaminant in both conventional and recycled water is 1,4-dioxane (1,4-D) (Zenker et al., 2003). It is a class 2B probable human carcinogen and an indicator compound for water reuse treatment design. California requires a 0.5-log removal of 1,4-D to validate the design of an AOP treatment for potable reuse (International Agency for Research on Cancer, 1999; California State Water Resources Control Board, 2014). However, UV-AOP removes 1,4-D at the expense of a large photon energy consumption. In contrast, harnessing the chemical reaction of HOCl rapidly mixing into NH_2Cl in the absence of UV irradiation for an efficient 1,4-D removal can greatly reduce the energy footprint. Furthermore, the mixed HOCl/NH_2Cl system can also be implemented in wastewater for the degradation of other organic contaminants if the reaction mechanism is understood.

To evaluate the application of the mixed HOCl/NH_2Cl system in water treatment, it is imperative to acquire a mechanistic understanding of the oxidative reactions via HOCl rapidly mixing into NH_2Cl. Accordingly, the objectives of the study were to provide mechanistic insights into the mixed HOCl and NH_2Cl system by an investigation of the reaction pathways, examination of the reactive species contribution, and exploration of the effects of water parameters on 1,4-D removal for potential optimization and implication of the technique in water treatments. 1,4-D was selected as the model organic contaminant because of its high occurrence and relevance to water treatment.

2. Materials and methods

2.1. Materials and reagents

All solutions were prepared using deionized water (18.2 MΩ•cm) from a Milli-Q system (Millipore Corp) and ACS reagent-grade or higher chemicals (Fisher Scientific and Sigma-Aldrich). A 50-mM NH_2Cl working solution was prepared freshly by dripping NaOCl into $(NH_4)_2SO_4$ buffered with 4 mM borate at pH 8.8, with an initial nitrogen-to-chlorine molar ratio of 1.2 and was equilibrated for a minimum of 2 hr before use. An $NHCl_2$ working solution was prepared by dripping concentrated perchloric acid slowly and gradually into the freshly made NH_2Cl solution until the solution pH approached 3. The final NH_2Cl working solutions contained a negligible amount of ammonium ion, nitrate, and nitrite. A 8–12 mM $ONOO^-$ stock solution was synthesized by the rapid acidification of a solution of hydrogen peroxide and sodium nitrite using hydrochloric acid that was immediately quenched with sodium hydroxide (Hughes and Nicklin, 1968a). Details on the preparation of the $ONOO^-$ solution is provided in Text S1 in the Supporting Information (SI).

2.2. Chemical oxidation experiments

To start an experiment, 1,4-D and NH_2Cl were added to a 50-mL petri dish reactor under rapid and constant agitation to achieve an initial concentration of 100 µM of 1,4-D and 3 mM of NH_2Cl, followed by the rapid addition of a small volume (no greater than 0.6 mL) of a 750-mM

HOCl solution to obtain a HOCl-to-NH_2Cl molar ratio ranging between 0.25 and 3. This range of molar ratio is typically observed in conventional drinking water treatment and water reuse applications. Solution pH was maintained at 3, 6, or 9 using 40-mM phosphate buffer (Text S1). These three pH levels were chosen to represent a wide spectrum of acidic, near-neutral, and alkaline conditions for a comprehensive understanding of the pH effects. Solution ionic strength was maintained at 50 mM. The reaction between HOCl and NH_2Cl was completed at approximately 1 min. Hence, 1 min after HOCl was rapidly mixed into NH_2Cl, a 2-mL sample was withdrawn from the reactor to quantify 1,4-D and identify chlorine species. To quantify $HO^{\bullet}$ and other reactive species generated in the reaction, 100 mM of *tert*-butanol (TBA) was added to the NH_2Cl solution in selective experiments prior to the rapid addition of HOCl to efficiently scavenge $HO^{\bullet}$ ($k = 6.0 \times 10^{9}$ M^{-1} s^{-1}) generated in the mixed system (Buxton et al., 1988). The difference between the system with and without TBA was calculated as the contribution of $HO^{\bullet}$ to 1,4-D removal. Details of the scavenging experiments and calculations are provided in Text S2, Table S1, and Fig. S1 in the SI. To investigate the chemical system in flow-concentration conditions relevant to potable reuse, additional experiments were conducted using 0.23 µM of 1,4-D, 42 µM of NH_2Cl with a HOCl-to-NH_2Cl molar ratio of 1 at pH 6 buffered by 40 mM of phosphate. 500 µM of TBA was used to quantify the contribution of $HO^{\bullet}$ for 1,4-D degradation. In addition, experiments on the hydrolysis of chloramines were conducted at pH 3, 6, and 9. All the experiments were conducted at 25 °C in triplicate.

