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Sulfate Radical-Based Advanced Oxidation Treatment for Groundwater Water Treatment
and Potable Water Reuse

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Environmental Toxicology

by

Wei Li

September 2017

Dissertation Committee:
      Dr. Haizhou Liu, Chairperson
      Dr. Sharon Walker
      Dr. Dan Schlenk

The Dissertation of Wei Li is approved:

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<div align="right">Committee Chairperson</div>

University of California, Riverside

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Dedication

This dissertation is dedicated to my great mom, Minjie Zhang. She was diagnosed with Lambert-Eaton disease in 2014, a year after I got into the Ph.D. program. Even though her health is getting worse every day, she has never complained about me going home late. She has helped me to raise my kids and relieve my worries about family so that I could be working at full strength. Her supportiveness and dedication pushes me through many difficulties which helped me complete my Ph.D. degree.

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ABSTRACT OF THE DISSERTATION

Sulfate Radical-Based Advanced Oxidation Treatment for Groundwater Water Treatment
and Potable Water Reuse

by

Wei Li

Doctor of Philosophy, Graduate Program in Environmental Toxicology
University of California, Riverside, September 2017
Dr. Haizhou Liu, Chairperson

Climate change and population growth pose increasing challenges to the availability of fresh water resources. Remediation of contaminated groundwater and recycling of wastewater are two promising solutions to increase fresh water supplies. Persulfate ($S_2O_8^{2-}$)-based advanced oxidation processes (AOPs) have gained increasing attention in recent years due to the generation of highly reactive and selective sulfate radicals ($SO_4^{\bullet-}$). $S_2O_8^{2-}$-based AOPs have been widely used in *in situ* chemical oxidation (ISCO) for groundwater remediation. $UV/S_2O_8^{2-}$ is also an alternative to UV/H_2O_2 that can be used to treat recycled wastewater into high quality drinking water.

In this dissertation work, the application of $S_2O_8^{2-}$-based AOPs in ISCO and UV/AOPs was examined. First, the effects of important groundwater chemical parameters, *i.e.*, alkalinity, pH and chloride on benzene degradation via heterogeneous $S_2O_8^{2-}$ activation by three Fe(III)- and Mn(IV)-containing aquifer minerals (*e.g.* ferrihydrite, goethite and pyrolusite) were examined. A comprehensive kinetic model was established to elucidate the mechanisms of radical generation and mineral surface complexation. Results showed

that an increase of alkalinity up to 10 meq/L decreased the rates of persulfate decomposition and benzene degradation. These results were associated with the formation of unreactive surface carbonato complexes. An increase in pH generally accelerated persulfate decomposition due to enhanced formation of reactive surface hydroxo complexation. A change in the chloride level up to 5 mM had a negligible effect on the reaction kinetics. Kinetics modeling also suggested that $SO_4^{\bullet-}$ was transformed into hydroxyl radicals ($HO^{\bullet}$) and carbonate radicals ($CO_3^{\bullet-}$) at higher pHs.

Secondly, we investigated 1,4-dioxane degradation by $UV/S_2O_8^{2-}$ in the presence of monochloramine (NH_2Cl), a membrane anti-fouling reagent. The mixing effects of NH_2Cl and $S_2O_8^{2-}$ on 1,4-dioxane degradation were examined at various oxidant doses, chloride concentrations, solution pHs and dissolved O_2 levels. Results showed that a NH_2Cl-to-$S_2O_8^{2-}$ molar ratio of 0.1 was optimal, beyond which the scavenging effects of NH_2Cl on $HO^{\bullet}$, $SO_4^{\bullet-}$, and $Cl_2^{\bullet-}$ radicals decreased 1,4-dioxane degradation rate. At the optimal ratio, the degradation rate of 1,4-dioxane increased linearly with the total oxidant dose up to 6 mM. The simultaneous photolysis of NH_2Cl and $S_2O_8^{2-}$ was sensitive to the solution's pH, due to a disproportionation of NH_2Cl into less photo-reactive dichloramine ($NHCl_2$) and radical scavenger NH_4^+ at pH lower than 6. An increase of chloride concentration transformed reactive $HO^{\bullet}$ and $SO_4^{\bullet-}$ to less reactive $Cl_2^{\bullet-}$, while the presence of dissolved O_2 promoted 1,4-dioxane degradation and gaseous nitrogen production by participating in the 1,4-dioxane and NH_4^+ oxidation steps.

Third, based on the experimental investigations, a kinetic model was developed and

the fundamental mechanisms of contaminant degradation by three UV/AOPs, *i.e.*, UV/hydrogen peroxide (H_2O_2), $UV/S_2O_8^{2-}$ and UV/chlorine (HOCl) were simulated. Results showed that the treatment efficiency of contaminants generally followed the order of $UV/S_2O_8^{2-}$ > UV/H_2O_2 > UV/HOCl under chemical conditions relevant to reverse osmosis (RO) permeate. The generation of $HO^{\bullet}$ was important in UV/H_2O_2 to degrade contaminants, whereas both $SO_4^{\bullet-}$ and $HO^{\bullet}$ contributed to degradation of contaminants in $UV/S_2O_8^{2-}$. $CO_3^{\bullet-}$ predominated in UV/HOCl. Among the three UV/AOPs, the treatment efficiency of $UV/S_2O_8^{2-}$ was most sensitive to pH, chloride and inorganic carbon. The results provided guidance on the design and optimization of UV/AOP systems for water reuse under diverse chemical conditions.

Finally, the oxidation byproducts (OBPs) of benzene and 1,4-dioxane by $S_2O_8^{2-}$-based AOPs were investigated, and the cytotoxicity and genotoxicity levels of the parent compound and oxidation byproducts were compared. Results showed that phenol and aldehyde were the major products from benzene degradation. 1,4-dioxane was transformed into six major intermediates after UV/AOP treatments including ethylene glycol diformate, formaldehyde, glycolaldehyde, glycolic acid, formic acid, and methoxyacetic acid. Toxicity assays showed that the aldehyde and phenol were extremely genotoxic and cytotoxic compared to benzene and 1,4-dioxane. Results suggested that evaluation of the efficiency of any AOPs applied to water treatment must not only include study of the disappearance of the parent compound, but also needs further study of the toxicity of the subsequent oxidation byproducts.

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Chapter 1

Introduction

1.1 Motivation: in Response to Fresh Water Crisis

Nearly seventy percent of the earth's surface is covered by water; however, fresh water that is essential for life is extremely limited and mostly stored as glaciers in the Arctic Pole and Antarctica.[1,2] Accessible surface wate and groundwater only account for less than 1% of total water on earth. In much of the developing world, fresh water is becoming an increasingly precious resource that requires labor and money to obtain.[3] In the U.S., people have taken water for granted and have become the most inefficient water users. In arid regions, such as California, many water-intensive crops, such as alfalfa and almond trees are grown. The average American water consumption is 300 gallons per day, twice as much as our European counterparts and 100 times more than in developing countries.[4] At the same time, unpredictable climate conditions, uncontrolled population/economic growth, and source water contamination as a result of industrialization exacerbate the water shortages.[2,5,6] Global warming alters precipitation patterns, melts mountain glaciers, and bring more frequent floods and droughts. Population growth is a major contributor to water scarcity. The increase in population means an increasing demand for more water, food, and commodities. The demand for more economic growth seen in nations including China and India has resulted in a need to harness more water for power generation and manufacturing. Economic, industry, and agriculture activities are depleting our fresh water resources, while at the same time dumping wastewater into water bodies. Agricultural runoff, industrial discharge, and untreated sewage are damaging our water quality.[7,8] Water pollution makes a large volume of fresh water unsuitable for use and worsens water scarcity. In response to the crisis, we are exploring water efficiency, desalinating sea water,

expanding wastewater reuse, and repairing damaged water bodies to increase our fresh water supplies. In this dissertation, we are focusing on the emerging chemical oxidation technologies for mitigating contaminated groundwater and recycling wastewater.

1.2 Persulfate-Based ISCO for Groundwater Remediation

Groundwater contamination, which nearly always results from human activities, is difficult and expensive to clean up.[8] Sources of groundwater contamination vary from residential and municipal to industrial and agricultural activities.[9] Leakage of septic systems, sewers and pipelines, improper disposal of hazardous waste, spill from underground petroleum storage tanks, and agricultural runoff that contains pesticide and fertilizer are all possible sources of contamination.[9] Since 1980, the EPA superfund site program has completely remediated more than one thousand heavily contaminated sites. However, there are still more than thirteen hundred superfund sites listed on the National priority list, plus newly discovered sites. Groundwater remediation is still an ongoing challenge.[10] Over the years, research efforts have been directed at advancing and improving the treatment technologies. Examples of these technologies include physical separation, solidification, pump and treat, recycling, phytoremediation, chemical oxidation, thermal treatment, bioremediation, flushing, fracturing, and extraction.[11] Of those technologies, *in situ* Chemical Oxidation (ISCO) is the most rapidly growing remedial technology which is applied at many EPA hazardous waste sites due to its cost-effective performance.[12]

ISCO is a form of advanced chemical oxidation treatment process mostly used for soil or groundwater remediation that utilizes strong oxidants. Example of oxidants used in

ISCO includes catalyzed hydrogen peroxide (H_2O_2), permanganate($KMnO_4$), Ozone (O_3) and persulfate ($S_2O_8^{2-}$) to oxidize contaminants to less toxic substances.[13] Catalyzed H_2O_2 propagations have been established for years and found to be effective for removing almost all aromatic compounds including halogenated compounds.[14] However, catalyzed H_2O_2 has relatively low reactivity with alkanes.[15] Furthermore, the stability of H_2O_2 in the subsurface poses a significant shortcoming. The half-life of H_2O_2 ranges from a few hours to up to 10 days depending on soil conditions.[16] $KMnO_4$ is the oxidant of choice for treating alkenes and chlorinated compounds.[14] However, the solubility of $KMnO_4$ is relatively low compared to other oxidants.[17] During its oxidation of organic substances, $KMnO_4$ is reduced to solid manganese dioxide, which is in the form of non-soluble crystals. In addition, $KMnO_4$ is also rapidly consumed by natural organic matters, hence, the natural oxidant demand for $KMnO_4$ is high.[18] O_3-based ISCO is less common due to its high cost.[14] Sometimes, O_3 is combined with H_2O_2 to increase the hydroxyl radical ($HO^\bullet$) yield.[19] However, both O_3 and $HO^\bullet$ are non-selective oxidants, which react with many other non-targeted chemicals.[20]

$S_2O_8^{2-}$ is an emerging oxidant used in ISCO. It has gained increasing attention due to its economic feasibility and capacity to remove recalcitrant organic contaminants, such as hydrocarbons[21] and CECs.[22,23] The half-life of persulfate can range from two to hundreds of days depending on the conditions of the soil constituents.[24,25] High solubility of $S_2O_8^{2-}$ enhances the rate of diffusion and transport of $S_2O_8^{2-}$ in the subsurface. $S_2O_8^{2-}$ is also a strong oxidant ($E_0=2.1V$).[26] Activated persulfate generates $SO_4^{\bullet-}$ ($E_0=2.6V$) to create

highly reactive remediation system to treat contaminants of concern.[6,21,27] Unlike $HO^\bullet$, $SO_4^{\bullet-}$ is more selective towards electron rich organics. [28]

Sulfate radicals can be generated inexpensively through photolytic catalysis of persulfate by UV radiation (R1),[29,30] heat (R1),[31,32] base (R2),[33] and hydrogen peroxide.[34] This strongly oxidative species can also be generated through iron chelate activation (R3).[35] However, the metal activation involves both radical generation and radical scavenging (R3 vs. R4).[36]

$$S_2O_8{}^{2-} \xrightarrow{UV/heat} 2SO_4{}^{\bullet-} \tag{R1}$$

$$S_2O_8{}^{2-} + H_2O \xrightarrow{OH^-} SO_4{}^{\bullet-} + SO_4{}^{2-} + 3H^+ + O_2{}^{\bullet-} \tag{R2}$$

$$S_2O_8{}^{2-} + M^{n+} \rightarrow SO_4{}^{\bullet-} + SO_4{}^{2-} + M^{n+1} \tag{R3}$$

$$SO_4{}^{\bullet-} + M^{n+} \rightarrow SO_4{}^{2-} + M^{n+1} \tag{R4}$$
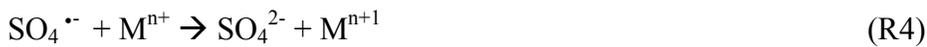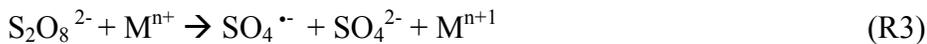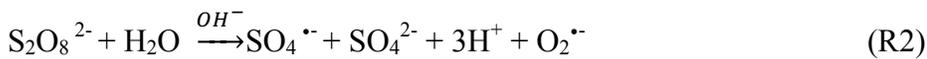
Fe(II) and Fe(III) are the most commonly used transitional metals when applying ISCO.[36] Other transition metals such as Cu(I) and Ag(I) are also capable of activating $S_2O_8{}^{2-}$, however, the application is limited due to their toxicity.[37] In addition, a few studies have demonstrated the ability of naturally-occurring aquifer minerals such as iron oxides and manganese oxides on $S_2O_8{}^{2-}$ activation.[38,39] The mechanism involves the oxidization of $S_2O_8{}^{2-}$ by metal oxides to yield Fe(II) or Mn(III) (R5), which then reduces $S_2O_8{}^{2-}$ to generate reactive radical species (R3).

$$S_2O_8{}^{2-} + M^{n+-} \rightarrow S_2O_8{}^{\bullet-} + M^{n+} \tag{R5}$$

Due to the complexity of the aquifer environment, the yield of $SO_4^{\bullet-}$ and the efficiency of $S_2O_8^{2-}$-based ISCO can be impacted by groundwater chemical constituents such as pH, Cl⁻ and alkalinity. A few chemical processes can occur. First, Cl⁻, HCO_3^- and pH can scavenge $SO_4^{\bullet-}$ to generate secondary radical species including chlorine atom (Cl•), carbonate radical ($CO_3^{\bullet-}$) and HO• via Reactions 6-8 (**Scheme 1**):[23,40,41]

$$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet} \qquad\qquad k=3.0 \times 10^8 \ \text{M}^{-1}\text{s}^{-1} \quad (R6)$$

$$SO_4^{\bullet-} + HCO_3^- \rightarrow SO_4^{2-} + H^+ + CO_3^{\bullet-} \qquad k=9.1 \times 10^6 \ \text{M}^{-1}\text{s}^{-1} \quad (R7)$$

$$SO_4^{\bullet-} + HO^- \rightarrow SO_4^- + HO^{\bullet} \qquad\qquad k= \times 10^{10} \ \text{M}^{-1}\text{s}^{-1} \quad (R8)$$
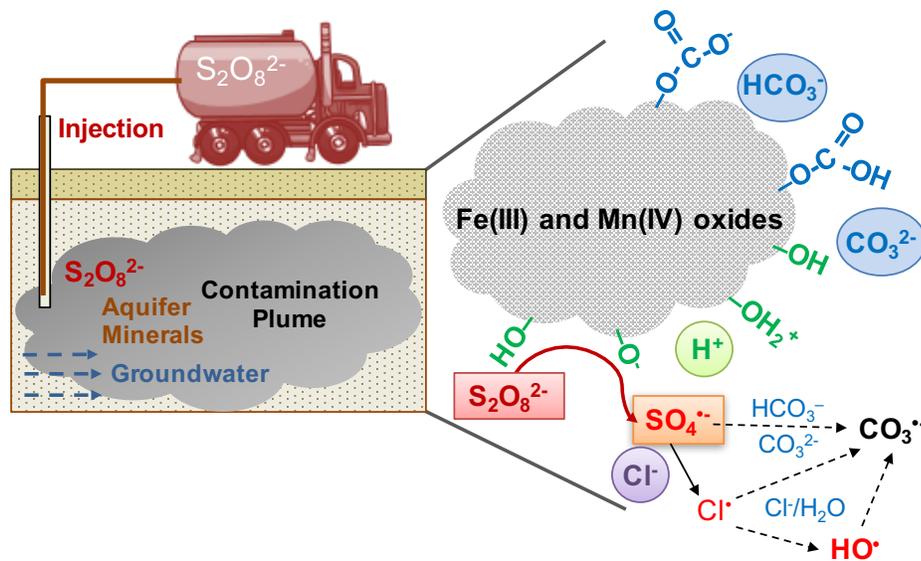
Scheme 1 Interaction of $S_2O_8^{2-}$ with aquifer chemical constituents during ISCO.

The treatment efficiency will therefore depend on the extent of the scavenging effects and the reactivity of secondary radical species with a contaminant.[42-48] $SO_4^{\bullet-}$, HO• and Cl• have similar reaction rates with aromatic compounds[49-50] However, the

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reactivity of $CO_3^{\bullet-}$ is usually a few orders of magnitude lower than $SO_4^{\bullet-}$, $HO^{\bullet}$ and $Cl^{\bullet}$ towards aromatic compounds.[51] In addition, the presence of Cl^- and HCO_3^- in groundwater can also form different chloro- and carbonato- surface complexes with Fe(III)- and Mn(IV)-oxides.[52,53] These surface complexes can change the redox reactivities of the surfaces of metal oxides, thus potentially impacting the rate of $S_2O_8^{2-}$ activation and the redox cycle of Fe and Mn-oxides (**Scheme 1**).[54] Thus, it is important to understand the mechanism and consequence of $S_2O_8^{2-}$ interaction with aquifer chemical constituents.

1.3 Persulfate-Based UV/AOPs for Potable Water Reuse

Potable water reuse offers a sustainable approach to address water scarcity and mitigate the long-term impacts of climate change.[55,56] However, conventional water and wastewater treatment processes are not sufficient for removing many trace organic contaminants in wastewater.[57] In a typical potable water treatment scheme, the secondary wastewater effluent from a conventional wastewater treatment plant is treated with a series of advanced treatment processes including micro- or nano-filtration,[58] reverse osmosis (RO),[59] activated carbon adsorption,[60] and advanced oxidation.[61]

UV-based AOPs have been widely applied in water industries to remove disinfection byproducts (DBPs) in drinking water and contaminants of emerging concern (CECs) in recycled water.[62-67] When UV-based AOPs are applied to portable reuse scenario, they are often used in the last step to remove trace contaminants that can pass through the filtration steps (**Scheme 2**). For example, small and non-charged molecules such as 1,4-dioxane and acetone can pass through RO membrane and cause potential health effects.[68] Advanced

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oxidation processes (AOPs) is the ultimate step to eliminate harmful micro organic residues in the final water product.
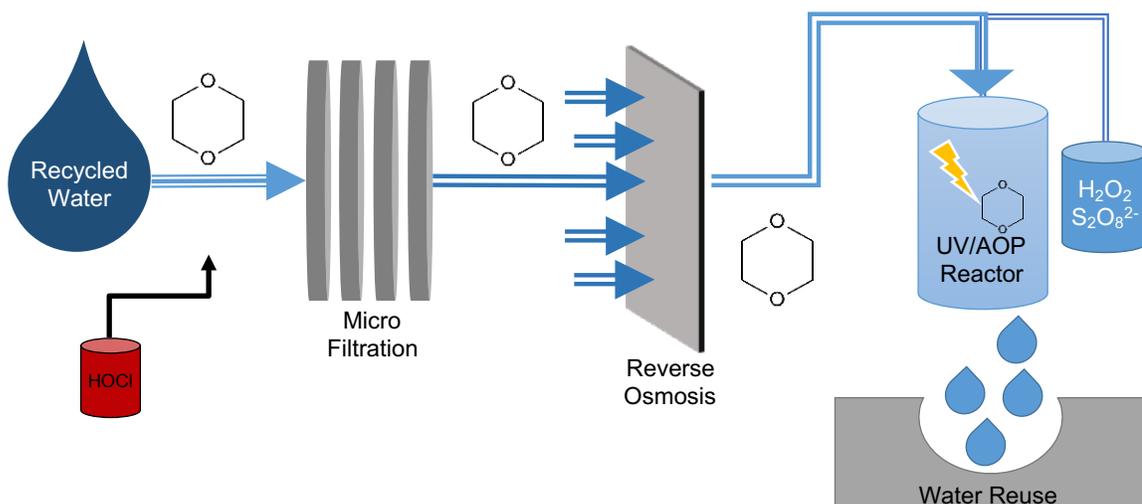
Scheme 2 Advanced treatment processes for portable water reuse. Derived from Patton & Li et. al. 2017.

UV/AOPs utilize photo energy to break the bonds of the oxidant precursor, commonly H_2O_2, to produce highly oxidative species such as $HO^{\bullet}$. UV/H_2O_2 is the most common AOP application in the States due to its low cost and non-toxic residual formation.[69] Increasingly stringent regulations urge water utilities to pursue alternative treatment schemes with higher efficacy and lower cost. The current application of H_2O_2 as the default oxidant for UV/AOPs may not be the best option due to the non-selectivity of $HO^{\bullet}$. Replacing H_2O_2 with $S_2O_8^{2-}$ might be more energy-efficient. The quantum yield of $SO_4^{\bullet-}$ is higher than $HO^{\bullet}$ (0.7 vs. 0.5), and they have similar oxidizing power (2.5-3.1 v *vs*. 1.9-2.8 v).[5] Furthermore, $SO_4^{\bullet-}$ is more selective towards electron-rich contaminants that are typically observed in wastewater effluent.[70,71,72] A prior study has demonstrated that

UV/$S_2O_8^{2-}$ shows better contaminant removal at the same molar concentration of H_2O_2.[30] It is also less influenced by other competing water chemical parameters such as alkalinity and chloride concentration.[73] When $S_2O_8^{2-}$ is activated by UV, it generates two $SO_4^{•-}$. In the presence of chloride, $SO_4^{•-}$ can be transformed into $Cl^{•}$, $Cl_2^{•-}$, and $HO^{•}$ (**Scheme 3**). UV/$S_2O_8^{2-}$ targets a wide range of contaminants of emerging concern, because different radicals have distinct reactivity with specific target contaminants.[50] UV/$S_2O_8^{2-}$ has been reported to successfully degrade phenolic compounds,[74] carboxylic acids,[75] PPCPs,[28] cyanobacterial toxin,[76] and even fluorinate organic compounds.[77] Thus, UV/$S_2O_8^{2-}$ can potentially substitute H_2O_2 and achieve better treatment efficiency.
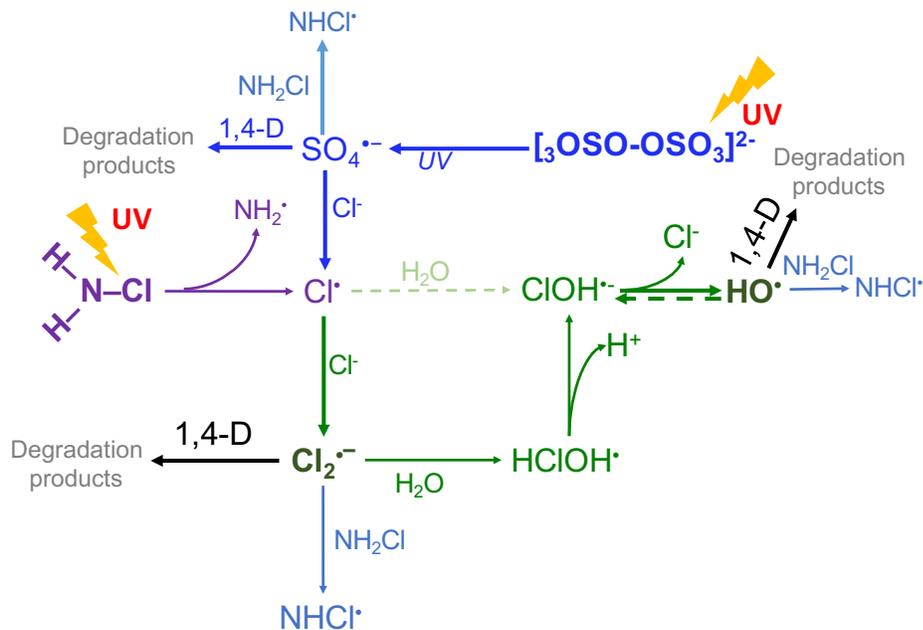
Scheme 3 Radical distribution in UV/$S_2O_8^{2-}$ and UV/NH_2Cl

In the advanced water treatment train, monochloramine (NH_2Cl) residual is often maintained in the feed water to control and minimize membrane fouling. Due to the small molecular size, monochloramine easily passes through RO membrane and undergoes photolysis in UV/AOPs.[78] Despite the vast application of monochloramine in advanced water treatment processes,[79] the fate of monochloramine during UV photolysis, and the impact of monochloramine on the chemistry of parent oxidant in UV/AOPs are not well understood. NH_2Cl has a high UV absorbance coefficient (371 $M^{-1}cm^{-1}$)[80] and similar quantum yield as $S_2O_8^{2-}$ (0.26-0.62 mol E^{-1})[81-83]. It can be used as a parent oxidant in the AOPs or combined with other parent oxidants to increase the overall radical yield.[82] The current understanding of chloramine aqueous photochemistry is limited to trichloramine photolysis in swimming pools,[84,85] and monochloramine or dichloramine photolysis in the pure water system.[80-83] However, the knowledge of applying the mixed system containing both $S_2O_8^{2-}$ and NH_2Cl in AOPs is underdeveloped [82]. Especially, little is known about the fundamental photochemistry of AOPs involving multiple parent oxidants. In the current AOPs where monochloramine is used as a disinfectant, the presence of monochloramine may alter the solution chemistry, reduce UV transmittance[86] and impact the degradation efficiency of micro-pollutants. In a case where $UV/S_2O_8^{2-}$ is employed, the sulfate radical ($SO_4^{\bullet-}$) produced from UV activation of $S_2O_8^2$ may further react with monochloramine to form less reactive radical species $NHCl^{\bullet}$ (R9).

$$SO_4^- + NH_2Cl \rightarrow HSO_4^- + NHCl^{\cdot} \qquad\qquad (R9)$$

NH$_2$Cl photolysis may also produce NH$_2^{\bullet}$ and Cl$^{\bullet}$ (R10). However, the reactivity of NH$_2^{\bullet}$ with trace organic contaminants in UV/AOPs remained unclear. Furthermore, NH$_2$Cl itself may act as a scavenger that decreases the quantum yield of NH$_2$Cl (R11-15). Therefore, it is important to understand the role of chloramine in aqueous photochemistry when combined with other oxidants.

$$HO^{\cdot} + NH_2Cl \rightarrow H_2O + NHCl^{\cdot} \hspace{3cm} \text{(R11)}$$

$$SO_4^- + NH_2Cl \rightarrow HSO_4^- + NHCl^{\cdot} \hspace{3cm} \text{(R12)}$$

$$Cl^{\cdot} + NH_2Cl \rightarrow H^+ + Cl^- + NHCl^{\cdot} \hspace{3cm} \text{(R13)}$$

$$Cl_2^- + NH_2Cl \rightarrow HCl + Cl^- + NHCl^{\cdot} \hspace{3cm} \text{(R14)}$$

$$NH_2^{\cdot} + NH_2Cl \rightarrow NH_2Cl + NHCl^{\cdot} \hspace{3cm} \text{(R15)}$$
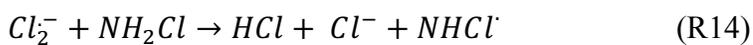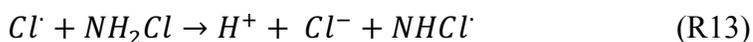
1.4 Toxicity Assessment for Oxidation Byproducts

The goal of introducing advanced treatment is to minimize health risks. However, during the application of AOPs, there lies a concern relating to the formation of various transformation byproducts from contaminants oxidized by reactive radicals.[87] To date, most oxidation byproducts of known contaminants and their cumulative toxicity profiles are largely unknown. The disappearance of the original contaminates may therefore not imply that the treatment is efficient, and hence oxidation byproducts of the reactions between oxidants and contaminants must always be considered. With increasing attention on disinfection byproduct formation,[88] the formation of more toxic intermediates or

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oxidation products during AOPs has also become an emerging concern. In several instances, the oxidation byproducts in AOPs may preserve the mode of action of the parent compound, and may pose a significant threat to environmental and human health.[89,90] Among numerous oxidation byproducts identified in AOPs-treated water samples, aldehyde compounds have received a great deal of attention from regulatory agencies and scientists due to a high level of carcinogenicity.[91,92] Studies have demonstrated that aldehydes induce nasal carcinomas in animal and humans.[93]

Research has only started to be developed regarding the identification of oxidation byproducts from AOPs, and limited research on the toxicity of these transformation products are available. For a complete risk assessment study on the oxidation byproducts formed during AOPs, identification of the oxidation byproducts and determination of their toxicity is crucial for a comprehensive risk assessment. The present study not only concerns the removal of the parent compounds, benzene and 1,4-dioxane, but also investigates their transformation products, evaluates the toxicity of the products using human cell-based bio-assays, and offers recommendations for minimizing the toxic substance formation.