Anaerobic control experiments on the HOCl/NH_2Cl mixed system were conducted using solutions purged with N_2 gas (dissolved oxygen concentration was below 0.5 mg/L) in a glovebox to evaluate the effects of dissolved oxygen on the generation of reactive species. Additional control experiments were conducted in pH 3 solutions continuously purged with carbon dioxide (CO_2) for 1 min without substantial loss of dissolved oxygen to evaluate the significance of $ONOO^-$ to 1,4-D degradation as dissolved CO_2 strongly scavenges $ONOO^-$. Details on the N_2- and CO_2-purged experiments are provided in Text S3.

2.3. Analytical methods

HOCl, NH_2Cl, and $NHCl_2$ were quantified by the *N,N*-diethyl-*p*-phenylenediamine (DPD) standard method with the addition of different amounts of potassium iodide using a VWR spectrophotometer (UV-3100PC UV–VIS) (Clesceri et al., 1989). Synthesized $ONOO^-$ stock solutions between 8 and 12 mM were measured spectrophotometrically at 302 nm ($\varepsilon = 1670$ M^{-1} cm^{-1}) (Hughes and Nicklin, 1968b). Generation of $ONOO^-$ via the hydrolysis of chloramines in the absence of chlorine was quantified in situ using folic acid as a fluorescence probe of $ONOO^-$ (Huang et al., 2007). Trace levels of $ONOO^-$ generated in the mixed HOCl/NH_2Cl system was quantified in situ using a highly-selective probe DAX-J2-PON Green sensor (AAT Bioquest, Sunnyvale, CA, USA) via a microplate reader (SYNERGY H1, BioTek) (Luo et al., 2017). 1,4-D was measured by high performance liquid chromatography (Agilent 1200 Series) coupled with a diode array detector (HPLC-DAD) (Mangalgiri et al., 2019). Trace levels of 1,4-D (≤0.23 µM) from flow-concentration condition experiments were measured by EPA Method 522 by gas chromatography coupled with mass spectrometry (GC-MS, Agilent). Details of analytical methods for 1,4-D and $ONOO^-$ are provided in Text S4.

3. Results and discussion

3.1. 1,4-Dioxane removal in the mixed HOCl/NH_2Cl system

No volatilization and degradation of 1,4-D were observed in the single oxidant system (HOCl or NH_2Cl alone) up to 30 min. In contrast, substantial and quick removal of 1,4-D was observed 1 min after HOCl was rapidly mixed into NH_2Cl at different HOCl-to-NH_2Cl ratios and solution pH (Fig. 1). The percentage of 1,4-D removal was highest at pH 6 and decreased significantly at more alkaline pH of 9 or more acidic pH of 3. The effects of pH were associated with the hydrolysis and decay of chloramines in the reaction system. As HOCl is mixed rapidly into NH_2Cl, HOCl converts NH_2Cl to $NHCl_2$ (R1 in Scheme 1; all the subsequent reactions are referred to Scheme 1), which further reacts with HOCl to form NCl_3 (R2) depending on the HOCl-to-NH_2Cl ratio (Valentine and Jafvert, 1992). The hydrolysis of $NHCl_2$ generates NH_2OH (R3) as the major pathway (Pham et al., 2021; Saunier and Selleck, 1979). NH_2OH further reacts with HOCl (R4; $k = 1.35 \times 10^{7}$ M^{-1} s^{-1}) or NH_2Cl (R5; $k = 1.8 \times 10^{2}$ M^{-1} s^{-1}) to produce HNO (Wahman et al., 2014; Giles, 1999). Meanwhile, NH_2Cl can hydrolyze to produce NH_2OH (R6) with a much slower rate than $NHCl_2$ hydrolysis (R3), (Anear and Yagil, 1962; Saunier and Selleck, 1979) and $NHCl_2$ can hydrolyze to HNO (R7) (Pham et al., 2021; Szczuka et al., 2020). These hydrolysis reactions (R6 and R7) provide a secondary and less important pathway that leads to HNO formation. HNO further deprotonates to form NO^- (R8) (Johnson et al., 2002). In the presence of dissolved oxygen, NO^- is rapidly converted into $ONOO^-$ (R9; $k = 2.7 \times 10^{9}$ M^{-1} s^{-1}), a critical precursor for the subsequent generation of $HO^{\bullet}$ and other reactive species for 1,4-D degradation (Shafirovich and Lymar, 2003). Therefore, the yield of reactive radical species is initiated by the hydrolysis and decay of NH_2Cl and $NHCl_2$. Meanwhile, as side reactions, NH_2OH can react with HNO to form nitrogen gas (R10), and HNO reacts with NH_2Cl (R11) and $NHCl_2$ (R12) to generate nitrogen gas as well (Johnson et al., 2002; Wahman et al., 2014).

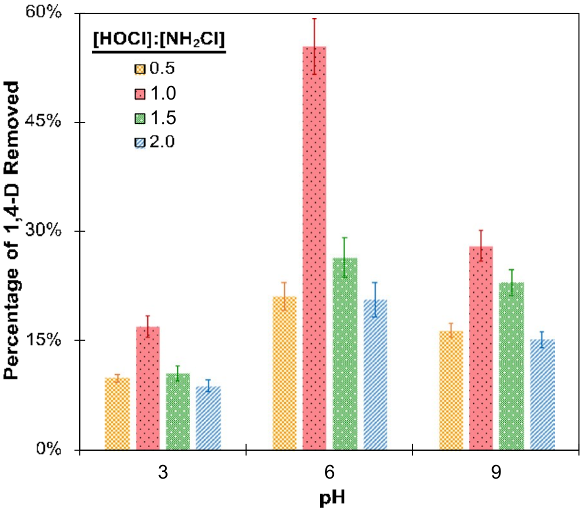
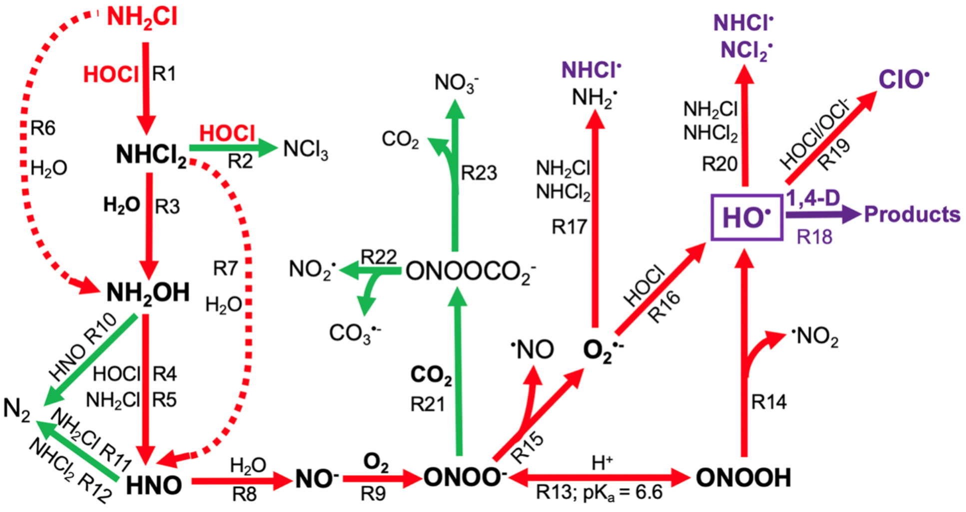


Fig. 1. The removal of 1,4-D from the chemical reaction of HOCl with NH_2Cl at the varying HOCl-to-NH_2Cl ratios and solution pH. $[1,4\text{-}D]_0 = 100$ µM, $[NH_2Cl]_0 = 3$ mM, $[TOTPO_4] = 40$ mM, Reaction Time = 1 min. Error bars represent the standard deviation of experimental triplicates.

In the mixed HOCl/NH_2Cl system, the effects of pH are multifold. Solution pH significantly affects the extent of transient formation of $NHCl_2$ and subsequently its hydrolytic decay rate, which impacts the yield of $ONOO^-$ and the oxidative capacity of the system. First, the generation of $NHCl_2$ via the reactions between HOCl and NH_2Cl is faster at more acidic pHs, as NH_2Cl reacts much faster with the protonated form of free chlorine (HOCl) than with the deprotonated form of free chlorine (OCl^-) (Pressley et al., 1972). Real-time $NHCl_2$ measurement confirmed that the cumulative formation of $NHCl_2$ was much faster at pH 3 than at higher pHs (Fig. S2). Second, the hydrolytic decay rate of $NHCl_2$ (R3 and R7) to initiate the chain reactions is much faster at higher pHs (Anear and Yagil, 1962; Saunier and Selleck, 1979). Additional control experimental data showed that the rate of $ONOO^-$ formation via hydrolytic decay of $NHCl_2$ increased by more than 20 times when the solution pH increased from 3 to 9 (Fig. S3A). Third, HNO generation by the hydrolytic decay of $NHCl_2$ (R3-R5) is much faster compared to the formation initiated by NH_2Cl hydrolysis (R6). For example, as the