1.5 Experimental Approaches

1.5.1 Examine the impact of groundwater chemistry on persulfate activation by aquifer minerals in ISCO using benzene as model contaminants.

The natural aquifer is rich in iron oxides and manganese oxides that can act as catalyst to activate $S_2O_8^{2-}$ by two steps of one-electron redox cycle.[39] To further examine the feasibility of using naturally occurred metal oxides to activate $S_2O_8^{2-}$ and produce reactive

radical species, Fe(OH)$_3$, a-Fe(OOH), and β-MnO$_2$ were first sieved to a uniformed size (38 μm ~150μm), and then sterilized to minimize microbes influence. 1mM of S$_2$O$_8^{2-}$ prepared in MilliQ water was mixed with 100g/L metal oxides with or without the addition of benzene. An aliquot of the mixed solution was transferred to a 9ml-glass tube without head space and rotated in the dark (**Scheme 4**). To examine the impact of chloride, bicarbonate, and pH on S$_2$O$_8^{2-}$ activation rate, varied levels of chloride (0 to 5mM), bicarbonate (0 to 10mM), and pH (8-13) were prepared with the test solutions. The pH was controlled with 50mM borate buffer or concentrated NaOH, and ionic strength was corrected by adding NaClO$_4$ across different pH levels. Samples were collected every five days for a total of 40 days. Collected samples were filtered through a 0.22 μm filter and S$_2$O$_8^{2-}$ was quantified by colorimetric analysis. [94] Initial chloride concentration was quantified by IC and bicarbonate concentration was monitored by standard sulfuric acid titration method. Benzene was quantified by HPLC using an A Zorbax Eclipse XDB-C18 column (4.6x50mm, 1.8 μm particle size) at a flow rate of 1.0 ml/min. Dissolved ion concentration at different pH levels was measured by ICP-MS. pH changes was monitored using pH meters.
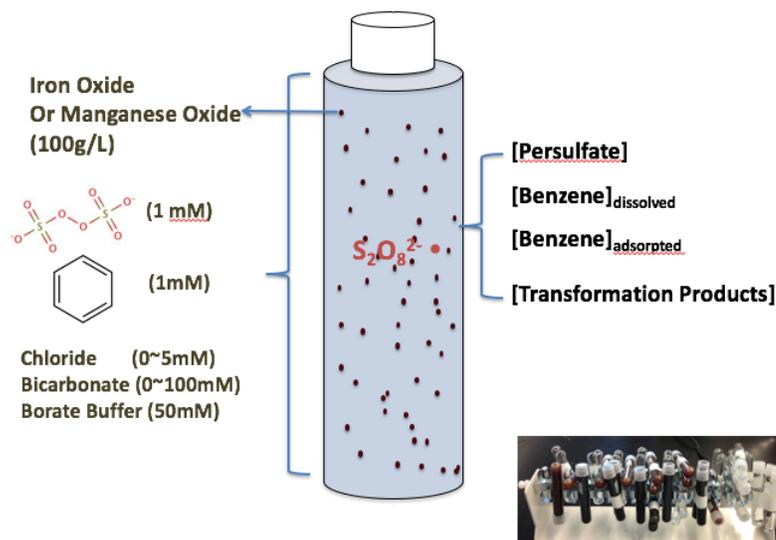
Scheme 4. Experimental set up for persulfate activation by aquifer minerals.

1.5.2 Investigate the application of UV/S$_2$O$_8^{2-}$ for potable water reuse, and the influence of NH$_2$Cl, chloride, pH, and oxygen using 1,4-dioxane as model contaminate

1,4-dioxane degradation rate by UV/S$_2$O$_8^{2-}$ in the presence of NH$_2$Cl at various concentrations (0-6 mM) was examined. The impact of chloride, pH, and oxygen content was also studied. In general, a requisite amount of 1,4-dioxane, benzoic acid, nitrobenzene, and buffer were first added to a volumetric flask and diluted with deoxygenated MilliQ water at a final concentration of 250 µM, 10 µM, 20 µM, respectively. NH$_2$Cl was added lastly to minimize the decay of NH$_2$Cl at lower pH. Prepared solutions were transferred to multiple 8 mL sealed quartz tubes without headspace. The tubes were then placed in a carousel UV chamber illuminated with a low-pressure monochromatic Hg lamp (λ=254 nm) at an intensity of 2.1 mW/cm^2 (Phillips TUV6T5, **Scheme 5**). Samples were withdrawn from sacrificial quartz tubes every five minutes for 25 minutes. NH$_2$Cl

concentration was measured immediately after sample collection using DPD colorimetric method.[95] The concentration of $S_2O_8^{2-}$ was measured using KI titration by a UV-Visible Spectrometer (Aqualog, Horiba Scientific).[94] The concentration of 1,4-dioxane, benzoic acid and nitrobenzene were measured by an Agilent 1200 liquid chromatography equipped with a diode array detector, and a Zorbax Eclipse SB-C18 column (4.6×150mm, 5-µm particle size). Total nitrogen (TNb) was measured by TOC analyzer (TOC; OI Analytical, College Station, TX). Gaseous nitrogen was determined by calculating the differences between the initial total nitrogen and total nitrogen at each collected data point. Ammonia, Nitrite, and nitrate concentration were measured by colorimetric methods.[95]
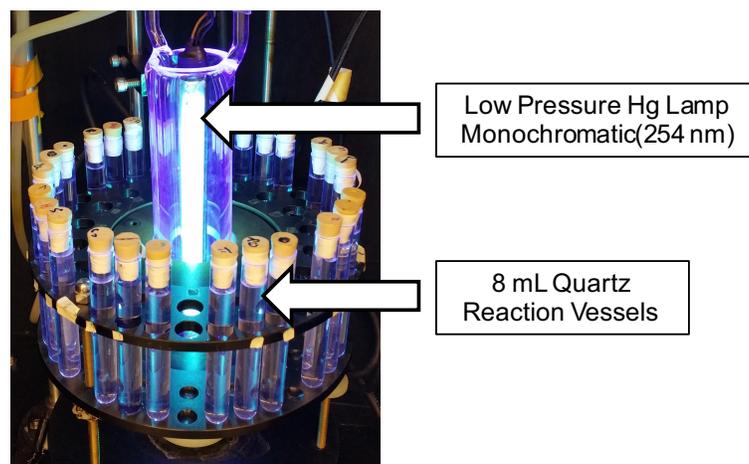
Scheme 5 UV photo reactor.

1.5.3 *Modeling approach to simulate UV/$S_2O_8^{2-}$, UV/H_2O_2, and UV/HOCl*

A kinetic model was developed with an open-source software Kintecus 4.55 to simulate the performance of UV/$S_2O_8^{2-}$, UV/H_2O_2, and UV/HOCl, which are the most

popular UV/AOPs in degrading trace organics present in RO permeate. The model was optimized based on the bench-scale experimentally-observed degradation rates of 1,4-dioxane and phenol by UV/$S_2O_8^{2-}$, UV/H_2O_2, and UV/HOCl. The overall degradation rates of six representative trace organic contaminants, 1,4-dioxane, carbamazepine, phenol, 17b-estradiol, aniline, and sulfamethoxazole, in full scale UV/AOP operations were simulated by the model. Three important water chemical parameters associated with RO permeate were examined: pH, chloride, and carbonate. The steady-state concentration of each radical and the contribution of each radical to the oxidation efficiency of trace contaminants were calculated.

1.5.4   *Investigate the oxidation byproducts of benzene and 1,4-dioxane, and quantify the toxicity potency of the oxidation byproducts using human cell-based assays*

To investigate the impact of different oxidants on product distribution, degradation of benzene by $Na_2S_2O_8$, H_2O_2, and $KMnO_4$ was investigated. $S_2O_8^{2-}$ and H_2O_2 at 5mM were activated by the three solids mentioned above with the addition of 1 mM benzene using same glass reactor setup. $KMnO_4$ at 5mM was directly mixed with 1 mM benzene. All experiments were controlled at pH 8 with 50mM borate buffer. Products were identified and quantified using HPLC, fractionated manually by HPLC, concentrated by purging nitrogen, and finally re-suspended in MilliQ water to a final desired concentration with HPLC solvent containing 0.05% DMSO.

Products of 1,4-dioxane oxidation by UV/$S_2O_8^{2-}$, UV/H_2O_2, and UV/NH_2Cl were identified using the state-of-arts instruments including HPLC and IC. The concentrations

of 1,4-dixoane, ethylene glycol diformate, formaldehyde, and glycolaldehyde were measured by an Agilent 1200 liquid chromatography equipped with a diode array detector and a Zorbax Eclipse SB-C18 column (4.6×150mm, 5-μm particle size). Glycolic acid, formic acid, and methoxyacetic acid were quantified using Dionex 1000 ion chromatograph equipped with a suppressed conductivity detector (Dionex, USA). The chemical standards were purchased based on the identified oxidation byproducts, and the toxicity study was conducted using known standards.

The genotoxicity of the individual transformation products was tested by using HCT-116 human colorectal carcinoma cells with an integrated beta-lactamase reporter gene under the control of p53 response elements (**Scheme 6**). HCT-116 cells after the fourth passage were transferred to each well of the black, clear-bottom, 96 well assay plates at a density of around 50,000 cells per well. The test compounds were then added to the assay plate at gradient concentrations. Mitomycin was used as positive control. The plate was incubated at 37 °C, 5% CO_2 for 16 hours, and then an aliquot of LiveBLAzer™ - FRET B/G substrate mixture was added to each well. The fluorescence intensity at 447 and 520 nm emission was measured with excitation at 405 nm using an EnVision microplate reader. The ratio of emissions at 460nm/530 nm was calculated by Excel and dose response curve was plotted using GraphPad Prism 7.
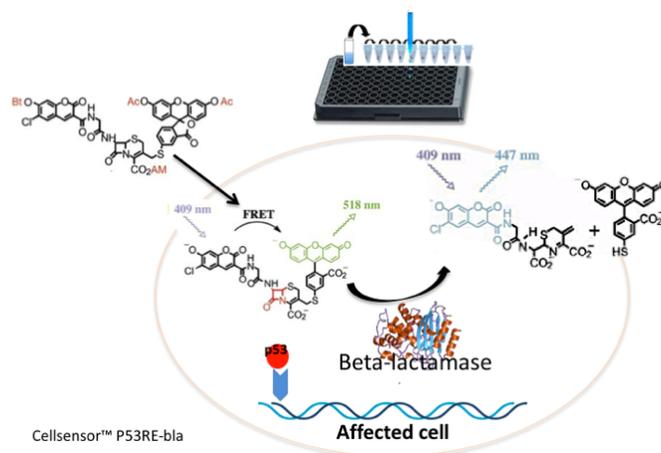
Scheme 6 Genotoxicity study using HCT-116 human colorectal carcinoma cells

Cell viability assay was also performed at the same time to test the cytotoxic effect of the compounds. After 16 hours incubation, an aliquot of 10 μL of MTT reagent (Life Technologies) was added to the wells. After 2 hours incubation at 37 °C, the assay medium was then aspirated and 100 μL DMSO was added into each well. After 2 hours incubation at room temperature, the absorbance was recorded at 570 nm and the percentage reduction in cell proliferation (relative cell density) was compared to that achieved in the growth medium controls and vehicle-treated controls. DMSO was used as a positive control to show a dose response curve. LC50 was then calculated using GraphPad Prism 7.

1.6 Research Objectives

The overall objective of the study was to conduct a series of applied experiments combined with computational kinetic modeling to explain the basis of $S_2O_8^{2-}$-based AOPs, and to apply the knowledge obtained from experimental observations to field study. In the meantime, an effort was taken to delve into the toxicity evaluation of the transformation

products during $S_2O_8^{2-}$ based ISCO and UV/AOPs and develop strategies for controlling the toxic substances formation during the process.

In Chapter 2, the objectives were to (1) investigate the impacts of groundwater alkalinity, pH, and chloride on benzene degradation via heterogeneous $S_2O_8^{2-}$ activation by Fe(III)- and Mn(IV)-containing minerals were investigated, (2) examine the fundamental mechanisms of radical chain reactions of persulfate activation in diverse chemical conditions, (3) quantify the kinetics and the efficiency of benzene degradation, and (4) assess the distribution of benzene degradation products. (5) A companying objective was to develop a comprehensive kinetic model to elucidate mineral surface complexation and radical chain reactions involving persulfate ISCO under diverse groundwater chemical conditions.

In Chapter 3, the objectives were to (1) quantify the formation of reactive radicals during the simultaneous photolysis of NH_2Cl and $S_2O_8^{2-}$, (2) examine the impact of oxidant dosage, pH, chloride and dissolved O_2 on the degradation of 1,4-dioxane, and (3) develop a kinetic model to predict the radical yield and transformation of with both oxidants.

In Chapter 4, the objectives of the work were to (1) develop a kinetic model to investigate radical generation mechanisms in UV/H_2O_2, $UV/S_2O_8^{2-}$ and UV/HOCl, (2) predict the degradation of trace contaminants in complex chemical conditions relevant to potable water reuse by three UV/AOPs, (3) elucidate the impact of individual chemical parameters including pH, chloride and organic carbon on three UV/AOPs.

In Chapter 5, The objectives were to (1) identify the oxidation byproducts of benzene and 1,4-dioxane in $S_2O_8^{2-}$-based AOPs, (2) compare the toxicity potency of the

oxidation byproducts to the original contaminant using human cell-based bioassays, (3) Recommend strategies for minimizing toxic byproducts formation.

In Chapter 6, conclusions from the doctoral work are given, as well as discussion on the application of $S_2O_8^{2-}$-based AOPs to mitigate the risk of contaminated groundwater and to promote wastewater reuse technology were presented. Chapter two and chapter 4 have been published in peer-reviewed journals. Chapter three and chapter five are currently undergoing the peer-review process with an anticipation of publication.

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Chapter 2

Persulfate-Based ISCO for Groundwater Remediation: Impacts of Alkalinity, pH and Chloride

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2.1 Introduction

Groundwater contamination is a global challenge due to rapid industrialization and population growth.[1-2] In particular, carcinogenic petroleum hydrocarbons including benzene are widely present in groundwater at hazardous waste sites.[3-6] A variety of physical, chemical and biological approaches have been developed to remediate groundwater.[7-10] *In situ* chemical oxidation (ISCO) using persulfate ($S_2O_8^{2-}$) has been increasingly applied as a novel chemical remediation approach.[11-17] Besides base activation, persulfate can also be heterogeneously activated by Fe(III)- and Mn(IV)-containing minerals via Fenton-like reactions to generate sulfate radical ($SO_4^{\bullet-}$).[18-21] Compared to hydroxyl radical ($HO^{\bullet}$), $SO_4^{\bullet-}$ is similarly oxidative but more selective towards electron-rich organic contaminants.[22-24] In addition, the half-life of persulfate in the aquifer is orders of magnitude longer than other conventional oxidants including hydrogen peroxide (H_2O_2) and permanganate (MnO_4^-).[25-29] These unique features can lead to an efficient delivery of persulfate to the contamination plumes at hazardous waste sites.[20,21]

Despite inherent advantages, persulfate-based ISCO remediation is affected by the presence of major groundwater chemical constituents, especially alkalinity, pH and chloride; however, the impacts of these important chemical parameters on the efficiency and kinetics of persulfate-based remediation are not well understood. Contaminated groundwater typically has chloride and alkalinity levels ranging from micro- to milli-mole, and pH from neutral to extremely high levels impacted by the base activation of persulfate.[30,31] Prior studies also reported inconclusive effects of pH and chloride on the

efficiency of contaminant degradation by $SO_4^{\bullet-}$. For example, some contaminants were degraded more quickly at higher pHs while others at lower pHs.[32-34] The effect of chloride on the degradation of organic contaminants was reported to be either negligible, inhibitive or positive at varying concentrations.[32,35-37] A better understanding of the impacts of groundwater chemical conditions on persulfate activation will significantly benefit large-scale remediation efforts.

In principle, a variety of groundwater constituents can transform $SO_4^{\bullet-}$ into chlorine atom ($Cl^{\bullet}$), carbonate radical ($CO_3^{\bullet-}$), $HO^{\bullet}$ and other radicals.[23,38,39] The reactivities of different radicals can vary by orders of magnitude.[22,40-43] Furthermore, alkalinity and pH affect the formation of carbonato and hydroxo complexes on the mineral surfaces and their redox reactivity.[44] In addition, Fe(III)- and Mn(IV)-containing minerals that are widely present in aquifer exhibit distinct rates of persulfate decomposition and efficiencies of radical yield.[20-21] However, the fundamental mechanisms controlling the impacts of groundwater chemical matrix on heterogeneous persulfate activation remain unknown.

The main objectives of this study were to investigate the impacts of groundwater alkalinity, pH and chloride on benzene degradation via heterogeneous persulfate activation by Fe(III)- and Mn(IV)-containing minerals, examine the fundamental mechanisms of radical chain reactions of persulfate activation in diverse chemical conditions, quantify the kinetics and the efficiency of benzene degradation, and assess the distribution of benzene degradation products. A companying objective was to develop a comprehensive kinetic model to elucidate mineral surface complexation and radical chain reactions involving

persulfate ISCO under diverse groundwater chemical conditions.2.2. Materials and Methods

2.2 Materials and Methods

2.2.1 Experimental system

All chemicals were purchased as ACS grade from Fisher Chemical or Sigma-Aldrich. Three Fe(III) and Mn(IV) minerals were employed in this study to simulate typical aquifer conditions: ferrihydrite $FeO(OH)_{(s)}$, goethite α-$FeO(OH)_{(s)}$ and pyrolusite β-$MnO_{2(s)}$. In particular, pyrolusite represents a Mn(IV)-containing aquifer mineral because it is present in the subsurface and exhibits a strong catalytic effect to activate persulfate.[21,45-47] Ferrihydrite and pyrolusite were purchased from Sigma-Aldrich. Goethite was synthesized by precipitating $Fe(NO_3)_3$ with NaOH.[48] All metal oxides were grounded and sieved through No. 100 and 400 sieves with a nominal particle size between 38 and 150 μm. Additional information on mineral preparation can be found in a previous study.[21] The surface area of each mineral was directly measured, and details are provided in **Table 1** and **Appendix A-1**.

Table 1 BET surface area of minerals used in this study.

Mineral	BET Surface Area (m^2/g)
Goethite (α-$FeO(OH)_{(s)}$)	21
Ferrihydrite ($FeO(OH)_{(s)}$)	180
Pyrolusite (β-$MnO_{2(s)}$)	0.11

To prepare persulfate activation and benzene degradation experiments, a 1-mM benzene solution was prepared directly in a 1-L volumetric flask with deionized (DI) water containing 50 mM borate buffer at pH 8.0 with no headspace. Chloride concentrations varying between 0 and 5 mM was prepared by adding a requisite amount of 100 mM NaCl. The solution pH was adjusted between 8 and 13 by adding 50 mM borate buffer and 5 M NaOH. Solution alkalinity was adjusted between 1.6×10^{-2} and 10 meq/L with a 0.5 M NaHCO$_3$ stock solution. The ionic strength was 10 mM in most experiments except that it was 100 mM in experiments with varying pH levels. Pure K$_2$S$_2$O$_8$ crystals were added to the flask to reach the targeted S$_2$O$_8^{2-}$ concentration of 1 mM. After mixing, the solution was quickly transferred to 10-mL glass vials without headspace. The vials were pre-loaded with 100 g/L of Fe(III) or Mn(IV) minerals, a typical dosage to simulate ISCO performance.[20,21] Each vial was then placed on an automatic rotator and left at 23 ^{o}C in darkness. All experiments were performed in duplicates or triplicates.

Samples were withdrawn from the sacrificial glass vials every five days, centrifuged at 2000 g for 5 minutes and filtered through 0.22-μm syringe filters before analysis.[21] The concentration of persulfate was measured using potassium iodine (KI) titration with a Horiba UV spectrometer.[49] Benzene and its oxidation product phenol were analyzed by an Agilent 1200 liquid chromatography (**Appendix A- 2**). Another major benzene degradation product, an aldehyde compound, was characterized by nuclear magnetic resonance (NMR) and liquid chromatography-mass spectrometry (LC-MS).[20] Chloride was measured by a Dionex 1000 ion chromatography equipped with a

conductivity detector. Alkalinity was measured by the standard sulfuric acid titration method.[50]

2.2.2. Development of a kinetic model

A comprehensive kinetic model of heterogeneous persulfate activation was established using the Kintecus software.[51] Details on the kinetic model were provided in **Appendix A-3**. In short, a total of 77 and 56 reactions were established to model persulfate decomposition by Fe(III) and Mn(IV) oxide, respectively (**Appendix A-5**). All rate constants were directly obtained from prior literature, except that the rate constants of four reactions involving homogeneous persulfate activation by soluble Fe(III) were optimized using experimental data from persulfate activation by soluble Fe(III). Rate constants of six reactions involving heterogeneous persulfate activation by ferrihydrite and goethite and three reactions involving heterogeneous persulfate activation by pyrolusite were optimized using experimental data at different alkalinity, pH and chloride levels. Metal surface hydroxo and carbonato complexes were modeled based on known equilibrium constants without considering the surface electrostatic interactions. The model ensured the surface hydroxo and carbonato complexes reactions reached equilibria instantaneously throughout the reaction regardless the presence or absence of persulfate in all conditions. The best model fitting was achieved by minimizing the root mean squares (RMS) between experimental and modeled data using Powell non-restricted algorithms. The steady-state concentrations of metal surface complexes and radicals were calculated based on the fully optimized kinetic model.

2.3 Results and Discussion

2.3.1 *Radical chain reactions during persulfate activation by aquifer minerals*

In the presence of 1 mM benzene, 100 g/L of minerals, negligible levels of alkalinity and chloride, and at pH 8, the surface area-normalized rates of persulfate decomposition followed the order of pyrolusite > goethite > ferrihydrite (**Figure 1A**). The high reactivity of pyrolusite was mainly associated with its surface hydroxo complexation and crystalline structure.[3,21,52-56] The activation of persulfate by ferrihydrite and goethite resulted from Fenton-like reactions involving the reduction of surface Fe(III) to Fe(II) by persulfate (Reaction 1-2 in **Table 2**; all subsequently referred reactions are listed in **Table 2**), followed by the oxidation of surface Fe(II) by persulfate to generate $SO_4^{\bullet-}$ (Reaction 3-4). Similar reactions involving surface Mn(IV) and Mn(III) took place for pyrolusite involving Mn(IV) and Mn(III) (Reactions 5-6).[20,21,57] Based on the kinetic model prediction, a predominant fraction of persulfate loss (>80%) was attributed to Fenton-like reactions involving oxidized and reduced surfaces sites of metal oxides (**Figure 1**), and the rest of persulfate was decomposed via thermal decomposition at 25 $^{\circ}$C (Reactions 7).
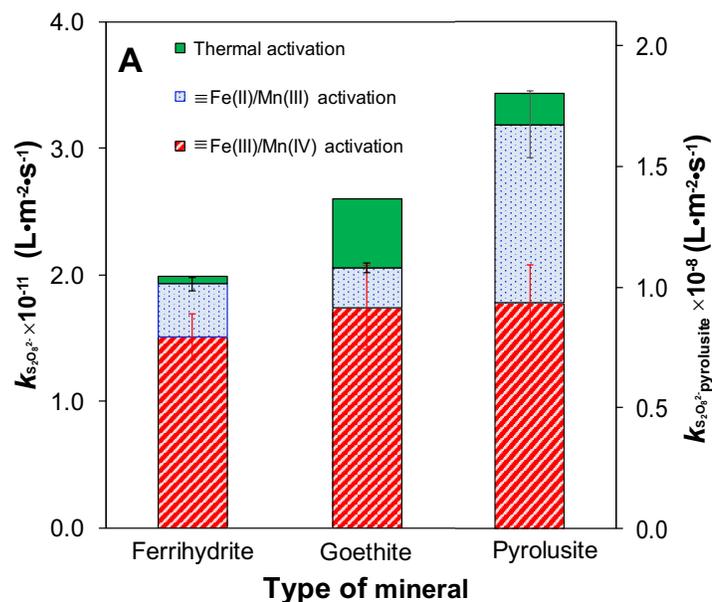
Figure 1. Surface area-normalized first-order decay rate constant of persulfate decomposition (pyrolusite rates on the secondary y-axis); $[S_2O_8^{2-}]$=1 mM, [benzene]=1 mM, $[Cl^-]$=0 mM, pH=8.0 [alkalinity]=1.6×10^{-2} meq/L, dosage of mineral=100 g/L, ionic strength=10 mM.
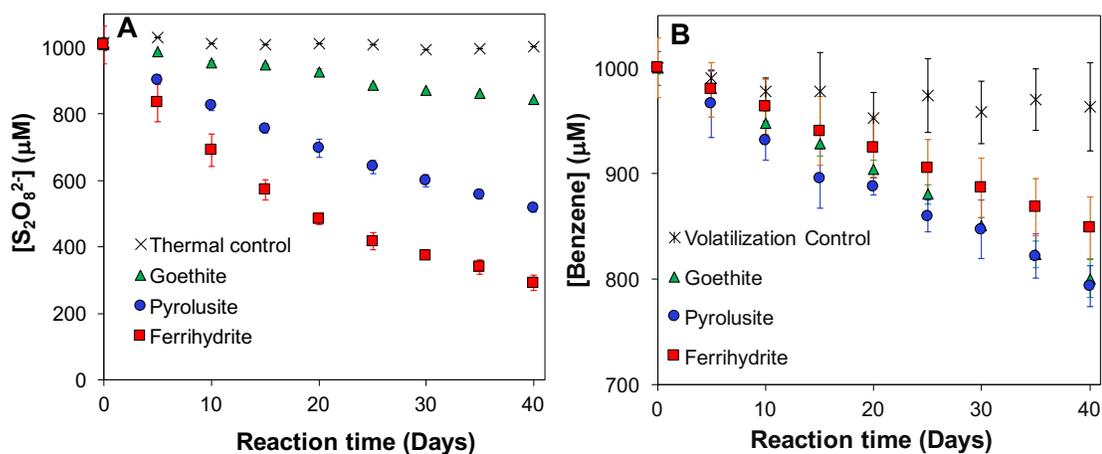
Figure 2. The kinetics of persulfate decomposition and benzene degradation in the presence of different metal oxides. (A) Persulfate decomposition time profile; (B) Benzene degradation time profile. $[S_2O_8^{2-}]$=1 mM, [benzene]=1 mM, [alkalinity]=1.6×10^{-2} meq/L, $[Cl^-]$=0 mM, pH=8.0, dosage of metal oxides=100 g/L, ionic strength=12 mM.

Table 2 Major radical chain reactions involving benzene degradation via persulfate activation by Fe(III) and Mn(IV) oxides.

No.	Reaction	Rate constant ($M^{-1}s^{-1}$)	Reference[*]
1	$\equiv Fe(III) - OH + S_2O_8^{2-} \rightarrow \equiv Fe(II) - OH + S_2O_8^{\cdot-}$	$(6.0\pm0.6)\times10^{-6}$	
2	$\equiv Fe(III) - O^- + S_2O_8^{2-} \rightarrow \equiv Fe(II) - O^- + S_2O_8^{\cdot-}$	$(2.8\pm0.8)\times10^{-6}$	
3	$\equiv Fe(II) - OH + S_2O_8^{2-} \rightarrow \equiv Fe(III) - OH + SO_4^{\cdot-} + SO_4^{2-}$	$(1.8\pm0.2)\times10^{-4}$	
4	$\equiv Fe(II) - O^- + S_2O_8^{2-} \rightarrow \equiv Fe(III) - O^- + SO_4^{\cdot-} + SO_4^{2-}$	$(2.2\pm0.3)\times10^{-5}$	
5	$\equiv Mn(IV) - O^- + S_2O_8^{2-} \rightarrow \equiv Mn(III) - O^- + S_2O_8^{\cdot-}$	$(2.2\pm0.4)\times10^{-3}$	
6	$\equiv Mn(III) - O^- + S_2O_8^{2-} \rightarrow \equiv Mn(IV) - O^- + SO_4^{\cdot-} + SO_4^{2-}$	$(4.9\pm1.3)\times10^{-3}$	
7	$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$ (25 °C)	1.2×10^{-8}	21 [a]
8	$C_6H_6 + SO_4^{\cdot-} \rightarrow C_6H_6^{\cdot+} + SO_4^{2-}$	3.0×10^{9}	58
9	$S_2O_8^{2-} + SO_4^{\cdot-} \rightarrow S_2O_8^{\cdot-} + SO_4^{2-}$	6.6×10^{5}	59
10	$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^- + HO^{\cdot}$	1.2×10^{1}	60 [a]
11	$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + HO^{\cdot}$	7.0×10^{7}	23
12	$SO_4^{\cdot-} + HCO_3^- \rightarrow CO_3^{\cdot-} + SO_4^{2-} + H^+$	9.1×10^{6}	39
13	$HO^{\cdot} + HCO_3^- \rightarrow CO_3^{\cdot-} + H_2O$	8.6×10^{6}	61
14	$\equiv Fe(II) - OH + SO_4^{\cdot-} \rightarrow \equiv Fe(III) - O^- + SO_4^{2-}$	$(9.5\pm1.0)\times10^{7}$	
15	$\equiv Fe(II) - O^- + SO_4^{\cdot-} \rightarrow \equiv Fe(III) - O^- + SO_4^{2-}$	$(1.0\pm5.0)\times10^{8}$	
16	$\equiv Mn(III) - O^- + SO_4^{\cdot-} \rightarrow \equiv Mn(IV) - O^- + SO_4^{2-}$	$(5.6\pm1.5)\times10^{10}$	
17	$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\cdot}$	6.6×10^{8}	62
18	$Cl^{\cdot} + H_2O \rightarrow ClOH^{\cdot-} + H^+$	4.5×10^{3}	63 [a]
19	$Cl^{\cdot} + OH^- \rightarrow ClOH^{\cdot-}$	1.8×10^{10}	64
20	$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot-}$	8.5×10^{9}	63
21	$Cl_2^{\cdot-} + H_2O \rightarrow HClOH^{\cdot} + Cl^-$	2.4×10^{0}	63 [a]
22	$HClOH^{\cdot} \rightarrow H^+ + ClOH^{\cdot-}$	1.0×10^{8}	63 [a]

23	$ClOH^{\cdot-} \rightarrow Cl^- + HO^{\cdot}$	6.1×10^9	65 [a]
24	$Cl^{\cdot} + HCO_3^- \rightarrow CO_3^- + H^+ + Cl^-$	2.2×10^8	66
25	$\equiv Fe(III) - OH + CO_3^{2-} + H^+ \rightarrow \equiv Fe(III) - OCO_2^- + H_2O$	1.0×10^{15}	75 [b]
26	$\equiv Fe(III) - OCO_2^- + H_2O \rightarrow \equiv Fe(III) - OH + CO_3^{2-} + H^+$	1.7×10^2	75 [a]
27	$\equiv Mn(IV) - OH + CO_3^{2-} + H^+ \rightarrow \equiv Mn(IV) - OCO_2^- + H_2O$	1.0×10^{15}	76 [b]
28	$\equiv Mn(IV) - OCO_2^- + H_2O \rightarrow \equiv Mn(IV) - OH + CO_3^{2-} + H^+$	7.1×10^0	76 [a]
29	$\equiv Fe(III) - OH + CO_3^{2-} + 2H^+ \rightarrow \equiv Fe(III) - OCO_2H^0 + H_2O$	1.0×10^{20}	75 [c]
30	$\equiv Fe(III) - OCO_2H^0 + H_2O \rightarrow \equiv Fe(III) - OH + CO_3^{2-} + 2H^+$	4.3×10^{-1}	75 [a]
31	$\equiv Mn(IV) - OH + CO_3^{2-} + 2H^+ \rightarrow \equiv Mn(IV) - OCO_2H^0 + H_2O$	1.0×10^{20}	76 [c]
32	$\equiv Mn(IV) - OCO_2H^0 + H_2O \rightarrow \equiv Mn(IV) - OH + CO_3^{2-} + 2H^+$	2.2×10^{-3}	76 [a]
33	$\equiv Fe(III) - OH_2^+ \rightarrow \equiv Fe(III) - OH + H^+$	2.6×10^2	78 [a]
34	$\equiv Fe(III) - OH + H^+ \rightarrow \equiv Fe(III) - OH_2^+$	5.0×10^9	78
35	$\equiv Mn(IV) - OH_2^+ \rightarrow \equiv Mn(IV) - OH + H^+$	1.3×10^9	79 [a]
36	$\equiv Mn(IV) - OH + H^+ \rightarrow \equiv Mn(IV) - OH_2^+$	5.0×10^9	79
37	$\equiv Fe(III) - OH \rightarrow \equiv Fe(III) - O^- + H^+$	5.9×10^0	78 [a]
38	$\equiv Fe(III) - O^- + H^+ \rightarrow \equiv Fe(III) - OH$	5.0×10^9	78
39	$\equiv Mn(IV) - OH \rightarrow \equiv Mn(IV) - O^- + H^+$	1.3×10^7	79 [a]
40	$\equiv Mn(IV) - O^- + H^+ \rightarrow \equiv Mn(IV) - OH$	5.0×10^9	79

[*] Reaction rate constants without references were obtained in this study from the kinetic model. All rate constants on Fe(III) in this table are for ferrihydrite. Rate constants for goethite are listed in **Appendix A-5**.
[a] rate constants are in unit of s^{-1}
[b] rate constants are in unit of $M^{-2} s^{-1}$
[c] rate constants are in unit of $M^{-3} s^{-1}$

After 40 days of reaction, 16% to 70% of persulfate was decomposed and approximately 20% of benzene was degraded (**Figure 2**). Surface area-normalized rates of benzene degradation followed the same order as persulfate decomposition for different minerals, and $SO_4^{\bullet-}$ was the major oxidative species (**Figure 3**). $SO_4^{\bullet-}$ predominantly reacted with benzene than with persulfate (Reaction 8 *vs.* 9). Although both $HO^{\bullet}$ and $CO_3^{\bullet-}$ were produced via $SO_4^{\bullet-}$ chain reactions (Reactions 10-13), they negligibly contributed to benzene degradation due to low steady-state concentrations (**Appendix A-4**).

Because benzene was the major sink for $SO_4^{\bullet-}$, its degradation was used to calculate the stoichiometric efficiency of $SO_4^{\bullet-}$ yield (denoted as $E_{S2O8}{}^{2-}$) in persulfate decomposition:

$$E_{S_2O_8^{2-}} = \frac{\Delta[Benzene]}{\Delta[S_2O_8^{2-}]} \times 100\% \qquad\qquad (1)$$

The experimentally observed stoichiometric efficiency of $SO_4^{\bullet-}$ yield was inversely correlated with the rate of persulfate decomposition for the three minerals (**Figure 4**). This trend was consistent with our prior observations on the reactivity of minerals.[20,21] As persulfate was decomposed and $SO_4^{\bullet-}$ was generated via heterogeneous activation by mineral surfaces, $SO_4^{\bullet-}$ was also scavenged by reactive mineral surface complexes (Reactions 14-16), which eventually lowered the radical yield.
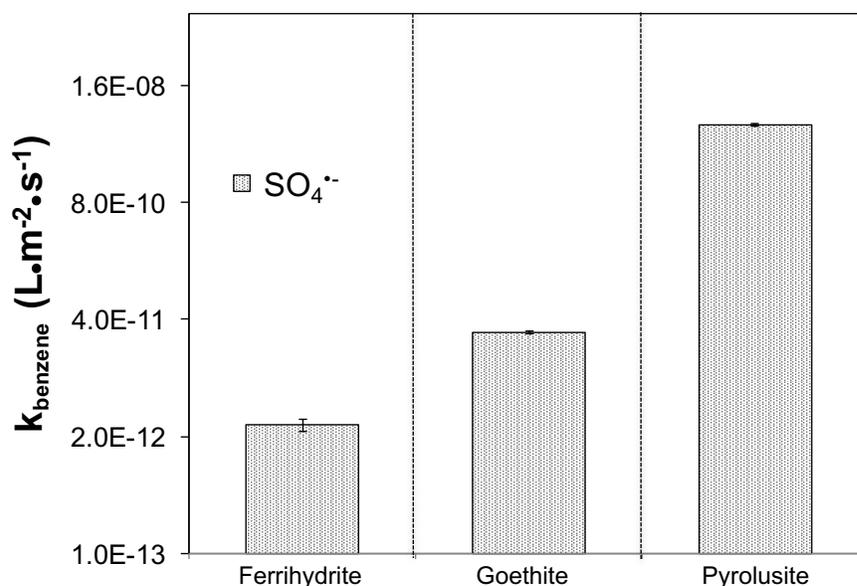
Figure 3 Surface area-normalized first-order rate constans of benzene degradation. Initial $[S_2O_8^{2-}]$=1 mM, initial [benzene]=1 mM, $[Cl^-]$=0 mM, [alkalinity]=1.6×10^{-2} meq/L. pH=8.0, dose of metal oxides=100 g/L, ionic strength=12 mM. The benzene degradation was predominantly contributed by $SO_4^{\bullet-}$ oxidation, calculated from kinetic model predictions.
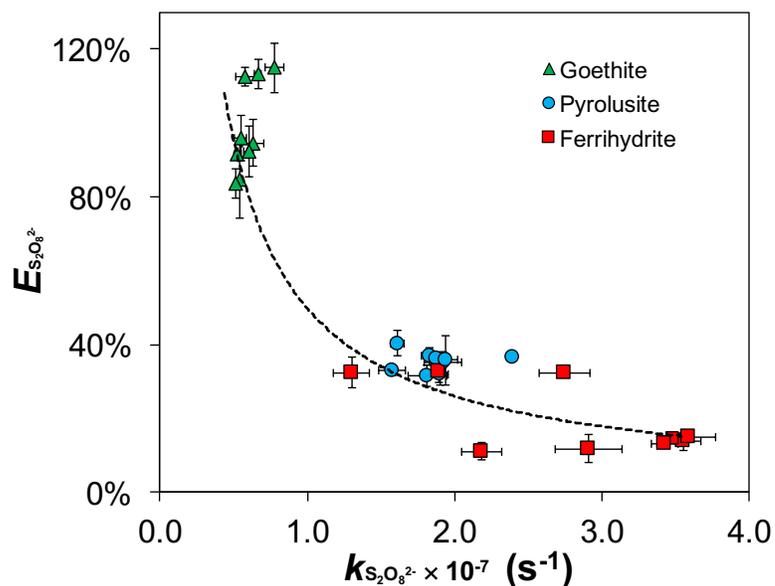
Figure 4. Correlation between the stochiomatric efficiency of radical yield ($E_{S2O8^{2-}}$) and the rate of persulfate decomposition ($k_{S2O8^{2-}}$). $[S_2O_8^{2-}]$=1 mM, [benzene]=1 mM, $[Cl^-]$=0 mM, pH=8.0 [alkalinity]=1.6×10^{-2} meq/L, dosage of mineral=100 g/L, ionic strength=10 mM.

2.3.2 Impact of groundwater chemistry on benzene degradation and persulfate

decomposition

The impact of groundwater chemical parameters on persulfate decomposition was systematically investigated on the basis of alkalinity, pH and chloride levels. When alkalinity increased from 1.6×10^{-2} meq/L (*i.e.*, the background level in air-saturated condition) to 10 meq/L, the rates of persulfate decomposition decreased by 40%, 3% and 15% in ferrihydrite, goethite and pyrolusite system, respectively (**Figure 5A, C** and **E**). Rates of benzene degradation also decreased by 24% and 15% in ferrihydrite and pyrolusite systems, and remained unchanged in goethite system (**Figure 5B, D and F**). The kinetic model predicted that the presence of alkalinity led to a transformation of $SO_4^{\bullet-}$ and $HO^{\bullet}$ to $CO_3^{\bullet-}$ (Reactions 12-13). Specifically, $[SO_4^{\bullet-}]_{ss}$ decreased by 12%-32%, $[HO^{\bullet}]_{ss}$ decreased by 20%-38%, and $[CO_3^{\bullet-}]_{ss}$ increased by three orders of magnitude with increasing alkalinity (). Different radicals exhibit distinct reactivities with organic contaminants. For example, $SO_4^{\bullet-}$, $HO^{\bullet}$ and $Cl^{\bullet}$ have comparable reaction rates with aromatic compounds.[42] However, $CO_3^{\bullet-}$ is much less reactive except for reacting with amine-containing compounds.[67-68]
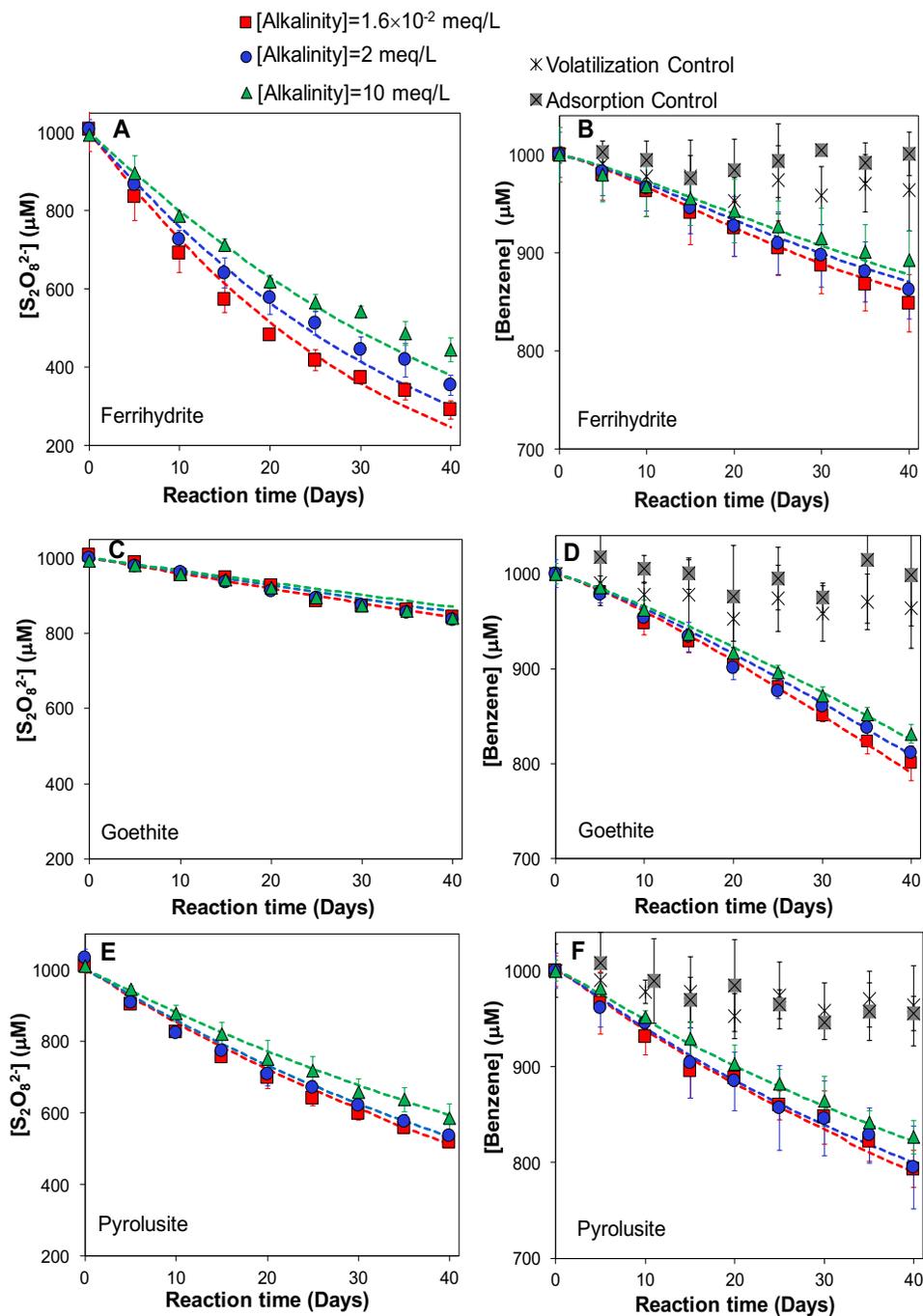
Figure 5. Impact of alkalinity on persulfate decomposition and benzene degradtion by three minerals. (A, C, E) Persulfate decomposition; (B, D, F) Benzene degradation. $[S_2O_8^{2-}]$=1 mM, [benzene]=1 mM, mineral dosage=100 g/L, pH=8.0, ionic strength=10 mM. Data points represent the experimental results. Dash lines represent the model-fitted values.

Solution pH significantly impacted the reaction kinetics. For all three minerals, when pH was increased from 8 to 12, the rates of persulfate decomposition increased by as much as 200% (**Figure 6A, C** and **E**), and the rates of benzene degradation was enhanced by up to 70% (**Figure 6B, D** and **F**). A further pH rise from 12 to 13 decreased the reaction kinetics. As the pH increased from 8 to 12, $SO_4^{\bullet-}$ was transformed to $HO^{\bullet}$ (Reaction 11). Consequently, $[HO^{\bullet}]_{ss}$ increased by more than 2 orders of magnitude for all three minerals (**Table 3**), corresponding to an 20% increase of the contribution of $HO^{\bullet}$ to benzene degradation (**Table 4**). Meanwhile, $CO_3^{\bullet-}$ was generated as a result of the scavenging effect of bicarbonate on $SO_4^{\bullet-}$ and $HO^{\bullet}$ (Reactions 12-13), and $[CO_3^{\bullet-}]_{ss}$ increased dramatically at higher pHs (**Table 3**). Because of the low reactivity of $CO_3^{\bullet-}$, benzene degradation slowed down from pH 12 to 13.

In addition, the change of pH did not significantly impact the solubility of metal oxides. The contribution of soluble Fe(III) due to dissolution of metal oxides to persulfate decomposition was minimal except at pH 13 (**Table 5**). Furthermore, control experiments in the absence of minerals showed that homogeneous persulfate decomposition was slow and not sensitive to pH ranging from 8 to 13 (**Figure 7**). This is consistent with previous observations that only extremely alkaline conditions at pH above 13 accelerated the base activation of persulfate in a homogeneous system.[14]
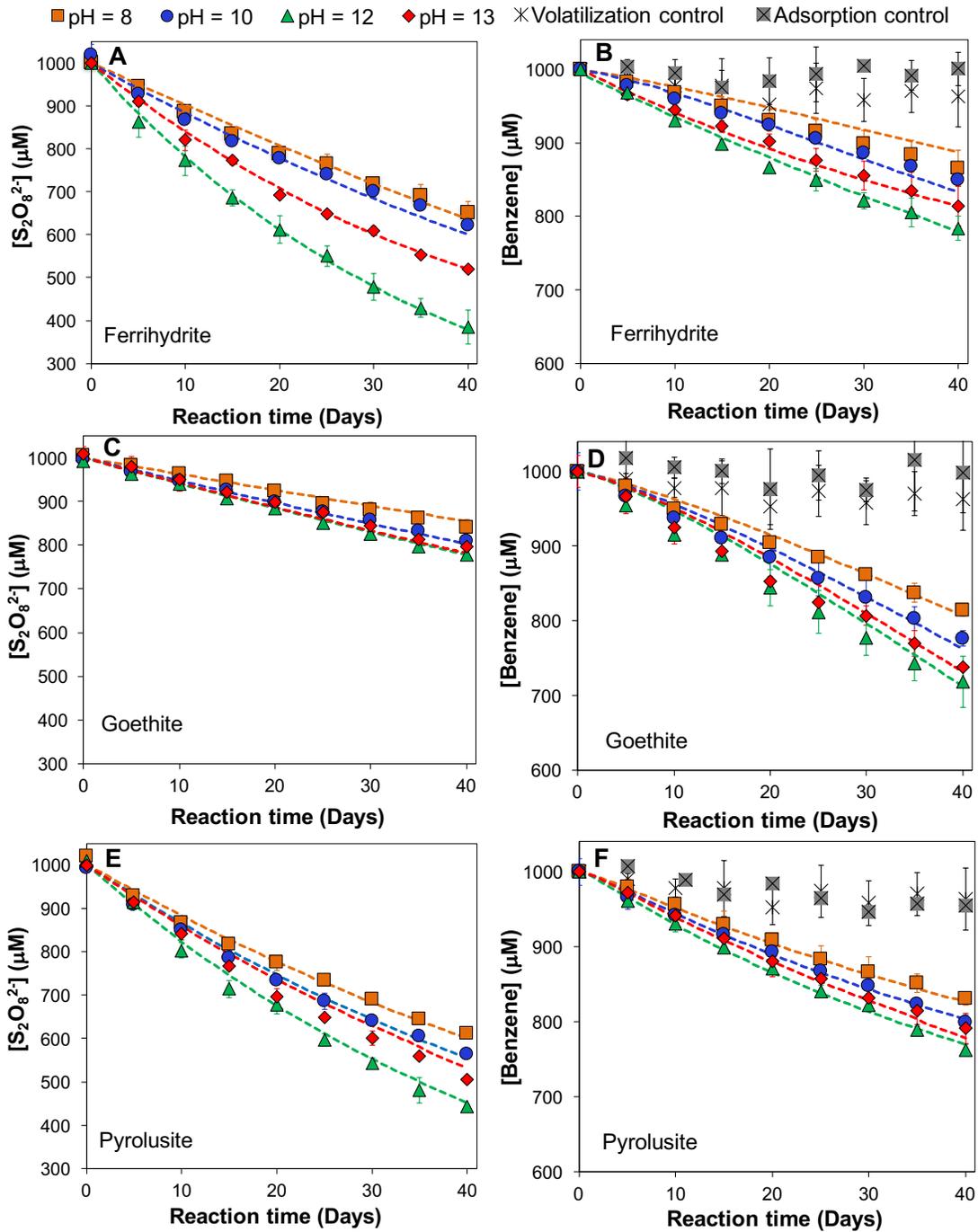
Figure 6 Impact of pH on the rates of persulfate decomposition and benzene degradtion by three minerals. (A, C, E) Persulfate decomposition; (B, D, F) Benzene degradaton. $[S_2O_8^{2-}]$=1 mM, [benzene]=1 mM, mineral dosage=100 g/L, ionic strength=100 mM. Data points represent the experimental results. Dash lines represent the model fitted values.