Scheme 1. Reaction scheme for the mixed HOCl/NH$_2$Cl system, with proposed reaction pathways for the generation of reactive species responsible for 1,4-D degradation. Major reaction pathways (red), generated reactive species for 1,4-D removal (purple) and scavenging reactions (green).

solution pH increased from 3 to 9, the ONOO$^-$ formation rate via the hydrolytic decay of NH$_2$Cl was much lower than that via the hydrolytic decay of NHCl$_2$ (Fig. S3B vs. Fig. S3A). Therefore, the combined opposing multifaced effects of pH—slow formation of NHCl$_2$ at high pH but rapid hydrolysis at high pH—result in an enhanced ONOO$^-$ formation at the near-neutral pH range, which supports the observation of maximum oxidative capacity of the mixture system was reached at the near-neutral pH of 6 (Fig. 1). The least efficient 1,4-D degradation was observed at pH 3, because the hydrolytic decay of NHCl$_2$ was extremely slow at this acidic pH (Fig. S3A).

Further, the HOCl-to-NH$_2$Cl molar ratio strongly affected the reactivity of the mixed HOCl/NH$_2$Cl system. An HOCl-to-NH$_2$Cl molar ratio of 1 exhibited the highest 1,4-D removal (Fig. 1). When the range of the HOCl-to-NH$_2$Cl ratio was expanded from 0.25 to 3, the mixed HOCl/NH$_2$Cl system exhibited a bell curve, with the highest 1,4-D removal at the HOCl-to-NH$_2$Cl ratio of 1 (Fig. 2). When the HOCl-to-NH$_2$Cl ratio is less than 1, the conversion of NH$_2$Cl to NHCl$_2$ by HOCl (R1) is limited by the HOCl availability in the system, and consequently decreases the formation of ONOO$^-$ and HO$^•$ (R9-R16). This trend was supported by the observation that only 50 % of residual NH$_2$Cl was consumed at an HOCl-to-NH$_2$Cl ratio of 0.5 (Fig. S4A). When the HOCl-to-NH$_2$Cl ratio is greater than 1, the scavenging reaction between HOCl and NHCl$_2$ (R2) becomes increasingly significant while the hydrolytic reactions of NHCl$_2$ (R3 and R7) are suppressed. This trend was supported by the high NH$_2$Cl consumption (Fig. S4A) and relatively low HOCl consumption (Fig. S4B) observed at the HOCl-to-NH$_2$Cl ratios of 1.5 and 2. In contrast, at the HOCl-to-NH$_2$Cl molar ratio of 1, the formation of NHCl$_2$ peaked and participated in the hydrolytic decay reactions to the highest extent.

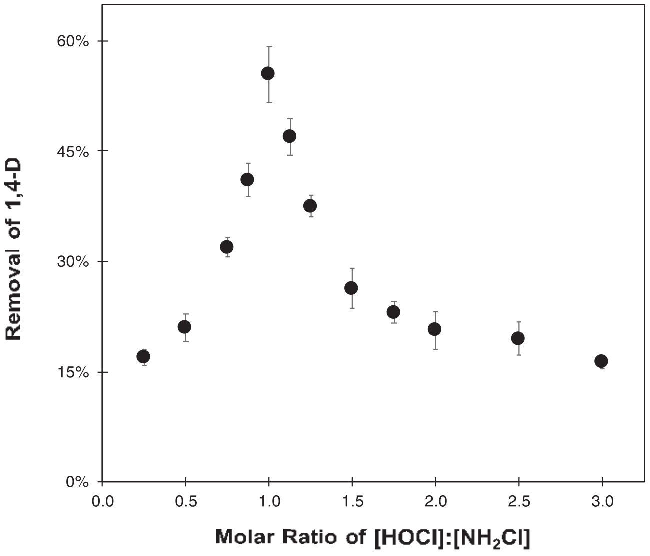


Fig. 2. The removal of 1,4-D from the chemical reaction of HOCl with NH$_2$Cl for HOCl-to-NH$_2$Cl ratios from 0.25 to 3 at pH 6. [1,4-D]$_0$ = 100 μM, [NH$_2$Cl]$_0$ = 3 mM, [TOTPO$_4$] = 40 mM, Reaction Time = 1 min. Error bars represent the standard deviation of experimental triplicates.

3.2. Impact of water chemistry on reactive species generation

The effect of solution pH on radical contribution was evaluated at an HOCl-to-NH$_2$Cl molar ratio of 1. HO$^•$ was quantified as a major contributor to 1,4-D removal (Fig. 3A). There are two pathways to generate HO$^•$ via ONOO$^-$. First, ONOO$^-$ protonates to form ONOOH with a pK_a of 6.6 (R13)[21], which decays into HO$^•$ and $^•$NO$_2$ (R14; $k = 3.5 \times 10^{-1}$ s^{-1}) (Goldstein et al., 2005). Second, ONOO$^-$ decomposes into NO$^•$ and O$_2^{•-}$ (R15; $k = 2.0 \times 10^{-2}$ s^{-1}) (Goldstein et al., 2005). O$_2^{•-}$ further reacts with HOCl to generate HO$^•$ (R16; $k = 7.5 \times 10^6$ M^{-1}s^{-1}), (Long and Bielski, 1980) or reacts with NH$_2$Cl and NHCl$_2$ (R17) to form NH$_2^•$ and NHCl$^•$. HO$^•$ degrades 1,4-D (R18; $k = 3.1 \times 10^9$ M^{-1}s^{-1}) (Eibenberger, 1980). Therefore, the yield of HO$^•$ was directly linked to the generation of ONOOH and the decomposition of ONOO$^-$. Because the generation of ONOOH (R13; pK_a = 6.6)[21] is directly associated with the formation of NHCl$_2$ and its hydrolytic decay (R1–R13) that exhibited the highest rate at pH 6, the contribution of HO$^•$ to 1,4-D degradation was highest at pH 6, accounting for 37 % of 1,4-D degradation (Fig. 3A). HO$^•$ also reacts with co-existing constituents (R19 and R20), including HOCl ($k = 1.2 \times 10^9$ M^{-1}s^{-1}), (Bulman et al., 2019) OCl$^-$ ($k = 6.37 \times 10^9$ M^{-1}s^{-1}), (Bulman et al., 2019) NH$_2$Cl ($k = 1.02 \times 10^9$ M^{-1}s^{-1}), (Chuang et al., 2017) and NHCl$_2$ ($k = 6.21 \times 10^8$ M^{-1}s^{-1}), (Zhang et al., 2019) to generate secondary species (ClO$^•$, NHCl$^•$, and NCl$_2^•$). These secondary species may oxidize 1,4-D and contributed to 6–18 % of 1,4-D degradation (Fig. 3A).

At pH 9, ONOOH deprotonated to ONOO$^-$ (R13; pK_a = 6.6)[21] and suppressed the direct HO$^•$ formation (R14) (Liu and Dodd, 2021). Meanwhile, OCl$^-$ became the dominant form of free chlorine and the reaction between HOCl and O$_2^{•-}$ (R16) was suppressed. As a result, the yield of HO$^•$ and other reactive species decreased at pH 9 (Fig. 3A). At pH 3, the hydrolytic decay of NHCl$_2$ was suppressed and resulted in a lower yield of ONOO$^-$. Eventually, the formation of HO$^•$ and other reactive species was significantly reduced either via the ONOOH decay