Table 3 Model-predicted steady-state concentrations of radicals generated during heterogeneous persulfate activation. *

Ferrihydrite	[Alkalinity] (meq/L)			pH				[Chloride] (mM)			
	1.6×10^{-2}	2	10	8	10	12	13	0	1	2	5
$[SO_4^{\bullet-}]_{ss}$	1.7×10^{-17}	1.4×10^{-17}	1.2×10^{-17}	1.7×10^{-17}	8.2×10^{-18}	4.2×10^{-18}	1.7×10^{-18}	1.7×10^{-17}	9.7×10^{-18}	9.1×10^{-18}	6.7×10^{-18}
$[HO^{\bullet}]_{ss}$	1.7×10^{-21}	1.5×10^{-21}	1.3×10^{-21}	1.7×10^{-21}	8.5×10^{-21}	4.4×10^{-19}	2.1×10^{-19}	1.7×10^{-21}	1.8×10^{-20}	3.0×10^{-20}	4.9×10^{-20}
$[CO_3^{\bullet-}]_{ss}$	1.7×10^{-18}	2.2×10^{-16}	1.3×10^{-15}	1.7×10^{-18}	3.3×10^{-16}	7.0×10^{-15}	2.8×10^{-13}	1.7×10^{-18}	1.6×10^{-15}	3.7×10^{-15}	7.2×10^{-15}
$[Cl^{\bullet}]_{ss}$	-	-	-	-	-	-	-	-	2.1×10^{-19}	2.4×10^{-19}	2.1×10^{-19}

Goethite	[Alkalinity] (meq/L)			pH				[Chloride] (mM)			
	1.6×10^{-2}	2	10	8	10	12	13	0	1	2	5
$[SO_4^{\bullet-}]_{ss}$	2.3×10^{-17}	2.2×10^{-17}	2.1×10^{-17}	2.3×10^{-17}	2.4×10^{-17}	2.9×10^{-17}	8.3×10^{-18}	2.3×10^{-17}	2.2×10^{-17}	2.1×10^{-17}	1.8×10^{-17}
$[HO^{\bullet}]_{ss}$	2.3×10^{-21}	2.2×10^{-21}	2.1×10^{-21}	3.4×10^{-21}	2.5×10^{-20}	3.0×10^{-18}	1.0×10^{-18}	3.4×10^{-21}	3.2×10^{-20}	5.5×10^{-20}	1.1×10^{-19}
$[CO_3^{\bullet-}]_{ss}$	4.3×10^{-17}	5.5×10^{-15}	2.8×10^{-14}	5.7×10^{-17}	1.5×10^{-16}	1.2×10^{-14}	8.6×10^{-13}	5.7×10^{-17}	2.9×10^{-14}	6.1×10^{-14}	1.0×10^{-13}
$[Cl^{\bullet}]_{ss}$	-	-	-	-	-	-	-	-	4.6×10^{-19}	5.6×10^{-19}	5.5×10^{-19}

Pyrolusite	[Alkalinity] (meq/L)			pH				[Chloride] (mM)			
	1.6×10^{-2}	2	10	8	10	12	13	0	1	2	5
$[SO_4^{\bullet-}]_{ss}$	2.2×10^{-17}	1.7×10^{-17}	1.5×10^{-17}	2.2×10^{-17}	1.8×10^{-17}	1.9×10^{-17}	7.6×10^{-18}	2.2×10^{-17}	1.9×10^{-17}	1.9×10^{-17}	1.9×10^{-17}
$[HO^{\bullet}]_{ss}$	2.4×10^{-21}	2.1×10^{-21}	1.9×10^{-21}	2.4×10^{-21}	2.2×10^{-20}	1.9×10^{-18}	9.4×10^{-19}	2.4×10^{-21}	4.1×10^{-20}	4.8×10^{-20}	1.3×10^{-19}
$[CO_3^{\bullet-}]_{ss}$	7.2×10^{-17}	7.6×10^{-15}	3.5×10^{-14}	7.2×10^{-17}	1.8×10^{-15}	2.7×10^{-14}	1.1×10^{-12}	7.2×10^{-17}	4.2×10^{-14}	6.8×10^{-14}	7.2×10^{-14}
$[Cl^{\bullet}]_{ss}$	-	-	-	-	-	-	-	-	5.3×10^{-19}	5.5×10^{-19}	5.8×10^{-19}

*When alkalinity varied between 1.6×10^{-2} and 10 meq/L: $[Cl^-]=0$ mM, pH=8.0; when pH varied between 8 and 13: $[Cl^-]=0$ mM, [alkalinity]=1.6×10^{-2} meq/L; when chloride concentration varied between 0 and 5 mM, [alkalinity]=1.6×10^{-2} meq/L, pH=8.0.

Table 4 The impact of pH on the percentile contributions of different reactive radicals to benzene degradation.*

Reactive radical	Ferrihydrite pH				Goethite pH				Pyrolusite pH			
	8	10	12	13	8	10	12	13	8	10	12	13
$SO_4^{\cdot-}$	100%	100%	77%	24%	100%	100%	76%	30%	100%	100%	78%	27%
$HO^{\cdot}$	0%	0%	21%	8%	0%	0%	22%	8%	0%	0%	20%	9%
$CO_3^{\cdot-}$	0%	0%	2%	68%	0%	0%	2%	62%	0%	0%	2%	64%

* Experimental condition: mineral dosage=100 g/L; alkalinity=1.6×10^{-2} meq/L; no chloride added.
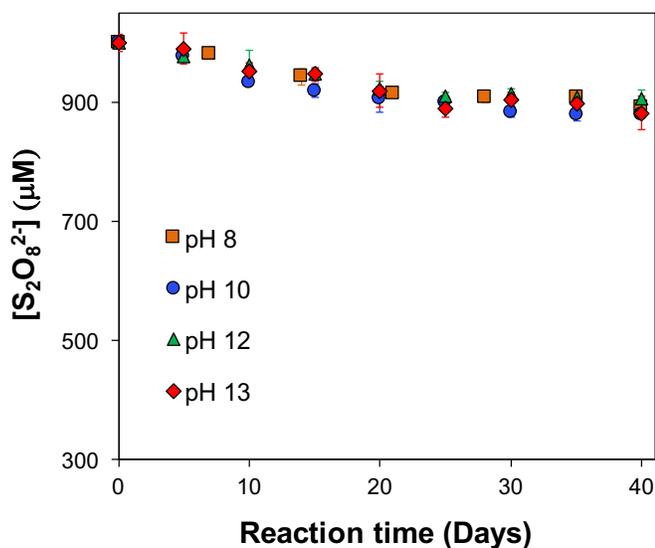
Figure 7 The impact of pH on persulfate decomposition in the absence of minerals. $[S_2O_8^{2-}]$=1 mM, [benzene]=1 mM, $[Cl^-]$=0 mM, [alkalinity]=1.6×10^{-2} -125 meq/L, ionic strength=100 mM.

Table 5 The impact of pH on the percentile contributions of different reaction pathways to persulfate decomposition. *

Reaction pathway for persulfate activation	Ferrihydrite pH				Goethite pH				Pyrolusite pH			
	8	10	12	13	8	10	12	13	8	10	12	13
≡Fe(III)-OH or ≡Mn(IV)-OH	57%	4%	0%	0%	63%	45%	1%	0%	0%	0%	0%	0%
≡Fe(II)-OH or ≡Mn(III)-OH	24%	2%	0%	0%	10%	5%	0%	0%	0%	0%	0%	0%
≡Fe(III)-O· or ≡Mn(IV)-O·	11%	83%	76%	41%	1%	30%	70%	71%	55%	52%	52%	51%
≡Fe(II)-O· or ≡Mn(III)-O·	1%	3%	5%	2%	0%	5%	13%	13%	38%	42%	41%	42%
Thermal activation	8%	7%	5%	5%	26%	15%	16%	16%	7%	7%	7%	7%
Soluble Fe(III) or Mn(IV)	0%	1%	14%	54%	0%	0%	0%	0%	0%	0%	0%	0%

* Experimental condition: mineral dosage=100 g/L, alkalinity=1.6×10^{-2} meq/L at pH 8, alkalinity=1.3×10^{-1} meq/L at pH 10, alkalinity=1.5 meq/L at pH 12, alkalinity=1.25×10^{2} meq/L at pH 13, no chloride added.

With respect to chloride, a change of chloride level up to 5 mM had no discernible effect on either persulfate decomposition or benzene degradation (**Figure 8**). The presence of chloride generated reactive chlorine atom radical ($Cl^{\bullet}$) via the scavenging reaction between chloride and $SO_4^{\bullet-}$ (Reaction 17). Although chain reactions involving $Cl^{\bullet}$ yielded reactive $HO^{\bullet}$ (Reactions 18-23), $Cl^{\bullet}$ also reacted strongly with bicarbonate and produced non-reactive $CO_3^{\bullet-}$ (Reaction 24), leading to a simultaneous increase of both $[HO^{\bullet}]_{ss}$ and $[CO_3^{\bullet-}]_{ss}$ (). As a result, the overall reactivity of the system remained more or less the same (), and benzene degradation was still mostly attributable to its reaction with $SO_4^{\bullet-}$ (**Table 6**). Prior literature reported the conversion of chloride to chlorate (ClO_3^-) by $SO_4^{\bullet-}$ and $HO^{\bullet}$ via radical-radical chain reactions in UV/persulfate system.[69] However, the steady-state concentrations of $SO_4^{\bullet-}$ and $HO^{\bullet}$ were very low in ISCO persulfate system (), and the extent of radical-radical reaction and the subsequent formation of chlorate was negligible.
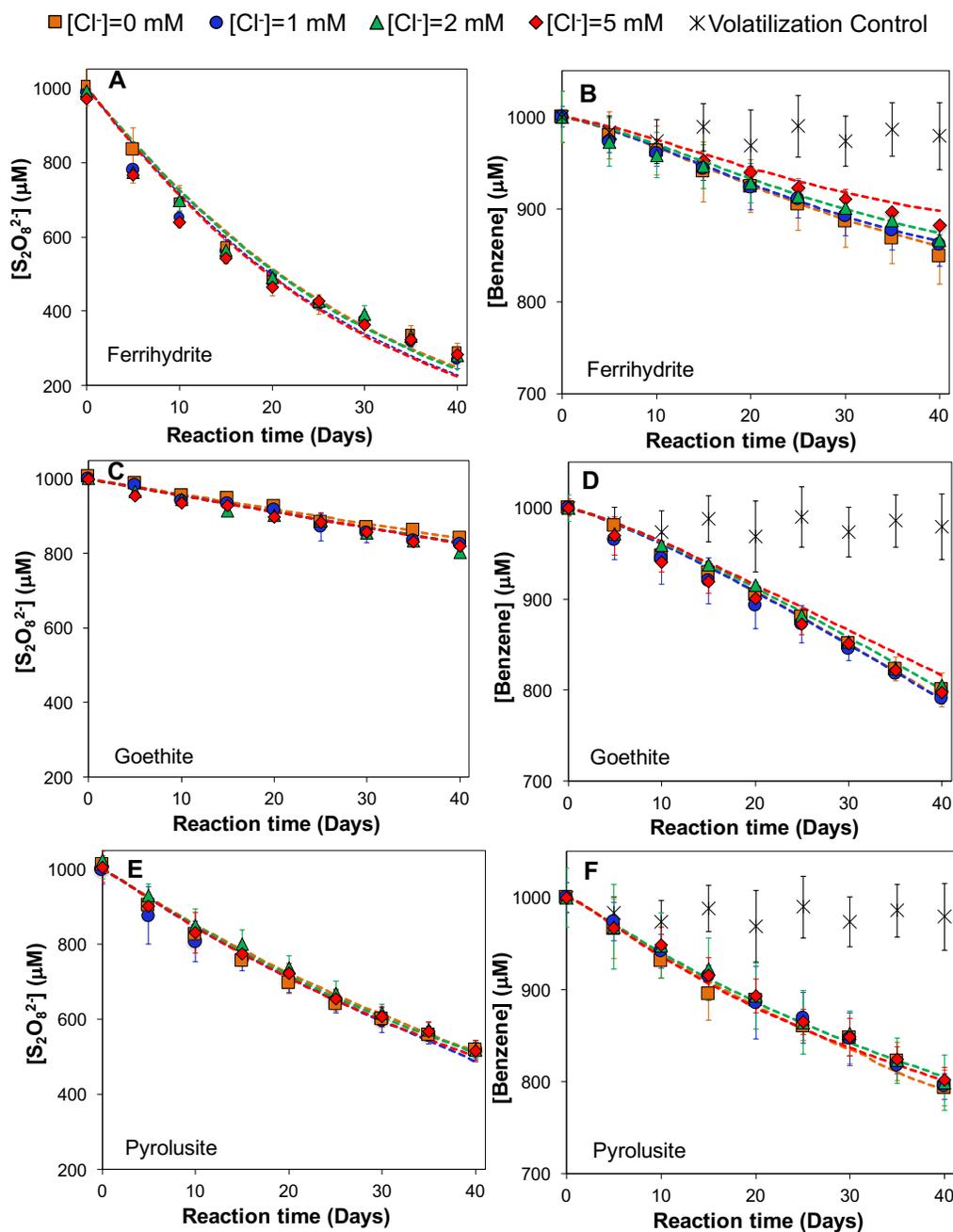
Figure 8 Impact of chloride on the rates of persulfate decomposition and benzene degradation by three minerals. (A, C, E) Persufate decomposition; (B, D, F) Benzene degradation. $[S_2O_8^{2-}]$=1 mM, [benzene]=1 mM, [alkalinity]=1.6×10^{-2} meq/L, pH=8.0, mineral dosage=100 g/L. Data points represent the experimental data. Dash lines represent the model-fitted values.

Table 6 The impact of chloride on the percentile contributions of different reactive radicals to benzene degradation.*

Reactive radical	Ferrihydrite [Cl⁻] (mM)				Goethite [Cl⁻] (mM)				Pyrolusite [Cl⁻] (mM)			
	0	1	2	5	0	1	2	5	0	1	2	5
$SO_4^{\cdot-}$	100%	96%	94%	91%	100%	94%	90%	85%	100%	91%	89%	88%
$HO^{\cdot}$	0%	0%	1%	2%	0%	0%	1%	1%	0%	1%	1%	2%
$Cl^{\cdot}$	0%	4%	5%	6%	0%	4%	5%	5%	0%	5%	5%	5%
$CO_3^{\cdot-}$	0%	0%	1%	2%	0%	2%	4%	8%	0%	3%	5%	5%

* Experimental condition: mineral dosage=100 g/L; alkalinity=1.6×10^{-2} meq/L; pH=8.0.

2.3.3 The impact of mineral surface complexation on persulfate activation

The reactivity of Fe(III) and Mn(IV) minerals on persulfate decomposition is mainly associated with metal surface complexation, especially carbonato and hydroxo complexes. Metal carbonato complexes including $\equiv$Me-OCO$_2$H^0 and $\equiv$Me-OCO$_2^-$ exist at the surface of Fe(III) and Mn(IV) oxides.[70-74] For example, ferrihydrite possesses $\equiv$Fe(III)-OCO$_2$H^0 and $\equiv$Fe(III)-OCO$_2^-$ surface carbonato complexes, each of which accounts for 28% and 72% of total carbonato complexes at varying pHs, respectively. The log value of equilibrium constant for $\equiv$Me-OCO$_2^-$ surface carbonato complexation reaction (denoted as logβ_1) is 12.78, 12.76 and 14.15 for ferrihydrite, goethite and pyrolusite, respectively (forward and reverse reactions of the equilibria are shown in Reactions 25-28). [75-77] The log value of equilibrium constant for $\equiv$Me-OCO$_2$H^0 surface carbonato complexation reaction (denoted as logβ_2) is 20.37, 18.30 and 22.65 for ferrihydrite, goethite and pyrolusite, respectively (Reactions 29-32). The formation of metal carbonato surface complexes can decrease the surface redox reactivity, because the carboxylic groups

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possess high electron density that can prevent their reactions with persulfate. Consequently, heterogeneous persulfate decomposition tends to slow down by surface carbonato complexation. This is consistent with prior observation that the formation of metal surface carbonato complexes decreased the redox reactivity on mineral surfaces.[44]

Furthermore, three hydroxo complexes exist at the mineral surfaces at solution pH ranging between 8 and 13: $\equiv$Me-OH$_2^+$, $\equiv$Me-OH^0 and $\equiv$Me-O$^-$. The equilibrium constants associated with the two steps of protonation (defined as pK$_1$ and pK$_2$) are 7.29 and 8.93 for ferrihydrite, 6.90 and 10.9 for goethite, and 0.6 and 2.6 for pyrolusite, respectively (forward and reverse reactions of the equilibria are shown in Reactions 33-40).[77-79] On the basis of pK values and the relevant range of groundwater pH, both $\equiv$Fe(III)-OH and $\equiv$Fe(III)-O$^-$ hydroxo complexes are important for ferrihydrite and goethite, and only $\equiv$Me-O$^-$ is relevant for pyrolusite. The deprotonated $\equiv$Fe(III)-O$^-$ is likely less reactive than the protonated $\equiv$Fe(III)-OH with persulfate for two reasons. First, the negative charges on $\equiv$Fe(III)-O$^-$ repulse the same negatively charged persulfate anion. Second, $\equiv$Fe(III)-O$^-$ possesses a higher electron density due to -O$^-$ groups, Therefore, it is less prone to withdraw additional electrons from persulfate to initiate the first step of activation.[80] The kinetic model fitting also showed that the rate constants of $\equiv$Fe(III)-OH reacting with persulfate was two times higher than those of $\equiv$Fe(III)-O$^-$ (Reaction 1 *vs.* 2 for ferrihydrite in **Table 2**; Reaction 54 *vs.* 56 for goethite in **Appendix A-5**).

With an increase of alkalinity up to 10 meq/L, the model-predicted steady-state concentrations (*i.e.*, equilibrium concentrations) of hydroxo surface complexes $\equiv$Me-OH

and $\equiv$Me-O$^-$ decreased by 10%-45%, and the equilibrium concentrations of carbonato surface complexes $\equiv$Fe(III)-OCO$_2$H^0 and $\equiv$Fe(III)-OCO$_2^-$ increased by nearly three orders of magnitude (**Table 7**). This significant increase of unreactive carbonato surface complexation with increasing alkalinity slowed down persulfate decomposition and decreased the yield of SO$_4^{\bullet-}$ (**Table 3**).

With an increase of pH from 8 to 12, model predictions suggested that the equilibrium concentrations of unreactive carbonato surface complexes $\equiv$Me-OCO$_2$H^0 and $\equiv$Me-OCO$_2^-$ decreased by several orders of magnitude, and reactive hydroxo complexes are predominant and remained relatively constant (**Table 7**). The combined effects are consistent with the observed acceleration of persulfate decomposition with increasing pH up to 12 (**Figure 6**). However, the concentrations of reactive hydroxo surface complex $\equiv$Me-OH decreased by 10 times from pH 12 to 13 due to hydroxo surface equilibrium (**Table 7**). This reversed change of surface reactivity is consistent with the experimentally observed decrease of persulfate decomposition from pH 12 to 13 (**Figure 6A, C** and **E**).

In addition, a variation in chloride levels had a negligible effect on the speciation of metal surface hydroxo or carbonato complexes (**Table 7**). The impact of chloride mainly resulted in changes of solution radical chain reactions. As Cl$^{\bullet}$ was generated via chloride (Reaction 17), HCO$_3^-$ was transformed to CO$_3^{\bullet-}$ by Cl$^{\bullet}$ (Reaction 24) instead of forming carbonato surface complexes (Reactions 25-32). These competing reactions slightly decreased the equilibrium concentrations of carbonato surface complexes, but the overall rates of persulfate decomposition and benzene degradation were not affected regardless

Table 7 Model-predicted steady-state concentrations of surface complexes of Fe(III) and Mn(IV) minerals. *

Ferrihydrite	[Alkalinity] (meq/L)			pH				[Chloride] (mM)			
	1.6×10^{-2}	2	10	8	10	12	13	0	1	2	5
$[Fe(III)\text{-}OH^0]_{ss}$	5.1×10^{-2}	5.0×10^{-2}	4.4×10^{-2}	5.1×10^{-2}	5.3×10^{-3}	5.7×10^{-5}	5.7×10^{-6}	5.1×10^{-2}	5.1×10^{-2}	5.1×10^{-2}	5.1×10^{-2}
$[Fe(III)\text{-}O]_{ss}$	6.0×10^{-3}	5.8×10^{-3}	5.1×10^{-3}	6.0×10^{-3}	6.2×10^{-2}	6.7×10^{-2}	6.7×10^{-2}	6.0×10^{-3}	6.0×10^{-3}	6.0×10^{-3}	6.0×10^{-3}
$[Fe(III)\text{-}OHCO_2^0]_{ss}$	4.3×10^{-6}	5.3×10^{-4}	2.7×10^{-3}	4.3×10^{-6}	3.0×10^{-7}	2.0×10^{-11}	1.7×10^{-12}	4.3×10^{-6}	4.2×10^{-6}	4.1×10^{-6}	4.0×10^{-6}
$[Fe(III)\text{-}OCO_2]_{ss}$	1.1×10^{-5}	1.4×10^{-3}	6.8×10^{-3}	1.1×10^{-5}	7.7×10^{-5}	5.0×10^{-7}	4.3×10^{-7}	1.1×10^{-5}	1.1×10^{-5}	1.1×10^{-5}	1.1×10^{-5}
$[Fe(II)\text{-}OH^0]_{ss}$	5.1×10^{-4}	4.8×10^{-7}	$4.2. \times 10^{-4}$	2.1×10^{-4}	1.8×10^{-5}	1.8×10^{-7}	2.1×10^{-8}	5.1×10^{-4}	5.2×10^{-4}	5.0×10^{-4}	5.2×10^{-4}
$[Fe(II)\text{-}O]_{ss}$	3.4×10^{-5}	3.5×10^{-5}	3.4×10^{-5}	3.7×10^{-5}	3.2×10^{-4}	5.3×10^{-4}	3.7×10^{-4}	3.4×10^{-5}	3.5×10^{-5}	3.6×10^{-5}	3.5×10^{-5}

Goethite	[Alkalinity] (meq/L)			pH				[Chloride] (mM)			
	1.6×10^{-2}	2	10	8	10	12	13	0	1	2	5
$[Fe(III)\text{-}OH^0]_{ss}$	2.0×10^{-3}	1.7×10^{-3}	1.1×10^{-3}	2.0×10^{-3}	2.5×10^{-3}	5.5×10^{-5}	5.6×10^{-6}	2.0×10^{-3}	2.0×10^{-3}	2.0×10^{-3}	2.0×10^{-3}
$[Fe(III)\text{-}O]_{ss}$	1.6×10^{-5}	1.4×10^{-5}	8.8×10^{-6}	1.6×10^{-5}	2.0×10^{-3}	4.4×10^{-3}	4.5×10^{-3}	1.6×10^{-5}	1.6×10^{-5}	1.6×10^{-5}	1.6×10^{-5}
$[Fe(III)\text{-}OHCO_2^0]_{ss}$	2.0×10^{-8}	2.3×10^{-6}	7.4×10^{-6}	2.0×10^{-8}	1.1×10^{-10}	1.6×10^{-13}	1.4×10^{-14}	2.0×10^{-8}	1.5×10^{-8}	9.3×10^{-9}	2.1×10^{-9}
$[Fe(III)\text{-}OCO_2]_{ss}$	5.8×10^{-6}	6.6×10^{-4}	2.1×10^{-3}	5.8×10^{-6}	3.2×10^{-6}	4.7×10^{-7}	4.0×10^{-7}	5.8×10^{-6}	4.2×10^{-6}	2.7×10^{-6}	6.1×10^{-7}
$[Fe(II)\text{-}OH^0]_{ss}$	2.3×10^{-4}	2.0×10^{-4}	1.7×10^{-4}	2.3×10^{-4}	1.7×10^{-4}	6.4×10^{-6}	6.0×10^{-7}	2.3×10^{-4}	2.5×10^{-4}	2.5×10^{-4}	2.7×10^{-4}
$[Fe(II)\text{-}O]_{ss}$	1.3×10^{-6}	1.1×10^{-6}	6.7×10^{-7}	1.3×10^{-6}	1.3×10^{-4}	3.5×10^{-4}	3.4×10^{-4}	1.3×10^{-6}	1.3×10^{-6}	1.3×10^{-6}	1.3×10^{-6}

Pyrolusite	[Alkalinity] (meq/L)			pH				[Chloride] (mM)			
	1.6×10^{-2}	2	10	8	10	12	13	0	1	2	5
$[Mn(IV)\text{-}OH^0]_{ss}$	1.9×10^{-10}	1.9×10^{-10}	1.9×10^{-10}	1.6×10^{-10}	1.5×10^{-12}	1.5×10^{-14}	1.5×10^{-15}	1.9×10^{-10}	1.8×10^{-10}	1.8×10^{-10}	1.8×10^{-10}
$[Mn(IV)\text{-}O]_{ss}$	4.6×10^{-5}	4.6×10^{-5}	4.5×10^{-5}	4.0×10^{-5}	3.8×10^{-5}	3.9×10^{-5}	3.8×10^{-5}	4.6×10^{-5}	4.5×10^{-5}	4.6×10^{-5}	4.5×10^{-5}
$[Mn(IV)\text{-}OHCO_2^0]_{ss}$	6.4×10^{-11}	8.2×10^{-9}	4.1×10^{-8}	5.6×10^{-11}	2.3×10^{-14}	1.0×10^{-18}	8.3×10^{-12}	6.4×10^{-11}	3.5×10^{-11}	2.2×10^{-11}	1.4×10^{-12}
$[Mn(IV)\text{-}OCO_2]_{ss}$	2.0×10^{-11}	2.6×10^{-9}	1.3×10^{-8}	1.8×10^{-11}	7.1×10^{-13}	3.2×10^{-15}	2.6×10^{-15}	2.0×10^{-11}	1.1×10^{-11}	7.1×10^{-12}	4.4×10^{-13}
$[Mn(III)\text{-}O]_{ss}$	1.3×10^{-5}	1.2×10^{-5}	1.2×10^{-5}	1.9×10^{-5}	2.1×10^{-5}	2.1×10^{-5}	2.1×10^{-5}	1.3×10^{-5}	1.4×10^{-5}	1.3×10^{-5}	1.4×10^{-5}

* When alkalinity varied between 1.6×10^{-2} and 10 meq/L: $[Cl^-]$=0 mM, pH=8.0; when pH varied between 8 and 13: $[Cl^-]$=0 mM, [alkalinity]=1.6×10^{-2} meq/L; when chloride concentration varied between 0 and 5 mM: [alkalinity]=1.6×10^{-2} meq/L, pH=8.0

of the chloride level (**Figure 8**).

In accord with these observations, the fraction of carbonato surface complexes, denoted as α, was calculated as:

$$\alpha = \frac{[\equiv Me-OCO_2H^0]_{ss}+[\equiv Me-OCO_2^-]_{ss}}{[\equiv Me-OH_2^+]_{ss}+[\equiv Me-OH^0]_{ss}+[\equiv Me-O^-]_{ss}+[\equiv Me-OCO_2H^0]_{ss}+[\equiv Me-OCO_2^-]_{ss}} =$$

$$\frac{K_1\beta_1[CO_3^{2-}][H^+]^2+K_1\beta_2[CO_3^{2-}][H^+]^3}{[H^+]^2+K_1[H^+]+K_1K_2+K_1\beta_1[CO_3^{2-}][H^+]^2+K_1\beta_2[CO_3^{2-}][H^+]^3} \quad (2)$$

$[\equiv Me\text{-}OCO_2H^0]_{ss}$, $[\equiv Me\text{-}OCO_2^-]_{ss}$, $[\equiv Me\text{-}OH_2^+]_{ss}$, $[\equiv Me\text{-}OH]_{ss}$ and $[\equiv Me\text{-}O^-]_{ss}$ are the equilibrium concentrations of the surface carbonato complex with bicarbonate, carbonate, and protonated and deprotonated hydroxo groups, respectively. K_i and β_i are surface hydroxo and carbonato complexation equilibrium constants.
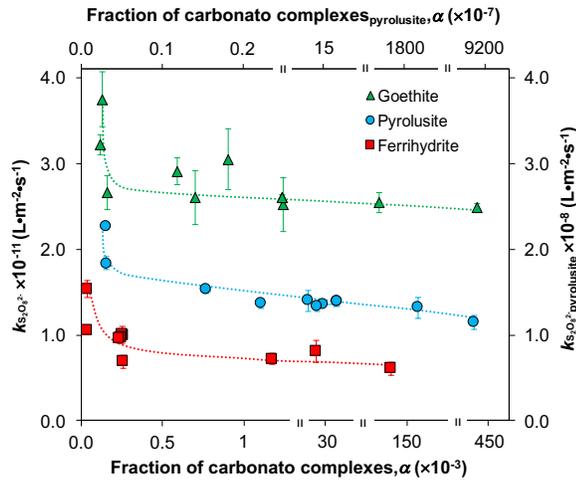
Figure 9 The correlation between the rate of persulfate decomposition and the fraction of carbonato complex on Fe(III) and Mn(IV) mineral (data for pyrolusite shown as secondary x- and y-axes). [$S_2O_8^{2-}$]=1 mM, [benzene]=1 mM, mineral dosage=100 g/L, pH=8.0, ionic strength=10 mM. Data points represent the experimental results. Dash lines are the trend lines.