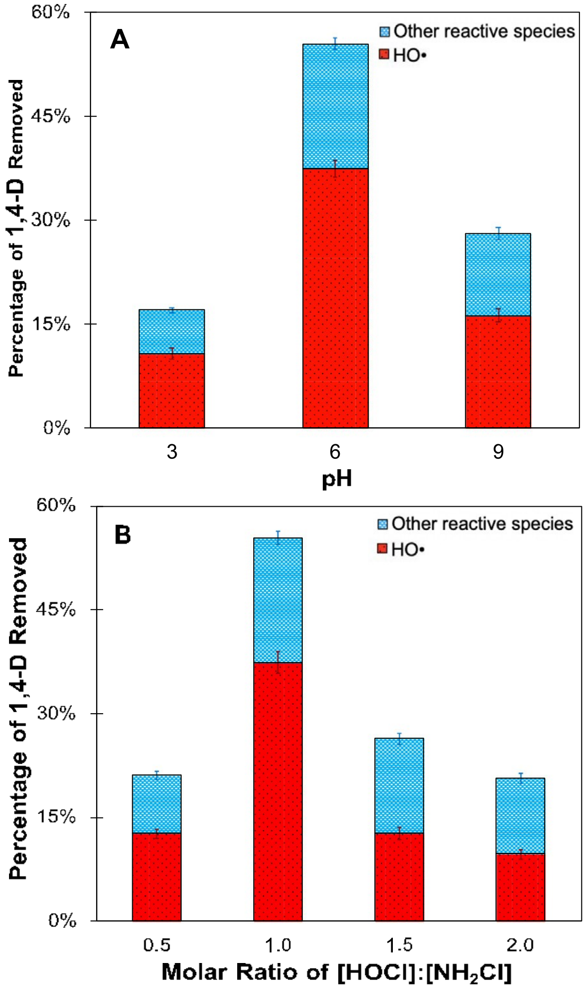


Fig. 3. Contribution of reactive species towards 1,4-D removal at different HOCl-to-NH$_2$Cl ratios and pH. [NH$_2$Cl]$_0$ = 3 mM; [*tert*-butanol]$_0$ = 100 mM, [TOTPO$_4$] = 40 mM, Reaction Time = 1 min (A) pH effect at the HOCl-to-NH$_2$Cl ratio of 1; (B) HOCl-to-NH$_2$Cl ratio effect at pH 6. Error bars represent the standard deviation of experimental triplicates. Detailed calculations are available in Text S2 and Fig. S1.

(R14) or $O_2^{\bullet -}$ pathway (R15 and R16).

The effects of the HOCl-to-NH$_2$Cl molar ratio on radical contribution were evaluated at pH 6. The contribution of HO$^\bullet$ was the highest at the HOCl-to-NH$_2$Cl ratio of 1, accounting for 37 % of 1,4-D removal (Fig. 3B). As the HOCl-to-NH$_2$Cl ratio deviates from 1, the yield of HO$^\bullet$ decreased. Additionally, when the HOCl-to-NH$_2$Cl ratio was greater than 1, the relative contributions of secondary reactive species increased that was a result of increased reaction of HO• with HOCl (R19; $k = 1.2 \times 10^9$ $M^{-1}s^{-1}$) and OCl$^-$ (R19; $k = 6.37 \times 10^9$ $M^{-1}s^{-1}$), (Bulman et al., 2019) leading to the formation of ClO$^\bullet$.

3.3. Reaction mechanisms of ONOO$^-$/ONOOH formation

In N$_2$-purged solution, 1,4-D removal was suppressed to negligible levels in the mixed HOCl/NH$_2$Cl system (Fig. 4A). The substantial reduction of oxidative capacity in the absence of dissolved oxygen confirmed the importance of dissolved oxygen in generating ONOO$^-$ (R9), which is a critical precursor leading to the generation of subsequent reactive species for 1,4-D removal. Importantly, ONOO$^-$ reacts with dissolved CO$_2$ to generate ONOOCO$_2^-$ (R21; $k = 2.9 \times 10^4$ $M^{-1}s^{-1}$), (Goldstein et al., 2005) which further decays into carbonate radical $CO_3^{\bullet -}$ and $NO_2^\bullet$ (R22), or CO$_2$ and NO_3^- (R23) (Lymar and Hurst, 1998). In a CO$_2$-purged solution at pH 3, 1,4-D removal was also suppressed to negligible levels compared to the air-saturated condition (Fig. 4B). These observations strongly supported that the formation of ONOO$^-$ via deprotonation of ONOOH in the mixed HOCl/NH$_2$Cl system was critical for subsequent reactive species formation that leads to eventual 1,4-D removal.

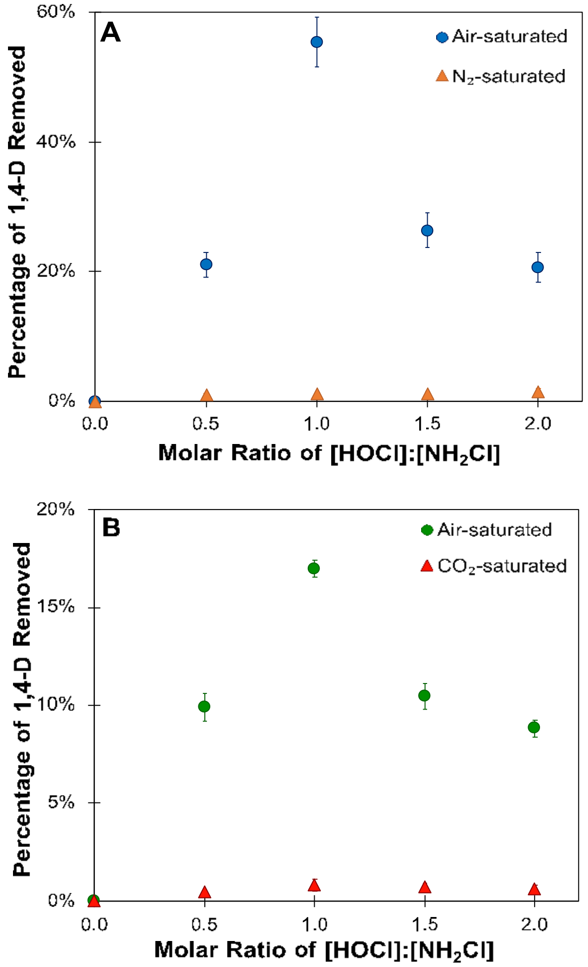


Fig. 4. Effects of dissolved oxygen and carbon dioxide on 1,4-D removal at different HOCl-to-NH$_2$Cl ratios. [1,4-D]$_0$ = 100 μM, [NH$_2$Cl]$_0$ = 3 mM, [TOTPO$_4$] = 40 mM, Reaction Time = 1 min (A) Dissolved oxygen effect on 1,4-D removal at pH 6; (B) Carbon dioxide effect on 1,4-D removal at pH 3. Error bars represent the standard deviation of experimental triplicates.

The generation of ONOO$^-$ in the mixed HOCl/NH$_2$Cl system was further confirmed by in situ measurement of ONOO$^-$ in different chemical systems at pH 6 (Fig. 5). In the single oxidant system with 3 mM HOCl, there was no ONOO$^-$ formation, because no hydrolytic delay reaction took place with HOCl alone. In the single oxidant system with 3 mM NH$_2$Cl, there was a small amount of 0.6 μM ONOO$^-$ formation, due to the slow hydrolytic decay of NH$_2$Cl and chain reactions (R6–R9). Furthermore, in a single oxidant system with 3 mM NHCl$_2$, the amount of ONOO$^-$ formation increased by 6.6 times to 4 μM (R7-R9), suggesting that the hydrolysis rate of NHCl$_2$ is much faster than the hydrolysis of NH$_2$Cl. In comparison, when 3 mM HOCl was rapidly mixed into 3 mM NH$_2$Cl, the formation of ONOO$^-$ reached 482 μM, two orders of magnitude higher than a single NHCl$_2$ system (Fig. 5). HNO, the crucial pre-cursor to ONOO$^-$, generated via either the direct reaction of the formed NH$_2$OH (R6) and HOCl/NH$_2$Cl (R4 and R5) or the direct hydrolysis of NHCl$_2$ (R7). In a single NH$_2$Cl or NHCl$_2$ system, the yield of HNO was low due to the suppressed generation of NH$_2$OH via R6, or the limited generation of HNO by R7. Hence, the highest ONOO$^-$ concentration was observed at the mixed HOCl/NH$_2$Cl system due to the substantial

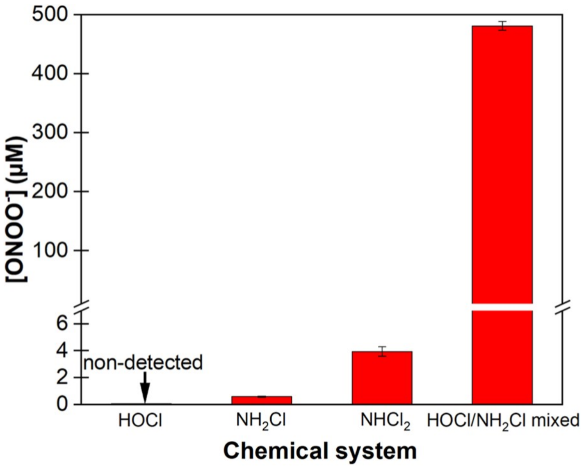


Fig. 5. Peroxynitrite quantification by fluorescence from the reaction of DAX-J2 PON Green with HOCl, NH_2Cl, $NHCl_2$ and HOCl/NH_2Cl, respectively. $[HOCl]_0 = 3$ mM, $[NH_2Cl]_0 = 3$ mM, $[NHCl_2]_0 = 3$ mM, pH = 6, Reaction Time = 1 min. Error bars represent the standard deviation of experimental triplicates.

generated HNO via R3–R5.