The experimentally observed rate of persulfate decomposition was associated with the model-predicted fraction of unreactive carbonato complexes in an inversely exponential relationship (**Figure 9**). The reactivity of minerals with persulfate decomposition plummeted by as much as 40% when a small fraction of mineral surface sites was occupied by carbonato complexes. This initial sharp decrease of reactivity was associated with a high sensitivity of surface speciation to carbonato complexation at pHs higher than 10. Under this chemical condition, the equilibrium concentration of reactive $\equiv$Me-OH reached a minimum, and a small extent of carbonato complex formation drastically decreased the surface reactivity. In contrast, as the fraction of carbonato complexes increased (this corresponded to conditions with solution pHs lower than 10), $\equiv$Fe(III)-OH and $\equiv$Mn(IV)-O$^-$ remained as the predominant reactive surface complexes. Consequently, the redox reactivity of mineral surface became less sensitive to carbonato complexation and exhibited a small variation (**Figure 9**).

2.3.4 Product distribution of benzene oxidation via heterogeneous persulfate activation

Two major oxidation products were simultaneously generated from benzene degradation, *i.e.*, phenol and a six-carbon aldehyde ring-cleavage product. The correlation between the yields of oxidation products and the branching ratio of $SO_4^{\bullet-}$ reacting with benzene exhibited a positively exponential relationship (**Figure 10A-B**). On the contrary, an inverse relationship existed between the yield of oxidation products and the branching ratio of $HO^\bullet$ or $CO_3^{\bullet-}$ (**Figure 10C-F**). These results indicated that $SO_4^{\bullet-}$ had a distinct oxidation pathway on benzene degradation compared to that of $HO^\bullet$ or $CO_3^{\bullet-}$. Prior studies

reported the distinct oxidation mechanisms for different radicals. For example, $SO_4^{\bullet-}$ reacted with benzene via direct electron transfer, $HO^{\bullet}$ reacted with benzene via OH addition, and $CO_3^{\bullet-}$ reacted via hydrogen abstraction.[42,43,81-84] The data suggested that $SO_4^{\bullet-}$-driven oxidation likely favored pathways that involve fewer steps of hydroxylation that accumulated phenol and aldehyde products, whereas $HO^{\bullet}$ or $CO_3^{\bullet-}$ oxidation promoted multiple steps of sequential hydroxylation of benzene and generated low-carbon-chain products. For example, a further oxidation of phenol can produce benzoquinone and hydroquinone intermediates.[85-86] The toxicity implications of the $SO_4^{\bullet-}$-driven oxidation products will be examined in the future.
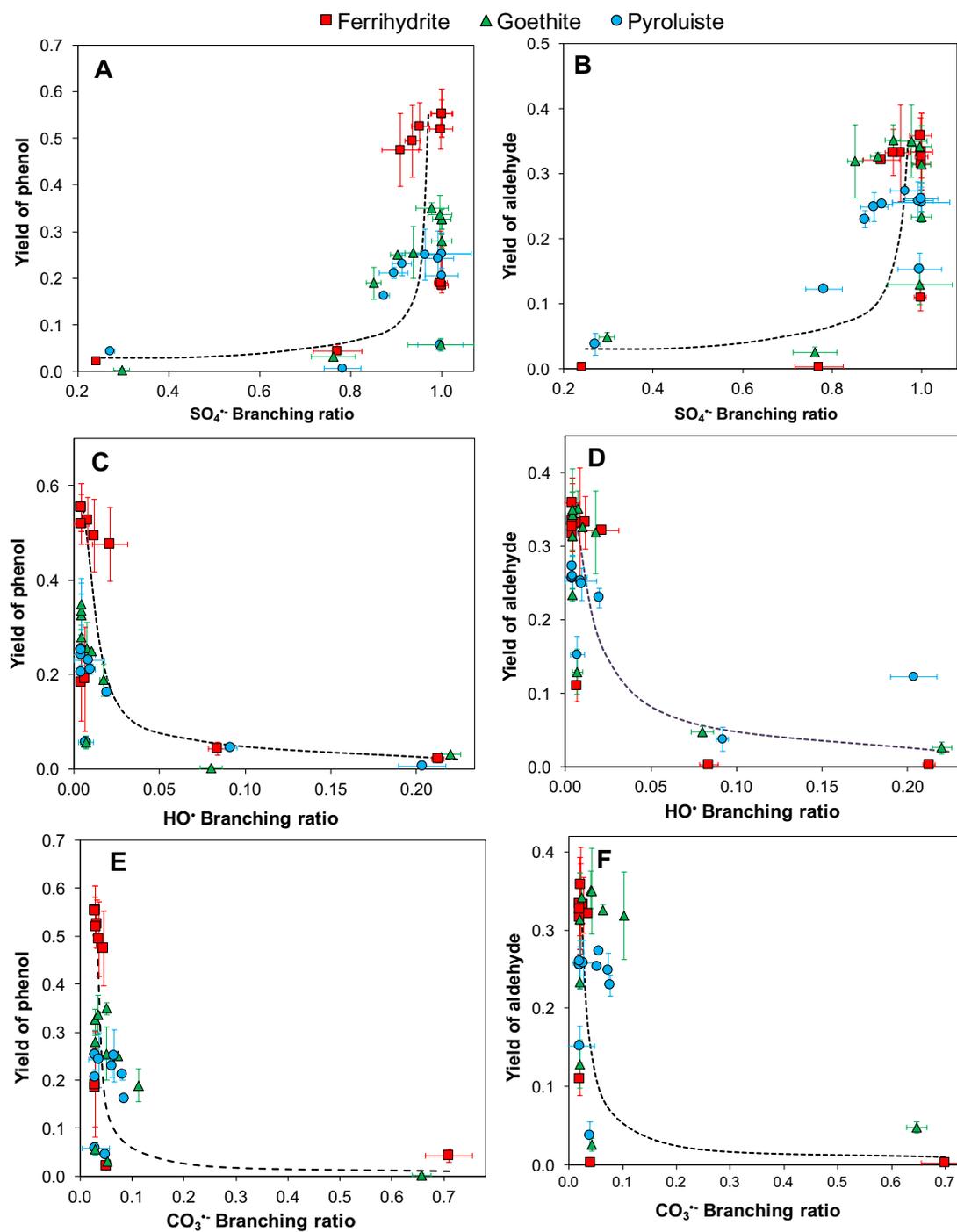
Figure 10. Correlation between the yields of benzene oxidation products and branching ratio of $SO_4^{\bullet-}$, $HO^{\bullet}$ and $CO_3^{\bullet-}$ reacting with benzene. (A,C,E) phenol; (B,D,F) aldehyde. Data points are experimental observations; dash lines are the trend lines.

2.4 Environmental Implications

One salient finding from this study is that persulfate-based ISCO remediation efforts need special attention to native alkalinity and pH levels in contaminated groundwater, because these chemical parameters indicate the in situ redox reactivity in the aquifer and the effectiveness on persulfate activation. Alkalinity and pH mainly impact the surface complexation of Fe(III)- and Mn(IV)-containing aquifer minerals. Higher alkalinity favors the formation of unreactive surface carbonato complexes, which tends to inhibit persulfate activation, while higher pH favors the formation of reactive surface hydroxo complexes and accelerates remediation efforts. Chloride in groundwater is found to impact solution radical distributions, but it poses a negligible effect on persulfate decomposition and contaminant removal. This indicates that persulfate ISCO is applicable to groundwater with elevated salinity. Results also suggest that aquifers with abundant goethite can increase the persistence of persulfate and increase remediation efficiency. Although aquifer minerals with higher abundance of ferrihydrite and pyrolusite can accelerate persulfate decomposition, these minerals tend to have lower stoichiometric efficiency of radical yields.

2.5 Acknowledgement

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Chapter 3

Persulfate-based UV/AOP for Potable Water Reuse: Impact of Chloramine, Chloride, pH, and Oxygen Levels on 1,4-dioxane Removal by UV/Persulfate

Submitted to Environmental Science & Technology

Li, Wei, Samuel Patton, Kenneth P. Ishida, Jamie Gleason, Stephen P. Mezyk, Guadalupe Lara, Alex Numa and Haizhou Liu " Simultaneous UV Photolysis of Chloramine and Persulfate on 1,4-dioxane Removal in Reserve Osmoses Permeate for Potable Reuse." Submitted to Environmental science & Technology

3.1 Introduction

Potable water reuse provides a viable solution to water scarcity by treating municipal wastewater. [1,2] UV-based advanced oxidation processes (UV/AOPs) have become an integral part of the treatment train to degrade trace organic contaminants. [3-9] For example, 1,4-dioxane (1,4-D), a solvent widely used in production of adhesives, dyes, textiles and cosmetics, has been widely detected in wastewater and classified as a potential human carcinogen. [10-13] Because small and neutral trace organic contaminants including 1,4-D can pass through reverse osmosis (RO) membranes, UV/AOP typically takes place subsequently to membrane treatment to ultimately eliminate recalcitrant trace contaminants from RO permeate.

During the upstream membrane step, chloramine is added in the feed water to minimize membrane bio-fouling. Due to their small molecular sizes and neutral charge, chloramines easily pass through RO membranes and are carried over to downstream UV/AOP step and undergo photolysis. [14] In addition, an oxidant is added to the UV/AOP step to produce highly oxidative species. Hydrogen peroxide (H_2O_2) is the default oxidant and produces hydroxyl radical ($HO^{\bullet}$). Although possessing a high oxidative capacity, $HO^{\bullet}$ is not selective and can be scavenged by carbonate and chloride and consequently adversely affects its efficiency. [6,15,16]

In recent years, persulfate ($S_2O_8^{2-}$) becomes an alternative oxidant in UV/AOP. [6,17,18] The quantum yield of $SO_4^{\bullet-}$ from $S_2O_8^{2-}$ is higher than that of $HO^{\bullet}$ from H_2O_2 (0.7 *vs.* 0.5), while both $SO_4^{\bullet-}$ and $HO^{\bullet}$ have similar oxidizing power (2.5-3.1 V *vs.*

1.9-2.8 V).[19-21] Furthermore, $SO_4^{\bullet-}$ is more selective towards electron-rich contaminants that typically observed in recycled water.[6,22,23] Therefore, $UV/S_2O_8^{2-}$ can potentially reach a higher efficiency and a lower energy footprint than H_2O_2. Given the existence of *de facto* UV/NH_2Cl because of NH_2Cl as carry-over membrane anti-fouling agents and the future application of $UV/S_2O_8^{2-}$, it is important to understand the unique radical generation under photolysis of both NH_2Cl and $S_2O_8^{2-}$.

The mechanism on the simultaneous photolysis of NH_2Cl and $S_2O_8^{2-}$ is not well developed. NH_2Cl has a high UV absorbance coefficient (371 $M^{-1}cm^{-1}$) and a quantum yield similar to H_2O_2.[4,24,-26] NH_2Cl can also act as a self-scavenger that decreases its radical yield upon UV irradiation.[14] However, most prior studies examined chloramine photolysis in solution conditions unrelated to potable reuse.[4,8,24-30] Our recent study showed that photolysis of NH_2Cl in RO permeate produce $HO^{\bullet}$ and $Cl_2^{\bullet-}$ that promote 1,4-D degradation. Furthermore, $SO_4^{\bullet-}$ produced from $S_2O_8^{2-}$ photolysis can react with NH_2Cl to generate secondary radicals, but the extent of chain reactions in RO permeate with the dual oxidants remains unknown.

The objectives of this study were to quantify the formation of reactive radicals during the simultaneous photolysis of NH_2Cl and $S_2O_8^{2-}$, examine the impact of oxidant dosage, pH, chloride and dissolved O_2 on the degradation of 1,4-D, and develop a kinetic model to predict the radical yield and transformation of with both oxidants.

3.2 Materials and Methods

All solutions were prepared from reagent-grade chemicals with deionized water (DI) (resistivity <18.2MΩ, Millipore System). A fresh 50 mM NH_2Cl stock solution was prepared daily by slowly titrating NaOCl with $(NH_4)_2SO_4$ at 1:1.2 molar ratio and buffered with 4 mM borate at pH 8.8.[31] The prepared NH_2Cl solution was equilibrated for 3 hours in the dark and its concentration was verified using permanganate.[32] An equal-molar chloride residue always co-existed with NH_2Cl due to chloramine equilibrium chemistry. A 100-mM persulfate stock solution was prepared daily using $Na_2S_2O_8$. Most experiments were conducted using N_2-purged DI water to minimize dissolved O_2. In some experiments, DI water was purged with ambient air for 20 minutes to create an air-saturated solution. The solution pH was adjusted to a targeted value between 5 to 8 with phosphate buffer, which also maintained the ionic strength constant at 50 mM. Chloride concentration was adjusted between 0.2 and 2 mM.

To start a UV experiment, solutions of NH_2Cl ranging between 0 and 6 mM and $S_2O_8^{2-}$ between 2 and 4 mM were mixed with 250 μM of 1,4-D. In addition, 10 μM benzoic acid (BA) and 20 μM nitrobenzene (NB) were added as radical probe compounds. The solution was quickly mixed, transferred to multiple 8-mL quartz tubes with no headspace, and placed in a carousel UV reactor (ACE Glass) equipped with a low-pressure monochromatic (λ=254 nm) mercury lamp (Philips TUV6T5, 6W).

Samples were withdrawn from the UV reactor at pre-determined time intervals. NH_2Cl concentration was measured immediately using the DPD colorimetric method.[32]

The presence of $S_2O_8^{2-}$ in the sample had no interference with the measurement. $S_2O_8^{2-}$ concentration was measured using KI titration by a Horiba UV spectrofluorometer after NH2Cl was removed by purging the solution with air.[33] To quantify the generation of nitrogen species during NH2Cl photolysis, total nitrogen (TN) was measured by a TOC analyzer with nitrogen detector (OI Analytical, Inc.); ammonium, nitrite and nitrate were measured using colorimetric methods with phenate, sulfanilamide and nicotinamide adenine dinucleotide phosphate, respectively;[32] gaseous nitrogen formation was calculated based on the loss of TN; the remaining fraction of nitrogen was accounted for as organic nitrogen. Chloride was measured by a Dionex-1000 ion chromatography equipped with a conductivity detector.

The steady-state radical concentrations were quantified based on the competitive kinetics of probe compounds. Using the observed first-order decay rates of the probe compounds (*i.e.* nitrobenzene (NB), benzoate(BA) and 1,4-dioxane (1,4-D), the steady-state concentrations of $HO^{\bullet}$, $SO_4^{\bullet-}$ and $Cl_2^{\bullet-}$ were calculated. The steady-state concentration of $HO^{\bullet}$ was calculated using NB, because NB predominantly reacted with $HO^{\bullet}$. First, the *pseudo* first-order decay rate of NB (k_{obs}) was obtained from experimental measurement. $[HO^{\bullet}]_{ss}$ was calculated based on Equation 1:

$$k_{obs} = -\ln\left(\frac{[NB]_t}{[NB]_0}\right) = k_{HO-NB}[HO^{\cdot}]_{ss}t \qquad \text{(Eq. 1)}$$

$$[HO^{\cdot}]_{ss} = \frac{k_{NB}}{k_{HO\cdot-NB}}$$

[NB]$_t$ is the concentration of nitrobenzene at a given reaction time t; [NB]$_0$ is the initial concentration of nitrobenzene (20 µM); k_{HO-NB} is the second-order rate constant between HO$^{\bullet}$ and NB, which is known as 6.0×10^9 M^{-1}s^{-1}.[34] k_{NB} is the experimentally obtained *pseudo* first-order decay rate of NB.

Second, based on the branching ratio calculation, the reaction between Cl$_2^{\bullet-}$ and BA was negligible (Equation 2):

$$\%_{BA-Cl_2^-} = \frac{k_{BA-Cl_2^-}[BA]}{k_{BA-Cl_2^-}[BA]+k_{1,4D-Cl_2^-}[1,4-D]+k_{H_2O-Cl_2^-}+k_{NH_2Cl-Cl_2^-}[NH_2Cl]} = <1\% \qquad \text{(Eq. 2)}$$

$\%_{BA-Cl_2^-}$ is defined as the branching ratio of BA with Cl$_2^{\bullet-}$. $k_{BA-Cl_2^-}$, $k_{1,4-D-Cl_2^-}$, and $k_{NH_2Cl-Cl_2^-}$ are the second-order rate constants between Cl$_2^{\bullet-}$ and benzoate, Cl$_2^{\bullet-}$ and 1,4-D, and Cl$_2^{\bullet-}$ and NH$_2$Cl, respectively, which are known as $k_{BA-Cl_2^-}=2.0\times10^6$ M^{-1}s^{-1},[35] $k_{1,4-D-Cl_2^-}$, $=3.3\times10^6$ M^{-1}s^{-1},[36] and $k_{NH_2Cl-Cl_2^-}=10^6$ M^{-1}s^{-1}. The rate constant for NH$_2$Cl and Cl$_2^{\bullet-}$ is obtained from this study, which is discussed in Text S4. $k_{H_2O-Cl_2^-}$ is the first-order rate constant between Cl$_2^{\bullet-}$ and H$_2$O, which is 1.3×10^3 s^{-1}.[37]

Because BA reacts with HO$^{\bullet}$, SO$_4^{\bullet-}$ and NH$_2^{\bullet}$, the *pseudo* first-order decay rate of BA was calculated based on Equation 3:

$$-ln\frac{[BA]_t}{[BA]_0} = (k_{BA-HO^{\cdot}}[BA][HO^{\cdot}]_{ss} + k_{BA-SO_4^-}[BA][SO_4^-]_{ss}+k_{BA-NH_2}[BA][NH_2^{\cdot}]_{ss})t \quad \text{(Eq. 3)}$$

and the steady-state concentration of SO$_4^{\bullet-}$ was obtained by solving the above equation:

$$[SO_4^-]_{ss} = \frac{k_{BA}-k_{HO^{\cdot}-BA}[HO^{\cdot}]_{ss}-k_{BA-NH_2^{\cdot}}[NH_2^{\cdot}]_{ss}}{k_{BA-SO_4^-}}$$

Here, $[BA]_t$ is the concentration of BA at a given reaction time t; $[BA]_0$ is the initial

concentration of BA (10 μM); $k_{HO\cdot-BA}$ is the second-order rate constant between $HO^\bullet$ and

BA (6.0×10^9 M^{-1}s^{-1}), $k_{BA-SO_4^-}$ is the second-order rate constant between $SO_4^{\bullet-}$ and BA

(1.2×10^9 M^{-1}s^{-1}),[38] and $k_{BA-NH_2^\cdot}$ is second-order rate constant between $NH_2^\bullet$ and BA

(3.0×10^6 M^{-1}s^{-1}).[39] k_{BA} is the experimentally obtained pseudo first-order decay rate of

BA. $[NH_2^\bullet]_{ss}$ was obtained from the kinetic model (All reactions of the model are listed in

Appendix B-2).

Finally, $[Cl_2^{\bullet-}]_{ss}$ was calculated based on Equation 4. $NH_2^\bullet$ was not included in the

equation because it has negligible reactivity with 1,4-D.[40]

$$-\ln\left(\frac{[1,4-D]_t}{[1,4-D]_0}\right) = (k_{HO\cdot-1,4-D}[HO^\cdot]_{ss} + k_{SO_4^--1,4-D}[SO_4^{\cdot-}]_{ss} + k_{Cl_2^--1,4-D}[Cl_2^{\cdot-}]_{ss})t \qquad \text{(Eq. 4)}$$

$$[SO_4^{\cdot-}]_{ss} = \frac{k_{1,4-D} - k_{HO\cdot-1,4D}[HO^\cdot]_{ss} - k_{Cl_2^--1,4-D}[Cl_2^{\cdot-}]_{ss}}{k_{SO_4^--1,4D}}$$

Here $[1,4-D]_t$ is the concentration of 1,4-D at a given reaction time t; $[1,4-D]_0$ is the initial

concentration of 1,4-D (250 μM); $k_{HO\cdot-1,4-D}$ is the second-order rate constant between

$HO^\bullet$ and 1,4-D (3.1×10^9 M^{-1}s^{-1}),[41] $k_{SO_4^--1,4-D}$ is the second-order rate constant between

$SO_4^{\bullet-}$ and 1,4-D (4.1×10^7 M^{-1}s^{-1}),[42] and $k_{Cl_2^--1,4-D}$ is the second-order rate constant

between $Cl_2^{\bullet-}$ and 1,4-D (3.3×10^6 M^{-1}s^{-1}).[36] $k_{1,4-D}$ is the experimentally observed *pseudo*

first-order rate constant of 1,4-D.

The concentrations of 1,4-D, BA and NB were measured by an Agilent 1200 liquid

chromatography equipped with a diode array detector and a Zorbax Eclipse SB-C18

column (4.6×150mm, 5-μm particle size). A kinetics model was developed using the Kintecus software (all reactions of the model are listed in **Appendix B-2**).[43] The model development and optimization can be found in Text S4 and prior literature.[18, 44]

3.3 Results and Discussion

### 3.3.1 Impact of NH$_2$Cl dosage on UV/S$_2$O$_8{}^{2-}$

The effect of NH$_2$Cl on 1,4-D degradation by UV photolysis of S$_2$O$_8{}^{2-}$ was investigated. The concentrations of S$_2$O$_8{}^{2-}$ and 1,4-D were fixed at 2 mM and 0.25 mM, respectively. The UV fluence-normalized rate of 1,4-D degradation increased from 7.5×10^{-4} to 9.7×10^{-4} cm^2·mJ^{-1} when the NH$_2$Cl dosage increased from 0 to 0.2 mM; however, the rate decreased to 5.3×10^{-4} cm^2·mJ^{-1} when the NH$_2$Cl dosage was increased further to 4 mM (**Figure 11**). Analysis with probe compounds showed that HO$^\bullet$ contributed the most to 1,4-D degradation, followed by SO$_4{}^{\bullet-}$ and Cl$_2{}^{\bullet-}$ (**Figure 11A**). The contribution of HO$^\bullet$ reached a maximum at the optimal NH$_2$Cl dosage of 0.2 mM –corresponding to a NH$_2$Cl-to-S$_2$O$_8{}^{2-}$ molar ratio of 0.1:1, and decreased by 27% when NH$_2$Cl dosage increased to 4 mM. The contribution of SO$_4{}^{\bullet-}$ to 1,4-D degradation dropped significantly to negligible when the NH$_2$Cl-to-S$_2$O$_8{}^{2-}$ ratio increased beyond 0.1, accompanied by a substantial increase in the contribution of Cl$_2{}^{\bullet-}$ to 1,4-D removal (**Figure 11A**).
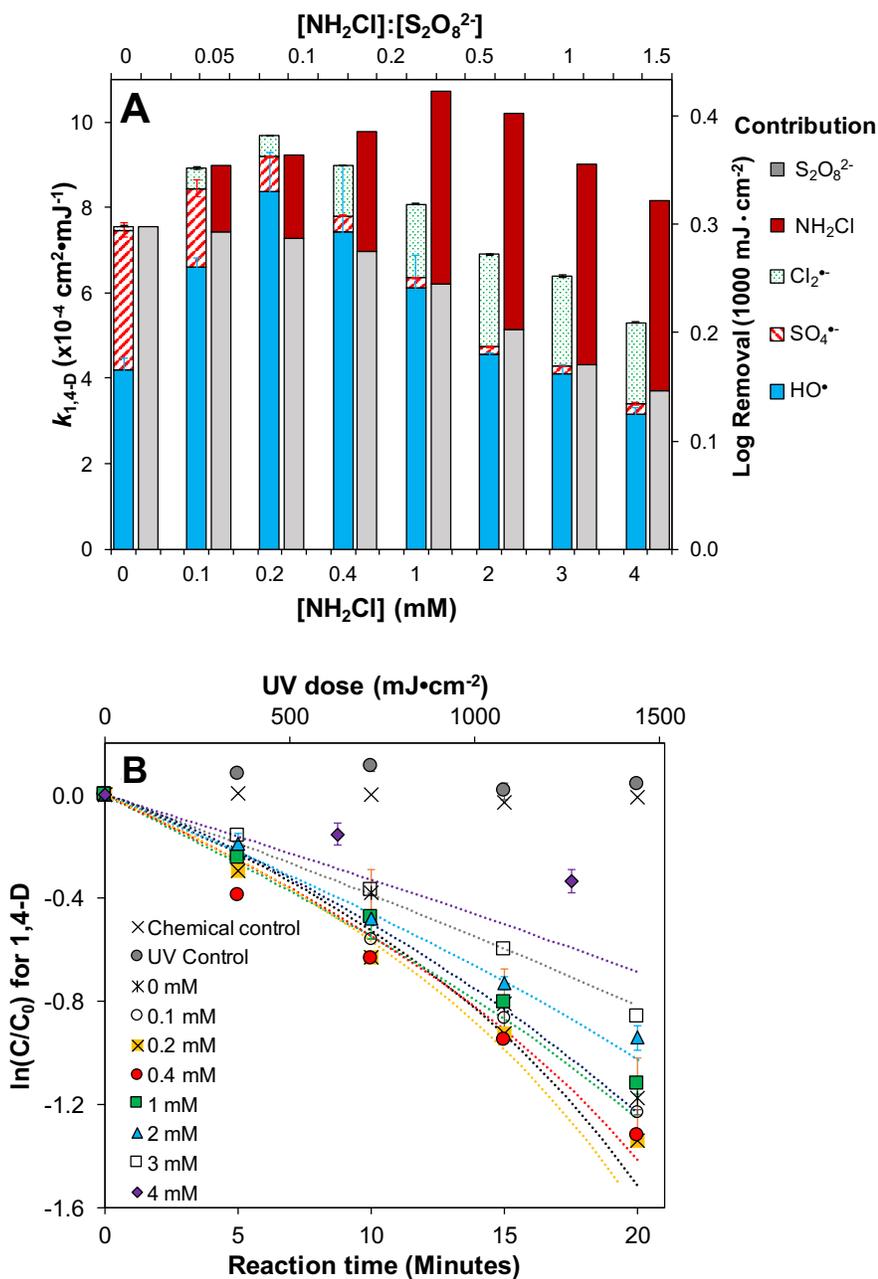
Figure 11 Effect of NH$_2$Cl dose on 1,4-dioxane degradation. (A) UV fluence normalized rate of 1,4-dioxane, S$_2$O$_8^{2-}$ and NH$_2$Cl; (B) first order decay of 1,4-dioxane. [S$_2$O$_8^{2-}$]=2 mM, [NH$_2$Cl]=0-4 mM [1,4-dioxane]=0.25 mM, [benzoic acid]=10 μM, [nitrobenzene]=20 μM, pH=5.8, UV dose = 2760 mJ cm^{-2}. Dash lines represent the modeled results.

As the concentration of NH_2Cl increased from 0 to 4 mM, photons were preferentially absorbed by NH_2Cl compared to $S_2O_8^{2-}$, which was supported by an increase in the photolysis rate of NH_2Cl and a decrease in the photolysis rate of $S_2O_8^{2-}$ (**Figure 12A**). The percentage of light absorbed by NH_2Cl (solid gray bar) and $S_2O_8^{2-}$ (red bar) in the mixed system was calculated (**Appendix B-4**) and shown in **Figure 11**. For instance, in the presence of 0.1 mM NH_2Cl, $S_2O_8^{2-}$ absorbed 98% of light as if no monochloramine were present, and only absorbed 51% of light when mixing with 4 mM NH_2Cl. Thus, the contribution of $S_2O_8^{2-}$ to 1,4-D decreased by 2%. Meanwhile, NH_2Cl photolysis produced less reactive-$Cl^•$ and $NH_2^•$ (Reaction 1 in **Scheme 7**, all subsequent reactions are referred to those in **Scheme 7**) as the primary radical.[14] As a result, the rate of 1,4-D degradation was compromised. In contrast, an increase in $S_2O_8^{2-}$ dosage in the presence of a constant NH_2Cl level always promoted radical generation (**Figure 12B**).
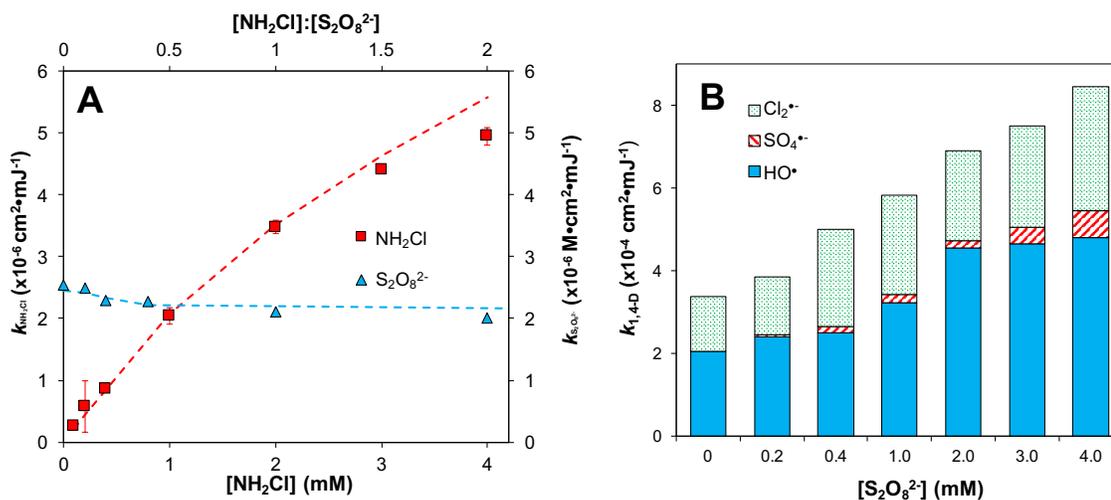
Figure 12 Impact of oxidant dosage on 1,4-D degradation. (A) correlation between 1,4-D degradation rates and oxidants photolysis rates (B) effect of $S_2O_8^{2-}$ dosage on 1,4-D degradation. $[S_2O_8^{2-}]$=0 - 4 mM, $[NH_2Cl]$=2 mM, [1,4-dioxane]=0.25 mM, [benzoic acid]=10 μM, [nitrobenzene]=20 μM, pH=5.8, UV dose = 2760 mJ cm^{-2}.

In addition, the experimentally observed 1,4-D degradation rate with both oxidants was always 10% to 40% lower than the theoretically additive value as if both oxidants existed separately (**Figure 11**, calculation provided in **Appendix B-5**). Furthermore, the degradation rate of 1,4-D was positively correlated with the photolysis rate of $S_2O_8^{2-}$, but inversely correlated with that of NH_2Cl (**Figure 13A**). These trends strongly suggested that in the mixed oxidant system, NH_2Cl rather than $S_2O_8^{2-}$ had a stronger scavenging effect on reactive radicals.
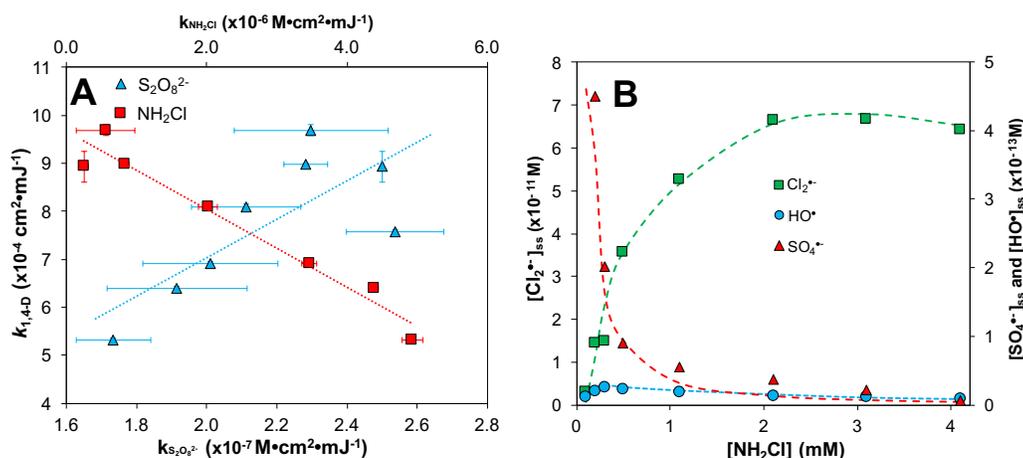
Figure 13. Effect of NH_2Cl dosage on the treatbility of 1,4-dioxane by UV/ $S_2O_8^{2-}$ and NH_2Cl. (A) correlation between 1,4-D degradation rates and oxidants photolysis rates; (B) steady-state radical concentration. $[S_2O_8^{2-}]$=2 mM, $[NH_2Cl]$=0-4 mM, [1,4-dioxane]= 0.25 mM, [benzoic acid]=10 µM, [nitrobenzene]=20 µM, pH= 5.8. UV dose = 2760 mJ·cm^{-2}. Dash lines represent the modeled resultes.

3.3.2 Radical distribution in UV photolysis of $S_2O_8^{2}$ and NH_2Cl

Impacts of NH_2Cl on the radical generation and scavenging pathways in UV/$S_2O_8^{2-}$ were elucidated in **Scheme 7**. Direct photolysis of $S_2O_8^{2-}$ and NH_2Cl generated $SO_4^{\bullet-}$, $Cl^{\bullet}$ and $NH_2^{\bullet}$ (Reactions 1-2 in **Scheme 7**). The co-existence of chloride with NH_2Cl leads to

the reaction of $SO_4^{\bullet-}$ with chloride to generate $HO^{\bullet}$ (Reactions 3-7). Consequently, when NH_2Cl dosage increased up to 0.2 mM, $[SO_4^{\bullet-}]_{ss}$ decreased by 75%, and the steady-state concentrations of $[HO^{\bullet}]_{ss}$ increased by 2-fold (**Figure 13B**). 1,4-D is more reactive with $HO^{\bullet}$ than with $SO_4^{\bullet-}$; consequently, its degradation kinetics were enhanced.[45]

Scheme 7 Radical reaction pathways in UV/persulfate with monochloramine.

However, as the NH_2Cl concentration increased from 0.2 to 4 mM, both $[HO^{\bullet}]_{ss}$ and $[SO_4^{\bullet-}]_{ss}$ decreased substantially, and $[Cl_2^{\bullet-}]_{ss}$ increased by 4-fold (**Figure 13B**). This trend resulted from the scavenging effects of NH_2Cl on $HO^{\bullet}$ and $SO_4^{\bullet-}$ (Reaction 8-9). For instance, up to 14% of $HO^{\bullet}$ and 8% of $SO_4^{\bullet-}$ were scavenged by 4 mM NH_2Cl (**Appendix B-5**). $HO^{\bullet}$ reacts with NH_2Cl at 5.1×10^8 $M^{-1}s^{-1}$, and the second-order rate constant between $SO_4^{\bullet-}$ and NH_2Cl of $2.4\pm0.1\times10^7$ $M^{-1}s^{-1}$ was estimated by pulse radiolysis (**Appendix B-6**).

$Cl_2^{\bullet-}$ could also be scavenged by NH_2Cl (Reaction 10). However, more $Cl_2^{\bullet-}$ was produced with increasing NH_2Cl dosage, thus $[Cl_2^{\bullet-}]_{ss}$ reached a plateau after NH_2Cl reached 2 mM (**Figure 13B**). 1,4-D is more reactive with $HO^{\bullet}$ and $SO_4^{\bullet-}$ than with $Cl_2^{\bullet-}$. Therefore, the overall degradation rate of 1,4-D slowed down significantly.

In addition, the co-existence of chloride with NH_2Cl acted as a scavenger to transform $SO_4^{\bullet-}$ to $Cl_2^{\bullet-}$ (Reaction 3-4). To eliminate the confounding effect by chloride, the initial NH_2Cl dosage was varied but chloride fixed at 4 mM. Results showed that the 1,4-D degradation rate decreased by 43% with increasing NH_2Cl concentrations (**Figure 14**). This trend further confirmed that indeed scavenging reactions with NH_2Cl (Reactions 8-10) decreased the radical yields.
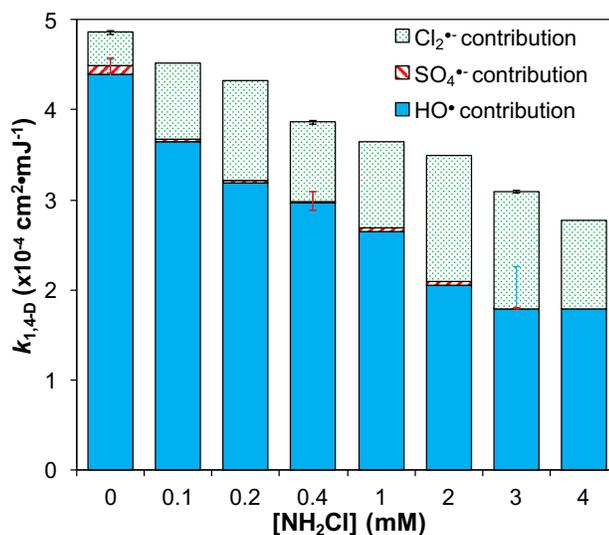
Figure 14. Effect of NH_2Cl dosage on 1,4-dioxane degradation by $UV/S_2O_8^{2-}$ and NH_2Cl at a fixed chloride concentration. $[S_2O_8^{2-}]$=2 mM, $[NH_2Cl]$=0-4 mM, $[Cl^-]$=4 mM, [1,4-dioxane]=0.25 mM, [benzoic acid]=10 μM, [nitrobenzene]=20 μM, pH=5.8, UV dose = 2760 mJ cm^{-2}.

3.3.3 Products from photolysis of $S_2O_8^{2-}$ and NH_2Cl

The major products of NH_2Cl photolysis were NH_4^+, nitrate, gaseous nitrogen and organic nitrogen (**Figure 15**). NH_4^+ production mainly resulted from the oxidation of NH_2Cl by $NH_2^\bullet$ (Reaction 11) and and the eventual oxidation to form gaseous nitrogen (Reaction 12). $NHCl^\bullet$ formed via $HO^\bullet$, $Cl^\bullet$, $SO_4^{\bullet-}$ and $Cl_2^{\bullet-}$ reacting with NH_2Cl (Reactions 8-10). $NHCl^\bullet$ can also combine to produce N_2 gas and Cl^- (Reaction 13). A small amount of NO_3^- was produced throughout the experiment, possibly due to the reaction between NH_2Cl and nitrite or H_2O.[26,46] Organic nitrogen was likely formed through the interaction of $NH_2^\bullet$ and $NHCl^\bullet$ with 1,4-D, benzoate, nitrobenzene and their degradation products. However, differentiating the organic nitrogen products was not the aim of this study, further investigation maybe required to examine the mechanism of organic nitrogen formation.
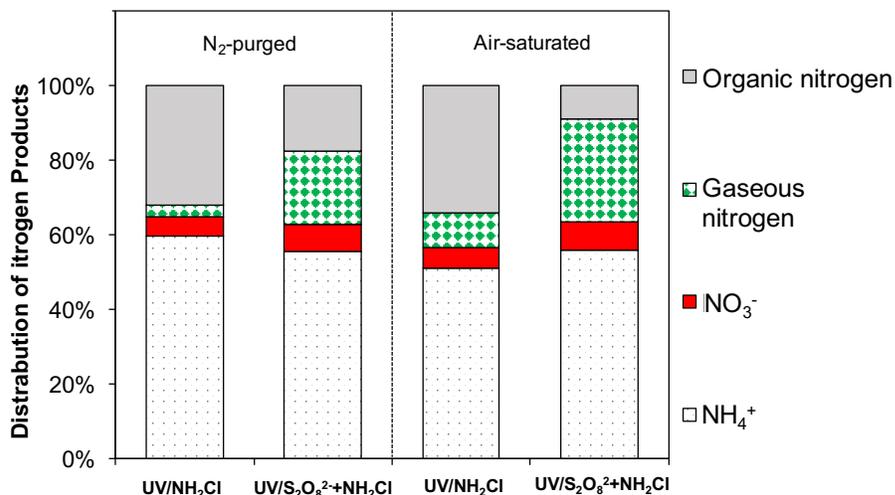
Figure 15. Impact of persulfate dosage and oxygen on NH_2Cl product distribution. $[S_2O_8^{2-}]$=0-2 mM, $[NH_2Cl]$=2 mM, [1,4-dioxane]= 250 μM, [benzoic acid]=10 μM, [nitrobenz ene]=20 μM, pH= 5.8, UV dose = 2760 mJ·cm^{-2}.

In the absence of $S_2O_8^{2-}$, approximately 55% of NH_2Cl was converted to NH_4^+, 30% to organic nitrogen, 3% to gaseous nitrogen and 5% to nitrate, respectively (**Figure 15**). In contrast, in the presence of $S_2O_8^{2-}$, NH_2Cl photolysis generated more gaseous nitrogen, but less organic nitrogen species. $SO_4^{\bullet-}$ directly oxidizes NH_2Cl (Reaction 9), yielding more N_2 (Reaction 13). This is consistent with the observation that gaseous nitrogen formation almost doubled with the inclusion of $S_2O_8^{2-}$ (**Figure 15**). O_2 reacts with NH_4^+ forming intermediate products including hydroxylamine (NH_2OH), nitrous acid (HNO_2), nitric oxide (NO) and nitroxyl (HNO), which are further oxidized to N_2.[47] The results suggest that O_2 and $S_2O_8^{2-}$ aid in the production of more highly oxidized nitrogen specieswhile SO_4^{2-}, with a 2:1 stoichiometry, was the only sulfur species observed from $S_2O_8^{2-}$ photolysis (**Figure 16**).
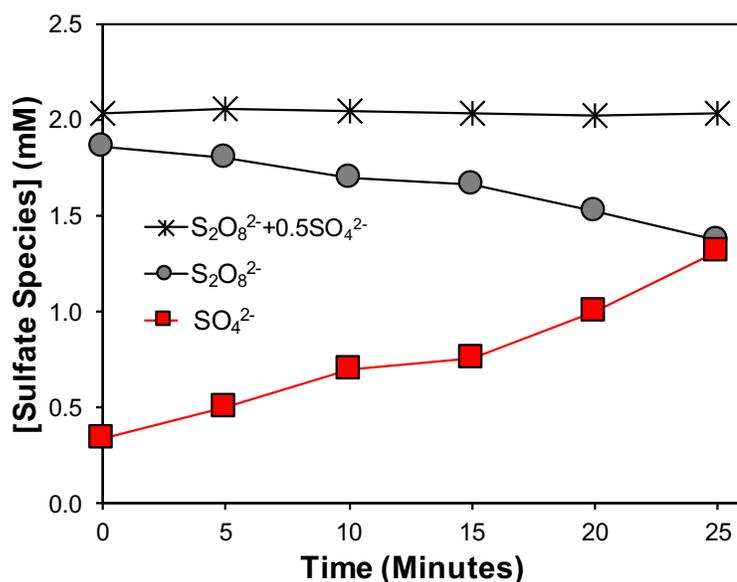
Figure 16 Persulfate photolysis products. $[S_2O_8^{2-}]=2$ mM, [1,4-dioxane]= 0.25 mM, [benzoic acid]=10 μM, [nitrobenzene]=20 μM. UV dose = 3450 mJ cm^{-2}.

3.3.4 Impact of total oxidant dosage on 1,4-doxiane degradation

The effect of total oxidant dosage in UV/$S_2O_8^{2-}$/NH_2Cl on 1,4-D degradation was examined at two NH_2Cl-to-$S_2O_8^{2}$ molar ratios, *i.e.*, 0.1:1 and 1:1. The 0.1:1-ratio generally achieved 33 to 240% more 1,4-D removal compared to the 1:1 ratio (**Figure 17A**). $[SO_4^{\bullet-}]_{ss}$ was approximately 5 times higher at the 0.1:1 ratio (**Figure 17B**), and $[HO^{\bullet}]_{ss}$ was 70 to 300% higher when the dosage exceeded 4 mM (**Figure 17B**). At the optimal ratio of 0.1:1, when the total oxidant (*i.e.*, $S_2O_8^{2-}$ and NH_2Cl) dosage exceeded 6 mM, major scavenging by $S_2O_8^{2-}$ reduced the $[HO^{\bullet}]_{ss}$ by 15% (Reaction 14, **Figure 17B**), thus 1,4-D degradation rate also dropped by 15%. In contrast, at the NH_2Cl-to-$S_2O_8^{2-}$ ratio of 1:1, the rate exhibited a bell-shape curve with the maximal rate observed at 4 mM (**Figure 17A**). At this oxidant ratio, more $SO_4^{\bullet-}$ was transformed to $Cl_2^{\bullet-}$ which was less reactive with 1,4-D. Despite the conversion of the $Cl_2^{\bullet-}$ to $HO^{\bullet}$ (Reactions 3-7), the 1:1-ratio generally resulted in higher $[Cl_2^{\bullet-}]_{ss}$ concentration and lower $[SO_4^{\bullet-}]_{ss}$ compared to 0.1:1-ratio (**Figure 17B**). When the total dosage exceeded 6 mM, more than 60% of $HO^{\bullet}$ was scavenged by NH_2Cl (**Appendix B-5**), which resulted in a 30% decrease of $[HO^{\bullet}]_{ss}$ (**Figure 17B**). Additionally, the $[Cl_2^{\bullet-}]_{ss}$ increased by 200% and contributed significantly to 1,4-D degradation, but the overall rates still decreased.
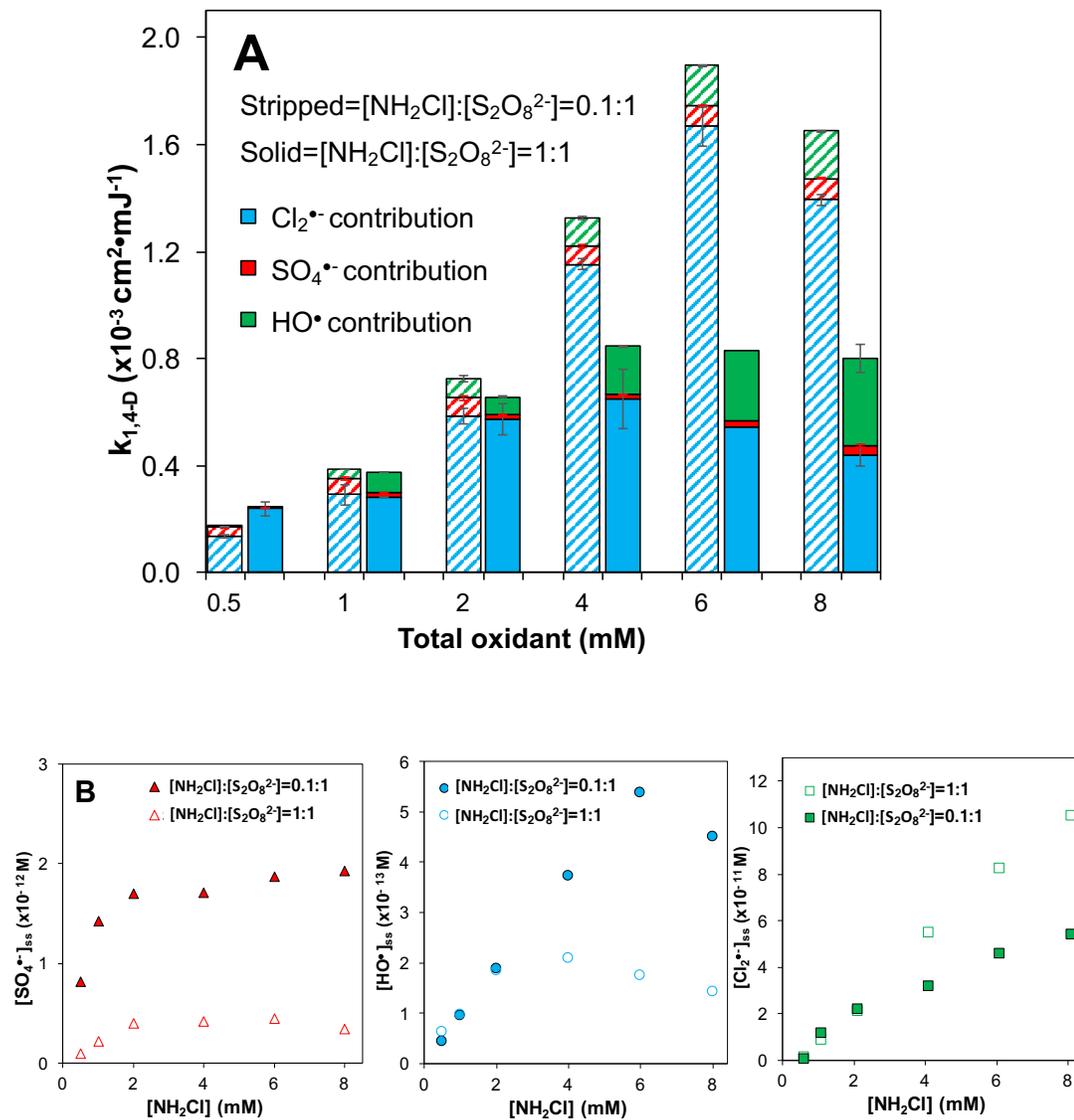
Figure 17. Impact of total oxidant dosage on the treatment of 1,4-dioxane by UV/ $S_2O_8^{2-}$ and NH_2Cl. (A) Effect of total oxiant dosage on 1,4-dioxane degradation rates; (B) Steady-state radical concentration. [1,4-dioxane]= 250 μM, [benzoic acid]=10 μM, [nitrobenzene]=20 μM, pH= 5.8. UV dose = 2760 mJ cm^{-2}.

3.3.5 Impact of chloride

An increase of chloride concentration from 0.2 to 2 mM slowed 1,4-D degradation by 28%, and preferentially reduced the contribution from $HO^\bullet$ (**Figure 18A**). There was a 40% and 80% reduction in $[HO^\bullet]_{ss}$ and $[SO_4^{\bullet-}]_{ss}$, respectively, whereas $[Cl_2^{\bullet-}]_{ss}$ increased by 240% (**Figure 18B**) that resulted from the chloride-assisted conversion of $HO^\bullet$ and $SO_4^{\bullet-}$ to $Cl_2^{\bullet-}$ (Reaction 3-4). Up to 87% of $OH^\bullet$ and 97% of $SO_4^{\bullet-}$ were scavenged by the 2 mM chloride (**Appendix B-5**); however, the $ClOH^{\bullet-}$ quickly dissociated and generated $HO^\bullet$ (Reactions 5-7). The presence of 2 mM chloride accelerated the reaction between $HO^\bullet$ and Cl^- by 200% (Reaction 15) and also accelerated the reaction of $HClOH^\bullet$ with Cl^- (Reaction 16). Approximately 9% of $HClOH^\bullet$ was scavenged by 2 mM chloride forming $Cl_2^{\bullet-}$ (**Appendix B-7**). These two reserve reactions led to elevated $[Cl_2^{\bullet-}]_{ss}$ and reduced $[HO^\bullet]_{ss}$.
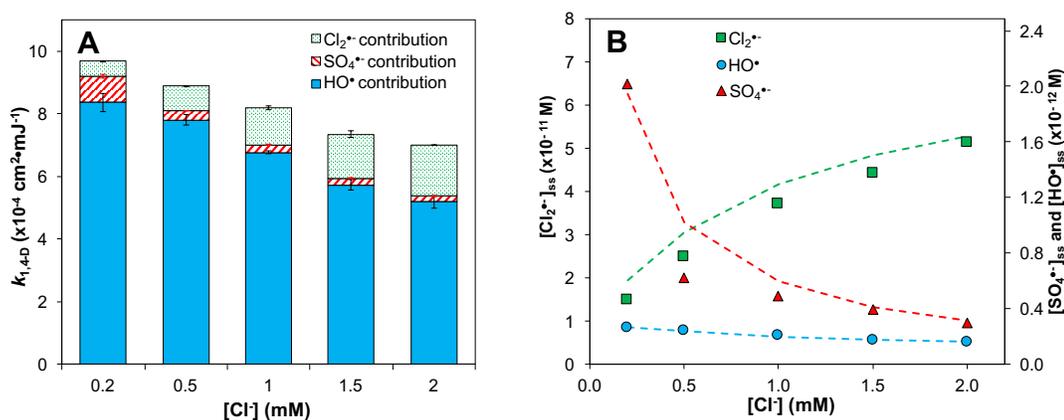
Figure 18. Impact of chloride on 1,4-dioxane treatment by $UV/S_2O_8^{2-}$ and NH_2Cl. (A) Impact of chloride on 1,4-dioxane degradation rate and radical contribution; (B) steady-state concentrations of radicals. $[S_2O_8^{2-}]$=2 mM, $[NH_2Cl]$=0.2 mM, $[Cl^-]$=0.2-2 mM, [1,4-dioxane]= 250 μM, [benzoic acid]=10 μM, [nitrobenzene]=20 μM. UV dose = 2760 mJ cm^{-2}. Dash lines represent the modeled resultes.