3.4. *Environmental Implication*

Significant HO$^\bullet$ exposure (1.1×10^{10} M•s) was observed under high-concentration conditions investigated in the study that generated significant quantities of ONOO$^-$ (Fig. S5). For conventional water treatment, the oxidative capacity of mixing HOCl with NH_2Cl can be harnessed to enhance contaminant degradation. 1,4-D is commonly detected in groundwater and surface water at a wide range of concentrations (μg/L to mg/L) (Adamson et al., 2014). Ammonia is also widely detected in groundwater and surface water (US EPA, WHO). Therefore, the traditional application of HOCl as a disinfectant creates a potential reactive system where NH_2Cl is formed and further mixing with HOCl takes place (Pressley et al., 1972). Enhanced 1,4-D removal and other organic contaminants can be achieved by optimizing the HOCl-to-NH_2Cl ratio and pH.

Under low-concentration conditions encountered in RO permeate during potable reuse applications, the experimental data showed HO$^\bullet$ exposure of 1.5×10^{10} M•s, which was comparable to the value obtained at high-concentration conditions (Fig. S5). Although fresh RO permeate can contain an oversaturated level of dissolved CO_2 due to the pressurized membrane process that increases CO_2 solubility from air, the generation of HO$^\bullet$ in RO permeate is still an important pathway when taking account into the CO_2 scavenging effects on ONOO$^-$ (detailed calculation provided in Text S5 and Table S2). Furthermore, a significant fraction of HO$^\bullet$ can react with 1,4-D after taking account into the potential HO$^\bullet$ scavenging effects of background bicarbonate in RO permeate (Text S6 and Table S3). Typically, a decarbonation step (i.e., aeration) is applied to the fresh RO permeate. This step significantly reduced the total carbonate concentrations and increase the dissolved oxygen level in the product water – two factors that favor the generation of HO$^\bullet$. Therefore, to fully take advantage of the oxidative capacity of the mixed HOCl//NH_2Cl system, water reuse facilities can implement the treatment train of the mixed system after the decarbonation step for micropollutant degradation.

In addition, although chlorine reaction with ammonia can lead to the formation of NDMA, a carcinogenic disinfection byproduct, (Pham et al., 2021; Sgroi et al., 2015; Wu et al., 2021; Mitch et al., 2003; Fujioka et al., 2012) this risk can be minimized by removing NDMA precursors from the feedwater through effective pre-treatment steps upstream. The mixed HOCl/NH_2Cl oxidative system in broader water treatment scenarios can benefit the degradation of trace organic contaminants. Future work to establish a kinetics model to predict the oxidative reactivity of the mixed HOCl and NH_2Cl system is warranted.

4. Conclusions

This study illustrated the pathways leading to the formation of reactive species that oxidize 1,4-D; and provided insights into the effects of water chemistry parameters on 1,4-D removal efficiency. ONOO$^-$ was identified as the critical reactive species formed in the mixed HOCl/NH_2Cl system. Chain reactions of ONOO$^-$ involving its protonation and subsequent decay result in the generation of HO$^\bullet$ and secondary reactive species that oxidize 1,4-D. The yield of HO$^\bullet$ favors low dissolved CO_2 and the presence of dissolved O_2. The optimum condition for efficient 1,4-D removal was found at the near-neutral pH of 6 with the HOCl-to-NH_2Cl ratio of 1. The findings of this study benefit future optimization of systems in which HOCl and NH_2Cl coexist and can be further applied to oxidatively degrade trace organic contaminants in water treatment and reuse scenarios. Future work is needed to investigate the effects of other chemical constituents (e.g., Cl^-, NO_2^-, NO_3^- and natural organic matter) to advance the understanding of matrix effects of the mixed HOCl/NH_2Cl system in real-world water treatment and reuse conditions.

CRediT authorship contribution statement

L.W.: Conceptualization, Investigation, Writing. *S.P.*: Conceptualization, Investigation. *H.L.*: Conceptualization, Supervision, Writing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Environmental Implication

1,4-dioxane (1,4-D) is a probable human carcinogen, and it must be removed from water during water treatments and reuse applications due to its wide occurrence and hazardous nature. The mixed HOCl/NH_2Cl system investigated in the study showed a promising potential for the implication of the technique in the real-world water treatment and reuse facilities for the rapid removal of the hazardous 1,4-D in realistic water parameters with a low energy footprint. The findings of this study also provided meaningful guidance for water treatment and reuse facilities to fully utilize the technique for achieving enhanced removal of 1,4-D.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.129760.

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