3.3.6 Impact of dissolved oxygen

1,4-D degradation rates in both $UV/S_2O_8^{2-}$ and $UV/S_2O_8^{2-}/NH_2Cl$ were modestly higher in air-saturated solution compared to N_2-purged solution (**Figure 19**). Dissolved O_2 is important to the oxidation of 1,4-D.[48] After reaction with radicals, 1,4-D is transformed into a dioxane radical, which reacts with O_2 to form peroxyl radical.[49] Peroxyl radical is strong and has rate constants ranging between 10^6–10^8 with various organics.[50,51] The peroxyl radical could potentially react with 1,4-D and accelerate the degradation process. Furthermore, in the presence of NH_2Cl, $NH_2^{\bullet}$ predominantly reacted with NH_2Cl instead of O_2 to produce non-reactive $NHCl^{\bullet}$ (Reaction 11 *vs*. 17).[52] Therefore, in the absence of O_2, the scavenging of NH_2Cl by $NH_2^{\bullet}$ to produce non-reactive radicals lowers the radical yield of NH_2Cl photolysis, and decreased the 1,4-D degradation rate.
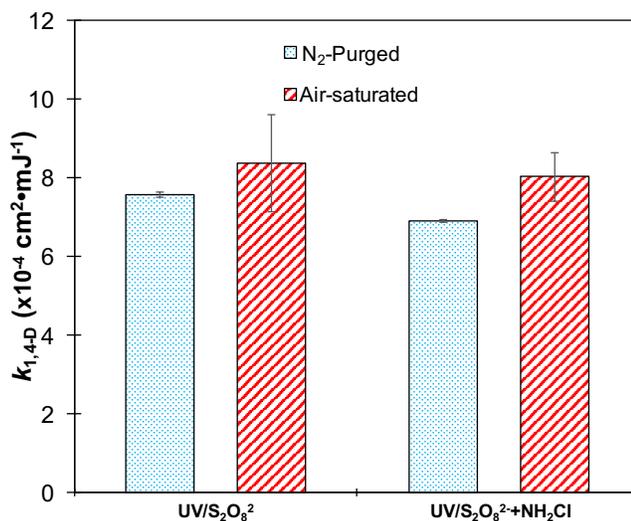
Figure 19 Impact of oxygen on 1,4-D treatability by $UV/S_2O_8^{2-}$ and NH_2Cl. (A) 1,4-dioxane degradation rates; (B) NH_2Cl photolysis rates. $[S_2O_8^{2-}]$=2 mM, $[NH_2Cl]$=2 mM, [1,4-dioxane]= 250 μM, [benzoic acid]=10 μM, [nitrobenzene]=20 μM. UV dose = 2760 mJ cm^{-2}.

3.3.7 Impact of pH on the photolysis of $S_2O_8^{2-}$ and NH_2Cl

RO permeate is typically acidic (pH=5.5-5.8) due to the application of the scale inhibitors to the feedwater. However, it is important to understand the effect of a wider range of pH on the performance of UV/AOP (**Figure 20A**). The higher pH at 8 enhanced the treatment efficiency. The increase of 1,4-D degradation kinetics from pH 5 to 8 was accompanied by an increase of $[HO^{\bullet}]_{ss}$ and $[SO_4^{\bullet-}]_{ss}$ (**Figure 20B**). The enhancement observed at higher pH (*e.g.* pH 7 and 8) was likely due to the stability of NH_2Cl. NH_2Cl disproportionates into $NHCl_2$ at pH 5 via an acid catalyzed reaction, which is further converted to trichloramine (NCl_3) under acidic conditions.[53,54] Dark control experiments showed that approximately 36% and 11% of NH_2Cl decayed into $NHCl_2$ after 20 minutes at pH 5 and 6, respectively (**Figure 21**). Furthermore, the disproportionation of NH_2Cl also generates NH_4^+ that scavenges $Cl^{\bullet}$ (Reaction 18).[26,55]
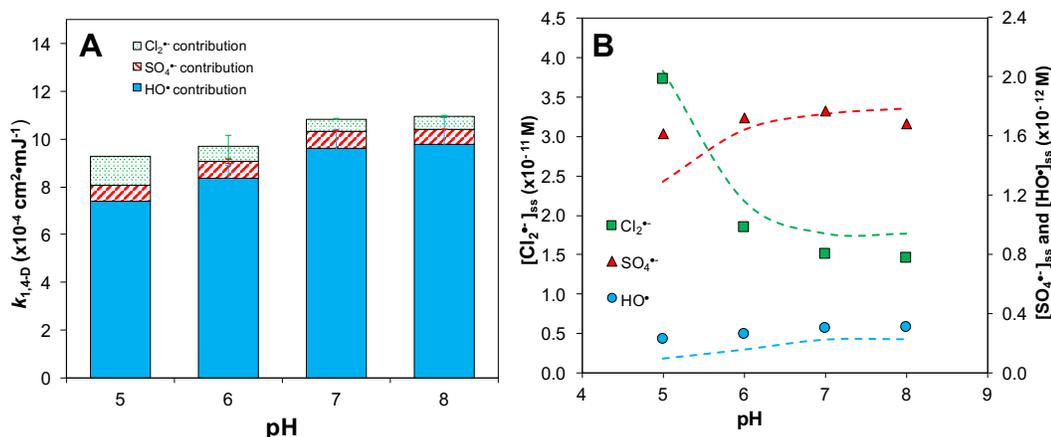
Figure 20 Impact of pH on 1,4-dioxane treatability by $UV/S_2O_8^{2-}$ and NH_2Cl. (A) Impact of pH on 1,4-dioxane degradation rate and radical contribution; (B) steady-state concentration of radicals. $[S_2O_8^{2-}]$=2 mM, $[NH_2Cl]$= 0.2 mM, [1,4-dioxane]= 250 μM, [benzoic acid]=10 μM, [nitrobenzene]=20 μM. UV dose = 2760 mJ cm^{-2}. Dash lines represent the modeled results.

To test the hypothesis that NH_4^+ could scavenge reactive chlorine species, additional $UV/S_2O_8^{2-}$ experiments were conducted by varying the NH_4^+ concentration between 0 and 6 mM with a constant chloride concentration of 4 mM. The presence of NH_4^+ decreased 1,4-D degradation by 30% (**Figure 22**). Collectively, the disproportionation of NH_2Cl and scavenging of $Cl^•$ and $Cl_2^{•-}$ by NH_4^+ (Reactions 18-19) resulted in approximately 10% decrease of photolysis rate at pH 5 compared to pH 8.
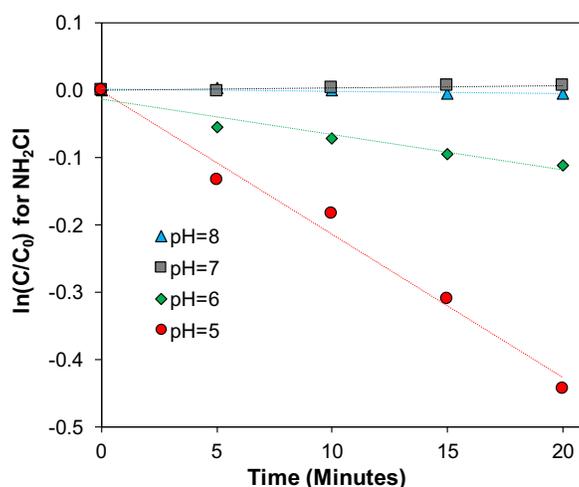
Figure 21. Effect of pH on 1,4-dioxane degradation without UV. [1,4-dioxane]= 250 µM
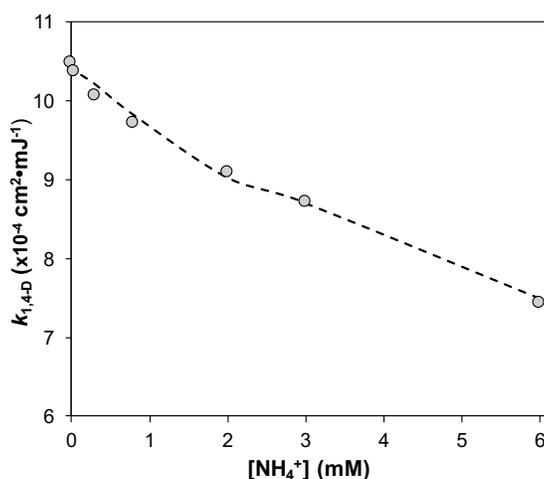
Figure 22. Effect of NH_4^+ on 1,4-dioxane degradation rates. $[S_2O_8^{2-}]$=2 mM, $[Cl^-]$=4 mM, $[NH_4^+]$=0-6 mM, [1,4-dioxane]= 0.25 mM, [benzoic acid]=10 µM, [nitrobenzene]=20 µM. pH=6, UV dose = 2760 mJ cm^{-2}. Dash line represents modeled results.

3.4 Environmental Implications

The study demonstrated the application of an alternative oxidant, $S_2O_8^{2-}$ in UV/AOP for 1,4-D removal for indirect potable reuse. The findings suggest that UV/$S_2O_8^{2-}$ is an efficient UV/AOP technology that may help the water utility to comply with ever strengthening regulations. Specifically, UV/$S_2O_8^{2-}$ can be operated efficiently in the presence of chloramine, a disinfectant that is wildly used in recycled water treatment trains. When the NH_2Cl-to-$S_2O_8^{2-}$ molar ratio is carefully controlled at 0.1:1, UV/$S_2O_8^{2-}$ performance is enhanced. However, beyond this optimal ratio, the performance is hindered because high NH_2Cl dosage has a photon filtering effect and significantly scavenges radicals, which decreases the yields of $HO^\bullet$ and $Cl_2^{\bullet-}$. In addition, UV/$S_2O_8^{2-}$ decreases the formation of undesired NH_2Cl decay products, NH_4^+ and organic nitrogen, and promoted gaseous nitrogen production. Although, the concentration of chloride is relatively low in RO permeate, the presence of chloride may slow down 1,4-D degradation through the transformation of reactive $HO^\bullet$ and $SO_4^{\bullet-}$ to less reactive $Cl_2^{\bullet-}$ that reacts with 1,4-D. This study also suggests that elevated pH could enhanced treatment efficiency. Results from this study elucidate the fundamental mechanisms of radical generation during the unique photolysis of duel oxidants, quantify the effects of inadvertent presence of NH_2Cl on the application of $S_2O_8^{2-}$ in water reuse, and assist in the development of more efficient UV/AOP technologies.

3.5 Acknowledgements

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Chapter 4

Modeling Approach for A Mechanistic Understanding of the Degradation of Trace Organic Contaminants by UV/Hydrogen Peroxide, UV/Persulfate and UV/Free Chlorine for Water Reuse

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4.1 Introduction

Water scarcity is one of the most challenging global issues. The availability of high-quality fresh water sources continues to decrease due to population growth, urbanization and climate change. [1-2] To address water scarcity, potable water reuse – a viable means to increase drinking water supplies from untraditional sources including treated wastewater – has been proposed and employed in the recent decade. [3-5] It is estimated that approximately 12 billion gallons of municipal wastewater effluent is discharged to the ocean in the U.S. everyday; this is equivalent to 27% of the total U.S. public water supply.[2] Reclamation of these effluent discharges would directly augment available drinking water resources. Currently, only approximately 10% of the effluent is reused in the U.S.[2]

Conventionally treated wastewater effluent contains a variety of trace organic contaminants including pesticides, pharmaceuticals and personal care products. [6-9] Ultraviolet-based advanced oxidation processes (UV/AOPs) have been increasingly required as part of the treatment train process to remove these contaminants. During UV treatment, an oxidant is photolyzed to generate short-lived radicals. Hydrogen peroxide (H_2O_2) is the most widely used oxidant to generate reactive hydroxyl radicals ($HO^\bullet$) (Reaction 1):

$$H_2O_2 \xrightarrow{h\nu} 2HO^\bullet \qquad\qquad (R1)$$

Recently, UV/persulfate ($S_2O_8^{2-}$) has been proposed and sulfate radicals ($SO_4^{\bullet-}$) are generated as the radical initiation step (Reaction 2):

$$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^{\bullet-} \tag{R2}$$

$SO_4^{\bullet-}$ has a similar oxidizing power ($E^0_{SO_4^{\bullet-}/SO_4^{2-}} = 2.5–3.1$ V) compared to $HO^\bullet$ ($E^0_{HO^\bullet/H_2O} = 1.9–2.7$ V), but possesses higher reaction rate constants with electron-rich contaminants.[10] This feature has made $SO_4^{\bullet-}$ an efficient oxidant for groundwater remediation.[11-12] Furthermore, $S_2O_8^{2-}$ has a 40% higher quantum yield ($\Phi=0.7$, Reaction 2)[13] compared to H_2O_2 under UV irradiation at 254 nm ($\Phi=0.5$, Reaction 1),[14] thus generating more radicals than H_2O_2.

In addition, UV/chlorine (denoted as UV/HOCl) has become more popular in recent years.[15-18] Chlorine is the most commonly used disinfectant and can be combined with a UV source as an AOP system.[19-20] HOCl in solution exists as hypochlorous acid (HOCl) or hypochlorite ion (OCl⁻) with a pK_a of 7.6. Photolysis of chlorine can simultaneously produce $HO^\bullet$ and chlorine atom ($Cl^\bullet$):

$$HOCl \xrightarrow{h\nu} HO^\bullet + Cl^\bullet \tag{R3}$$

$$OCl^- \xrightarrow{h\nu} O^{\bullet-} + Cl^\bullet \tag{R4}$$

The redox potential of $Cl^\bullet$ is comparable to that of $HO^\bullet$ and $SO_4^{\bullet-}$ ($E^0_{Cl^\bullet/Cl^-} = 2.41$ V).[21] $O^{\bullet-}$ can further react with H_2O to generate $HO^\bullet$.[22] The quantum yield of HOCl is 40% higher than that of OCl⁻ ($\Phi=0.7$ in Reaction 3 *vs.* $\Phi=0.5$ in Reaction 4). [20,23]

A better understanding of the detailed mechanisms of radical distribution and transformation in UV/AOPs associated with contaminant removal are needed. Hundreds of radical reactions can impact the reaction pathways. While it is impossible to directly measure each radical under different chemical conditions, the application of a kinetic model can provide valuable insight into the radical pathways and predict the performance of AOPs. Prior studies have developed a variety of models including the steady-state radical model, [24-31] AdOx model, [32] probe model [33] and computational fluid dynamic model. [34-36] Although prior models had good estimations, there lacks a comprehensive model that can predict different UV/AOP performances in chemical conditions relevant to potable water reuse.

Ultimately, the efficiency of UV/AOPs on contaminant removal depends on the yields of reactive radicals (*e.g.*, HO$^{\bullet}$, SO$_4^{\bullet-}$, and Cl$^{\bullet}$), their reactivities with specific contaminants, and the solution chemical conditions that can impact the distribution and transformation of radicals. Solution chemical conditions including pH, bicarbonate, chloride and bromide can transform HO$^{\bullet}$, SO$_4^{\bullet-}$, and Cl$^{\bullet}$ into secondary radicals such as carbonate radical (CO$_3^{\bullet-}$) and reactive halide radicals (*e.g.*, Cl$_2^{\bullet-}$, ClOH$^{\bullet-}$ and Br$^{\bullet}$). These secondary radicals can exhibit distinct reactivities with trace organic contaminants compared to primary radicals, and consequently impact the rate of contaminant degradation. [22,37]

The objective of this work was to develop a kinetic model in order to investigate radical generation mechanisms in three UV/AOP systems, *i.e.*, UV/H$_2$O$_2$, UV/S$_2$O$_8^{2-}$ and

UV/HOCl. The kinetic model was further employed to predict the degradation of trace contaminants in complex chemical conditions relevant to potable water reuse. Selective experiments were also conducted and together with the validated model to elucidate the impact of individual chemical parameters including pH, chloride and organic carbon on UV/AOP performance for water reuse. The versatile kinetic model provides a useful tool to compare the performances of different UV/AOP systems for treating a variety of contaminants of concern in a complex environment. It ultimately provides water utilities with a better direction for the design of UV/AOPs based on varying water chemical conditions.
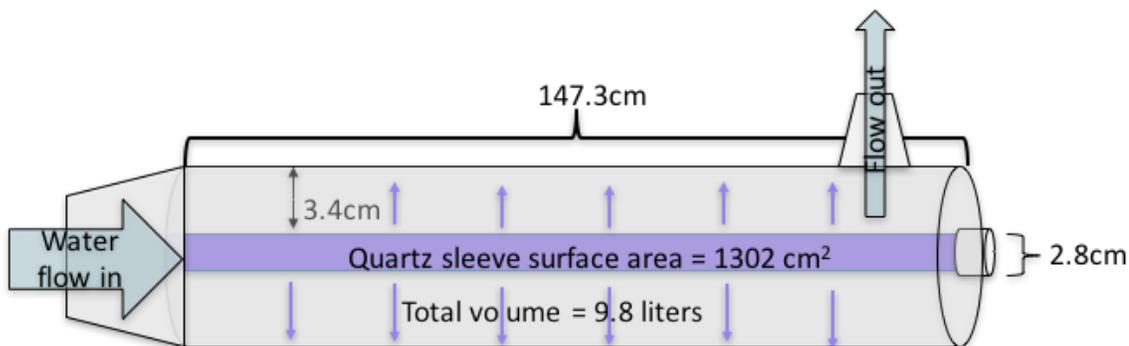
Scheme 8 A diagram of the single UV flow-through reactor (Trojan Technologies, London, ON). The kinetics modeling is based on the configuration of this reactor.

4.2 Materials and Methods

4.2.1 Modeling of radical reactions in UV/AOPs

The photolysis rate (r_p) of H_2O_2, $S_2O_8^{2-}$ and HOCl with monochromatic low-pressure high-output (LPHO) mercury vapor UV lamp ($\lambda=254$nm) was calculated as:

$$r_p = -2 \times \Phi \times I_0 \times f_{oxidant} \times f_{solution} \tag{E1}$$

where Φ is the primary quantum yield of the oxidant (mole/Einstein), I_0 is volume-normalized surface irradiance from the UV reactor (Einsteins·L^{-1}·s^{-1}) that was calculated as 1.27×10^{-5} Einstein·L^{-1}·s^{-1} based on a single UV flow-through reactor (Trojan Technologies, London, ON) (Detailed information is provided in **Appendix C-1** and **Scheme 8**), $f_{oxidant}$ is the fraction of incident light absorbed by the oxidant and $f_{solution}$ is the fraction absorbed by the total solution.

$$f_{oxidant} = \frac{\varepsilon_p c_p}{\sum \varepsilon_i c_i} \tag{E2}$$

$$f_{solution} = 1 - 10^{-(\alpha + \sum \varepsilon_i c_i)l} \tag{E3}$$

α is the absorption coefficient of the solution at the wavelength of 254 nm, ε_p and c_p are the molar extinction coefficient and the concentration of the oxidant, respectively (M^{-1}·cm^{-1} and M), ε_i and c_i are the molar extinction coefficient and concentration of solution constituents, including natural organic matter (NOM) and contaminants, and l is the effective light path of the reactor (cm). A total of 221 elemental reactions were incorporated in the model (**Appendix C-2**). Major radical reactions are listed in **Table 8**. The kinetic model was built on the platform of Kintecus 4.55 software.[38]

Table 8 Major radical chain reactions that impact the distribution of radicals in UV/AOPs.

No.	Reaction	Rate Constant	Reference
1	$H_2O_2 \xrightarrow{h\nu} 2HO^{\cdot}$	1.0×10^{-3} s^{-1}	This study
2	$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^{\cdot-}$	1.4×10^{-3} s^{-1}	This study
3	$HOCl \xrightarrow{h\nu} HO^{\cdot} + Cl^{\cdot}$	3.9×10^{-3} s^{-1}	This study
4	$OCl^- \xrightarrow{h\nu} O^{\cdot-} + Cl^{\cdot}$	3.2×10^{-3} s^{-1}	This study
5	$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^- + HO^{\cdot}$	6.6×10^2 s^{-1}	[39]
6	$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\cdot}$	3.0×10^8 M^{-1}s^{-1}	[40]
7	$Cl^{\cdot} + H_2O \rightarrow ClOH^{\cdot-} + H^+$	2.5×10^5 s^{-1}	[21]
8	$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot-}$	8.5×10^9 M^{-1}s^{-1}	[41]
9	$Cl_2^{\cdot-} + OH^- \rightarrow Cl^- + ClOH^{\cdot-}$	4.5×10^7 M^{-1}s^{-1}	[42]
10	$ClOH^{\cdot-} \rightarrow HO^{\cdot} + Cl^-$	6.1×10^9 s^{-1}	[21]
11	$HOCl + HO^{\cdot} \rightarrow ClO^{\cdot} + H_2O$	2.0×10^9 M^{-1}s^{-1}	[43]
12	$HCO_3^- + HO^{\cdot} \rightarrow CO_3^{\cdot-} + H_2O$	8.6×10^6 M^{-1}s^{-1}	[22]
13	$HCO_3^- + SO_4^{\cdot-} \rightarrow CO_3^{\cdot-} + SO_4^{2-} + H^+$	9.1×10^6 M^{-1}s^{-1}	[44]
14	$HCO_3^- + Cl^{\cdot} \rightarrow CO_3^{\cdot-} + Cl^- + H^+$	2.2×10^8 M^{-1}s^{-1}	[78]
15	$HO^{\cdot} + Br^- \rightarrow BrOH^{\cdot-}$	1.1×10^{10} M^{-1}s^{-1}	[43]
16	$SO_4^{\cdot-} + Br^- \rightarrow Br^{\cdot} + SO_4^{2-}$	3.5×10^9 M^{-1}s^{-1}	[78]
17	$Cl^{\cdot} + Br^- \leftrightarrow ClBr^{\cdot-}$	1.2×10^{10} M^{-1}s^{-1}	[43]
18	$ClBr^{\cdot-} \rightarrow Cl^- + Br^{\cdot}$	6.1×10^4 s^{-1}	[45]
19	$BrOH^{\cdot-} \rightarrow HO^{\cdot} + Br^-$	3.3×10^7 s^{-1}	[46]
20	$HO^{\cdot} + Cl^- \rightarrow ClOH^{\cdot-}$	4.3×10^9 M^{-1}s^{-1}	[21]
21	$Cl_2^{\cdot-} + HCO_3^- \rightarrow CO_3^{\cdot-} + 2Cl^- + H^+$	8.0×10^7 M^{-1}s^{-1}	[43]
22	$S_2O_8^{2-} + Cl^{\cdot} \rightarrow S_2O_8^{\cdot-} + Cl^-$	8.8×10^6 M^{-1}s^{-1}	[47]

4.2.2 Modeling of contaminant removal

Six representative trace organic contaminants were selected in this study due to their wide presence in wastewater effluent (**Table 9**). 1,4-dioxane is a widely used industrial solvent[48] with a drinking water notification level of 1 μg/L.[49] Phenol is a typical transformation product from aromatic contaminants.[50-51] 17β-estradiol is a natural estrogenic hormone.[52] Anilines, sulfamethoxazole and carbamazepine are frequently prescribed pharmaceuticals found in wastewater.[53-55]

Table 9 Compound structure and their quantum yield, extinction coefficient and direct photolysis rate

Compound Name	Structure	Direct Photolysis Rate (s^{-1})	Reference
17b-estradiol		Negligible	56
1,4-dioxane		Negligible	57
Phenol		2.1×10^{-4}*	58
Aniline		Negligible	59
Carbamazepine		4.6×10^{-4}*	60
Sulfamethoxazole		1.1×10^{-4}*	61
Natural Organic Matter (NOM)		1.8×10^{-10}*	62
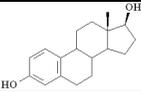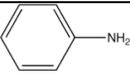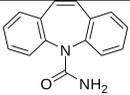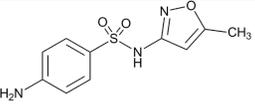
Based on the kinetic model, the overall degradation rate of each contaminant (k) was a summation of direct photolysis rate (k_d), indirect photolysis rate (k_i) and the direct chemical reaction rate with an oxidant (k_o):

$$k = k_d + k_i + k_o \tag{E4}$$

k_d is the direct photolysis rate for the test chemicals exposed to UV radiation based on equations E1–E3. k_i is controlled by reactions between the contaminant and each individual reactive radical:

$$k_i = \sum k_R \cdot [R^\cdot]_{ss} = k_{HO^\cdot}[HO^\cdot]_{ss} + k_{SO_4^{\cdot-}}[SO_4^{\cdot-}]_{ss} + k_{Cl^\cdot}[Cl^\cdot]_{ss} + k_{Cl_2^{\cdot-}}[Cl_2^{\cdot-}]_{ss} +$$

$$k_{CO_3^{\cdot-}}[CO_3^{\cdot-}]_{ss} + k_{Br^\cdot}[Br^\cdot]_{ss} + k_{Br_2^{\cdot-}}[Br_2^{\cdot-}]_{ss} + k_{BrCl^{\cdot-}}[BrCl^{\cdot-}]_{ss} +$$

$$k_{BrOH^{\cdot-}}[BrOH^{\cdot-}]_{ss} + k_{ClOH^{\cdot-}}[ClOH^{\cdot-}]_{ss} \tag{E5}$$

$[R^\cdot]_{ss}$ is the steady-state concentration of each individual radical $R^\cdot$. It is determined by the photolysis rate of an oxidant (r_p) and the consumption rate of scavenging reactions:

$$[R^\cdot]_{ss} = -\frac{r_p}{\sum k_{R^\cdot,s}[scavenger]_i} \tag{E6}$$

$[scavenger]_i$ is the concentration of scavengers, $e.g.$, Cl⁻, HCO₃⁻, Br⁻, and NOM. k_R is the second-order rate constant of a reaction between a contaminant and $R^\cdot$ (**Table 10**). $k_{R,s}$ is the rate constant of a reaction between $R^\cdot$ and a scavenger. These values were obtained from radiolysis literature or estimated based on prior literature.[63] When the rate constants were estimated (**Table 10**), the reaction rates were averaged by using the highest possible rate constants and the lowest possible rate constants, and the uncertainty was represented

as error bars. Although the transformation products of contaminants can react with radicals, those reactions were not considered in the kinetic model due to their lower concentrations and resultant smaller branching ratios in competitive kinetics.

Table 10 Rate constants of reactions between selected organic contaminants and radicals

Contaminant	$HO^{\cdot}$ ($M^{-1}s^{-1}$)	$SO_4^{\cdot-}$ ($M^{-1} s^{-1}$)	$Cl^{\cdot}$ ($M^{-1} s^{-1}$)	$Cl_2^{\cdot-}$ ($M^{-1} s^{-1}$)	$ClOH^{\cdot-}$ ($M^{-1} s^{-1}$)
17β-estradiol	1.4×10^{10}	1.2×10^{9}	$1.3-1.6\times10^{10}$*	$2.0-2.4\times10^{7}$ *	$2.0-2.4\times10^{7}$ *
Phenol	6.6×10^{9}	8.8×10^{9}	2.5×10^{10}	3.2×10^{8}	$5.0-6.0\times10^{6}$ *
Aniline	8.6×10^{9}	9.0×10^{9}	4.0×10^{10}	$3.4-4.1\times10^{8}$	$3.4-4.1\times10^{8}$
Sulfamethoxazole	4.9×10^{9}	1.3×10^{10}	$4.4\sim5.4\times10^{9}$*	$4.0-4.8\times10^{8}$ *	$4.0-4.8\times10^{8}$ *
1,4-dioxane	3.1×10^{9}	4.1×10^{7}	$2.8-3.4\times10^{9}$*	$1.0\times10^{5-6}$*	$1.0\times10^{5-6}$*
Carbamazepine	2.1×10^{9}	8.8×10^{9}	$1.8-3.7\times10^{9}$*	$2.1-2.5\times10^{6}$ *	$2.1-2.5\times10^{6}$ *

Contaminant	$CO_3^{\cdot-}$ ($M^{-1} s^{-1}$)	$Br^{\cdot}$ ($M^{-1} s^{-1}$)	$Br_2^{\cdot-}$ ($M^{-1} s^{-1}$)	$ClBr^{\cdot-}$ ($M^{-1} s^{-1}$)
17β-estradiol	2.2×10^{7}	$1.3-1.6\times10^{9}$*	$2.0-2.4\times10^{7}$ *	$2.0-2.4\times10^{7}$ *
Phenol	4.9×10^{6}	$5.9-7.3\times10^{8}$ *	6.0×10^{6}	$5.0-6.0\times10^{6}$ *
Aniline	5.4×10^{8}	$7.7-9.5\times10^{8}$ *	2.1×10^{8}	$3.4-4.1\times10^{8}$
Sulfamethoxazole	4.4×10^{8}	$4.4-5.4\times10^{8}$*	$4.0-4.8\times10^{8}$ *	$4.0-4.8\times10^{8}$ *
1,4-dioxane	$1.0\times10^{2-6}$*	1.2×10^{6}	$1.0\times10^{5-6}$*	$1.0\times10^{5-6}$*
Carbamazepine	2.3×10^{6}	$7.9-9.7\times10^{9}$*	$2.1-2.5\times10^{6}$ *	$2.1-2.5\times10^{6}$ *

* Rates constants are estimated base on the known reactivity of radicals with other similar compounds

k_o was only considered important during chlorine oxidation of aniline and carbamazepine in UV/HOCl.[64] In those cases, k_o was calculated as k_{HOCl}[HOCl], where k_{HOCl} is the second-order rate constant between the contaminant and chlorine, and [HOCl] is the concentration of hypochlorous acid. Rate in Eq. 4 are normalized by UV irradiance and expressed in units of $cm^2 \cdot mW^{-1} \cdot s^{-1}$. Reactions with OCl⁻ were not considered because OCl⁻ was not the major free chlorine species at pH 5.8 (pk_a=7.53).

In water reuse UV/AOP is typically applied after reverse osmosis (RO) membrane treatment. Therefore, the solution chemistry of UV/AOP is characteristic of RO permeate. Three important water chemical parameters associated with RO permeate were examined: pH, chloride, and carbonate. Trace levels of bromide and NOM were also present (**Table 11**). The ranges of concentrations were selected based on a water reuse facility in Southern California and would be applicable to UV/AOP coupled with RO in typical treatment train step utilized for potable water reuse. Concentrations of trace organic contaminants in wastewater effluent are in the range of nM and μM.[50, 65-68] In this study the initial concentrations of contaminants were set at 50 nM.[69]

Table 11 Chemical compositions for selected water matrix.

Chemical Parameter	RO Permeate[*]	Typical Range	Unit
Chloride	80	10 – 280	μM
Inorganic Carbon	200	40 – 400	μM
Bromide	0.2	0 – 2.0	μM
TOC	0.15	0.15	mg C/L
pH	5.8	5 – 7	--
Trace Organic Contaminant	50	50	nM

[*]RO permeate water quality chosen in this study, based on data from wastewater reuse treatment facility in Southern California. Typical nitrate (NO_3^-) concentration in RO permeate ranges from 10 to 20 μM. The absorption coefficient at 254nm and the quantum yield for $HO^\bullet$ are low,[70-71] therefore, the contribution of NO_3^- is not considered in the model.

4.2.3 Experimental investigation of UV/AOP performance

All chemicals used were ACS reagent grade and used without further purification. 1,4-dioxane degradation by UV/H_2O_2, UV/$S_2O_8^{2-}$ and UV/HOCl was conducted using a carousel photochemical reactor (ACE Glass Inc.) equipped with a 6-W monochromatic UV lamp with a wavelength of 254 nm. A solution containing 2 mM of oxidant (H_2O_2, $S_2O_8^{2-}$, or HOCl) and 250 µM 1,4-dioxane in synthetic RO permeate (**Table 11**) was prepared. A combination of 10 µM benzoic acid, 20 µM nitrobenzene and 20 µM N,N-dimethylaniline was added as probe compounds for $HO^•$, $SO_4^{•-}$, $Cl^•$, $Cl_2^{•-}$ and $CO_3^{•-}$. (detailed calculation on steady-state concentrations of radicals was described in **Appendix C-3**). To start a UV experiment, the reaction solution was transferred to multiple 8-mL quartz tubes without headspace and placed on the UV carousel reactor. At targeted time intervals, samples from sacrificial quartz tubes were withdrawn from the reactor. The concentration of the oxidant was measured using standard colorimetric method.[72-73] The samples were further quenched with methanol and analyzed for concentrations of trace organic contaminants and probe compounds using an Agilent-1200 liquid chromatography system equipped with a diode array detector and a Zorbax Eclipse SB-C18 column (4.6×150 mm, 5-µm particle size).

4.3 Results and Discussion

4.3.1 Degradation of contaminants in RO permeate by three UV/AOPs

The modeling predicted UV photolysis rates of oxidants in the order of HOCl > $S_2O_8^{2-}$ > H_2O_2 (Reactions 1–4 in **Table 8**, all reactions henceforth refer to **Table 8**). The

photolysis rates of HOCl and $S_2O_8^{2-}$ were approximately 300% and 40% higher than that of H_2O_2, respectively (**Figure 23**). The degradation rates (k) of the selected organic contaminants varied by more than one order of magnitude among UV/H_2O_2, UV/$S_2O_8^{2-}$, and UV/HOCl (**Figure 24**).
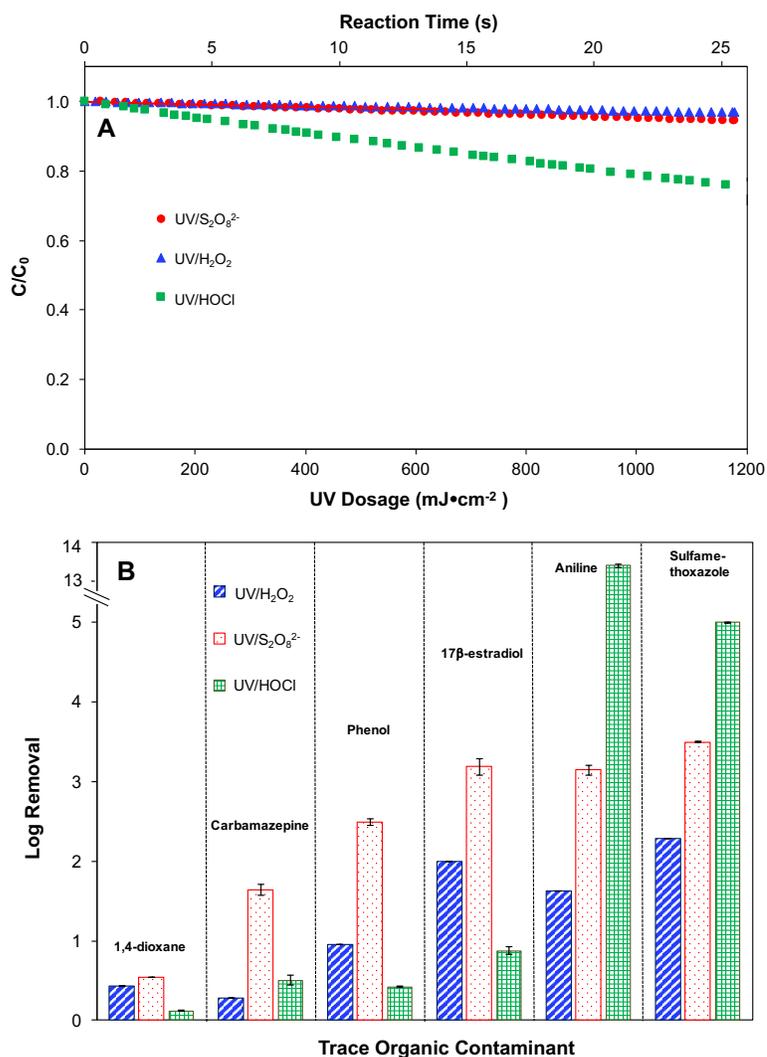
**Figure 23** Comparison of UV/H_2O_2, UV/$S_2O_8^{2-}$ and UV/HOCl treatment based on the kinetic model. (A) Consumption of H_2O_2, $S_2O_8^{2-}$ and HOCl by UV irradiance. (B) Log removal of organic contaminants. [Oxidant]=88 μM, [contaminant]=50 nM, [Cl⁻]=80 μM, [inorganic carbon]=200 μM, [Br⁻]=0.2 μM, TOC=0.15 mg C/L, pH=8, UV irradiance= 45.3 mW/cm², UV dosage=1178 mJ/cm² in 26 seconds.

In UV/H$_2$O$_2$, the irradiance-normalized rates ranged from 5.6×10^{-4} to 4.5×10^{-3} cm^2·mW^{-1}·s^{-1}. HO$^\bullet$ contributed the most to the contaminant degradation with the exception that CO$_3^{\bullet-}$ was important for aniline and sulfamethoxazole degradation. Direct photolysis was only important for sulfamethoxazole, which was also reported previously.[74]

In UV/S$_2$O$_8^{2-}$, the degradation rates ranged from 1.1×10^{-3} to 6.8×10^{-3} cm^2·mW^{-1}·s^{-1}, *i.e.*, 24%–470% higher than those in UV/H$_2$O$_2$. Both HO$^\bullet$ and SO$_4^{\bullet-}$ are important for contaminant degradation. The contribution by Br$^\bullet$ was also significant for carbamazepine, phenol, 17β-estradiol and aniline.

In UV/HOCl, the degradation rates ranged from 2.3×10^{-4} to 2.6×10^{-2} cm^2·mW^{-1}·s^{-1}, *i.e.*, 56%–73% lower than those in UV/H$_2$O$_2$ (**Figure 24**), mainly due to a lower yield of HO$^\bullet$ in RO permeate chemical conditions in UV/HOCl. The exceptions were for carbamazepine, aniline and sulfamethoxazole wherein the contribution by Br$^\bullet$, CO$_3^{\bullet-}$, and HOCl chemical oxidation were also important. The log removal varied from 0.1 to 13.5 with a UV dosage of 1178 mJ/cm^2 (**Figure 23B**). Generally, higher log removal could be achieved in UV/S$_2$O$_8^{2-}$, followed by UV/H$_2$O$_2$, and then UV/HOCl except for aniline and sulfamethoxazole, which achieved better log removal in UV/HOCl.
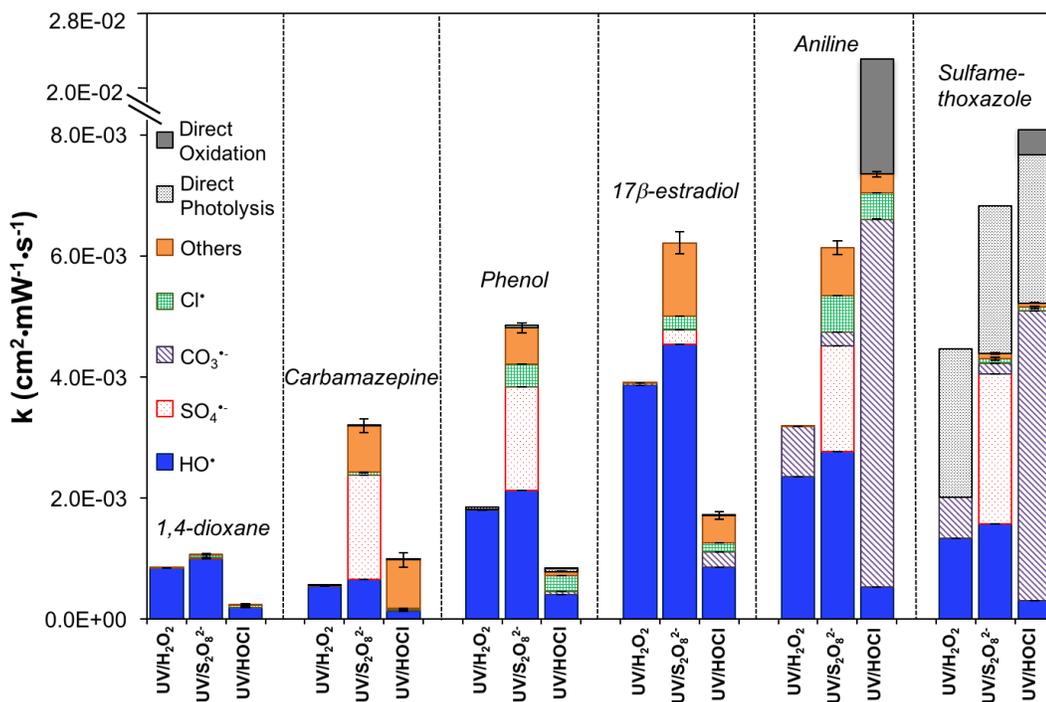
Figure 24 The comparison of three UV/AOP systems on the degradation of six selected trace organic contaminants based on the kinetic model. [Oxidant]=88 μM, [contaminant]=50 nM, [Cl⁻] =80 μM, [inorganic carbon] = 0.2 mM, [Br⁻]=0.2 μM, TOC=0.15 mg C/L, pH=5.8, UV irradiance=45 mW/cm².

4.3.2 Mechanisms of the degradations of contaminants in UV/AOPs

Scheme 9 illustrates major reaction pathways of radical generation and distribution in the presence of Cl^-, HCO_3^-, and Br^-. Although the three UV/AOPs exhibited different photolysis rates at the radical initiation steps, they share similar radical transformation pathways.

Scheme 9 Generation and transformation of radicals from UV/H_2O_2, $UV/S_2O_8^{2-}$ and $UV/HOCl$ in the presence of chloride and inorganic carbon. All referred reactions are listed in **Table 8**.

4.3.2.1 Contribution of HO•

HO• is one of the most reactive radicals. It reacts non-selectively with organics at the near diffusion-limited rate constants of approximately 10^{10} $M^{-1}s^{-1}$.[63,75] It reacted with the six select contaminants with rate constants between 2.1×10^9 and 1.4×10^{10} $M^{-1}s^{-1}$ (**Table 10**). In UV/H$_2$O$_2$, HO• was the major radical ($[HO•]_{ss}=1.2\times10^{-11}$ M, **Table 12**) and contributed significantly to contaminant degradation (**Figure 24**). More HO• was generated in UV/S$_2$O$_8^{2-}$ compared to UV/H$_2$O$_2$ with a steady-state concentration 65% higher than that of SO$_4$•$^-$ (**Table 12**). The higher radical yield in UV/S$_2$O$_8^{2-}$ was mainly due to the higher photolysis rate of S$_2$O$_8^{2-}$ compared to H$_2$O$_2$ (Reactions 1–2,**Table 8**). The contribution to contaminant degradation by HO• was 20% higher in UV/S$_2$O$_8^{2-}$ than that in UV/H$_2$O$_2$ (**Figure 24**). HO• was generated from SO$_4$•$^-$ via two pathways: hydrolysis of SO$_4$•$^-$ (Reaction 5) and Cl$^-$ scavenging effects on SO$_4$•$^-$ to produce Cl• (Reactions 6–10). In contrast, the contribution of HO• was significantly less in UV/HOCl (**Figure 24**). This was mainly due to a strong scavenging effect of HOCl on HO• (Reaction 11).

4.3.2.2 Contribution of SO$_4$•$^-$

SO$_4$•$^-$ generated in UV/S$_2$O$_8^{2-}$ is reactive with compounds containing electron-donating functional groups including olefinic bonds, amine and hydroxyl groups.[76-78] Therefore, carbamazepine, phenol, aniline and sulfamethoxazole were reactive with SO$_4$•$^-$ ($k_{SO4•-}\approx k_{HO•}\approx10^9$ $M^{-1}s^{-1}$), whereas 1,4-dioxane and 17β-estradiol exhibited much slower reactivity with SO$_4$•$^-$ than with HO• (*i.e.,* $k_{SO4•-} \leq 10\%\times k_{HO•}$). As a result, these four

contaminants exhibited enhanced degradation rates in $UV/S_2O_8^{2-}$ compared to UV/H_2O_2 (**Figure 24**).

4.3.2.3 Contribution of $CO_3^{\bullet-}$

$CO_3^{\bullet-}$ was a major radical that formed in all three UV/AOPs (**Table 12**). $CO_3^{\bullet-}$ was generated via the transformation of $HO^{\bullet}$, $SO_4^{\bullet-}$ and $Cl^{\bullet}$ in the presence of bicarbonate (Reactions 12–14). The effect was strongest in UV/HOCl, because HCO_3^- reacts with $Cl^{\bullet}$ 25 times faster than reacting with $HO^{\bullet}$ or $SO_4^{\bullet-}$. However, $CO_3^{\bullet-}$ reacts selectively towards compounds with amine and sulfur groups. [79,80] Amine-containing aniline and sulfamethoxazole react faster with $CO_3^{\bullet-}$ ($k_{CO_3\bullet-}$ >10^8 $M^{-1}s^{-1}$, **Table 10**), and their degradation was significantly enhanced in UV/HOCl in addition to direct photolysis and direct oxidation by HOCl (**Figure 24**).

4.3.2.4 Contribution of reactive halide radicals

Two groups of halide radicals were generated by UV/AOP in the presence of Cl^- and Br^-: reactive chlorine species (RCS) and reactive bromine species (RBS). RCS including $Cl^{\bullet}$, $Cl_2^{\bullet-}$ and $ClOH^{\bullet-}$ can react with contaminants with rate constants as high as 10^9 $M^{-1}s^{-1}$ (**Table 10**), but their steady-state concentrations were orders of magnitude lower than those of $HO^{\bullet}$, $SO_4^{\bullet-}$, and $CO_3^{\bullet-}$ (**Table 12**). As a result, contributions from RCS to contaminant degradation were limited. RBS include $Br^{\bullet}$, $Br_2^{\bullet-}$, $BrOH^{\bullet-}$, and $ClBr^{\bullet-}$, but only $Br^{\bullet}$ is considered reactive with contaminants.[63] Br^- reacted with $HO^{\bullet}$, $SO_4^{\bullet-}$, and $Cl^{\bullet}$ to

produce BrOH$^{\bullet-}$, Br$^{\bullet}$, and ClBr$^{\bullet-}$, respectively (Reactions 15–19). Br$^{\bullet}$ reacts with organic

contaminants in similar mechanisms to HO$^{\bullet}$ with reaction rate constants of 10^9–10^{10}

M^{-1}s^{-1}.[63,81]

Table 12 The steady-state concentrations of radicals in three UV/AOPs. The calculation was based on typical RO permeate chemical matrix with 88 μM of oxidant and 1178 mJ/cm^2 of UV irradiation.

Radical	Quasi Steady-State Concentration, [R$^{\bullet}$]$_{ss}$ (M)		
	UV/H$_2$O$_2$	UV/ S$_2$O$_8^{2-}$	UV/HOCl
HO$^{\bullet}$	1.2×10^{-11}	1.5×10^{-11}	2.6×10^{-12}
SO$_4^{\bullet-}$	--	8.8×10^{-12}	--
CO$_3^{\bullet-}$	7.0×10^{-11}	1.9×10^{-11}	5.1×10^{-10}
Cl$^{\bullet}$	5.2×10^{-17}	6.8×10^{-13}	4.9×10^{-13}
Cl$_2^{\bullet-}$	5.4×10^{-16}	7.0×10^{-12}	5.5×10^{-12}
ClOH$^{\bullet-}$	7.0×10^{-16}	8.5×10^{-16}	1.8×10^{-16}
Br$^{\bullet}$	9.2×10^{-15}	3.8×10^{-11}	1.4×10^{-11}
Br$_2^{\bullet-}$	1.3×10^{-15}	4.5×10^{-12}	1.8×10^{-12}
ClBr$^{\bullet-}$	1.3×10^{-15}	4.8×10^{-12}	2.0×10^{-12}
BrOH$^{\bullet-}$	7.3×10^{-16}	8.3×10^{-16}	1.7×10^{-16}

4.3.4 Model validation

1,4-dioxane and phenol degradation by UV/AOP were examined by bench-scale experiments. The kinetic model predictions matched well with the experimental data (**Figure 25** and **Figure 26**). Approximately 0.5 to 1.0 log of removal was achieved for 1,4-dioxane and phenol, respectively. In UV/S$_2$O$_8^{2-}$, both SO$_4^{\bullet-}$ and HO$^{\bullet}$ contributed to

1,4-dioxane degradation, but only $SO_4^{\bullet-}$ was important for phenol degradation. In UV/H_2O_2, $HO^{\bullet}$ was the major reactive radical. In UV/HOCl, because of the natural co-existence of chloride in free chlorine solution, chlorine dimer $Cl_2^{\bullet-}$ was produced and contributed significantly to 1,4-dioxane degradation, whereas for phenol, direct oxidation by HOCl was predominant (**Figure 25D**). The experimental data validated the kinetic model.
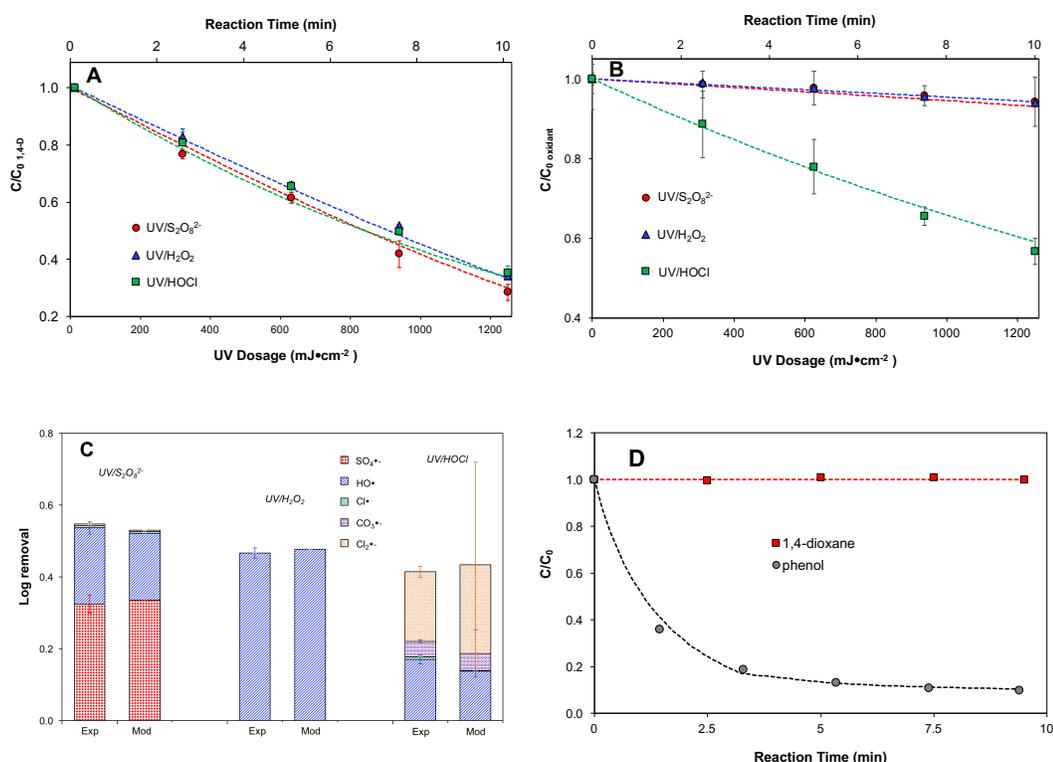
Figure 25 1,4-dioxane removal byUV/H_2O_2, UV/$S_2O_8^{2-}$ and UV/HOCl. (A) First order decay of 1,4-dioxane. (B) First-order decay of H_2O_2, $S_2O_8^{2-}$ and HOCl by UV irradiance. (C) contribution of radicals to 1,4-dioxane decay. (D) Direct oxidation of 1,4-dioxane and phenol by HOCl. [Oxidant]=2 mM, [1,4-dioxane]=250 μM, [Cl⁻]=80 μM, [inorganic carbon]=200 μM, [Br⁻]=0.2 μM, TOC=0.15 mg C/L, pH=5.8, UV irradiance= 45.3 mW/cm², UV dosage=1178 mJ/cm² in 26 seconds. Dash lines are modeled results.
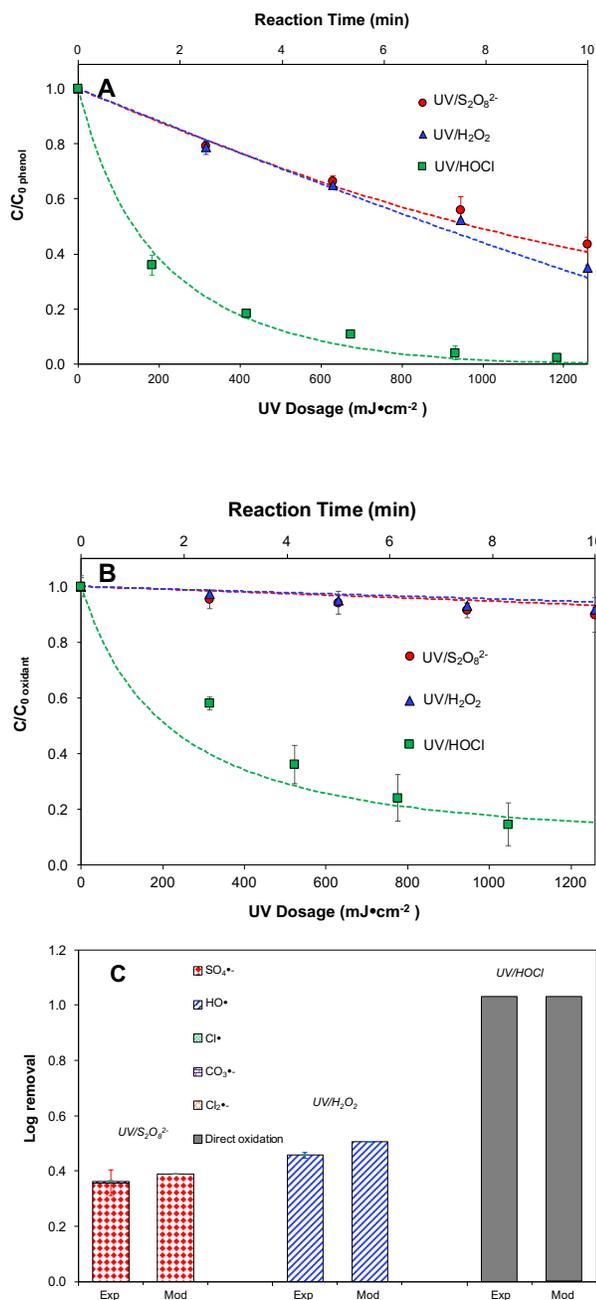
Figure 26 Phenol removal by UV/H$_2$O$_2$, UV/S$_2$O$_8^{2-}$ and UV/HOCl. (A) First order decay of phenol. (B) First order decay of H$_2$O$_2$, S$_2$O$_8^{2-}$ and HOCl by UV irradiance. (C) Contribution of radicals to phenol decay. [Oxidant]=2 mM, [phenol]=250 μM, [Cl$^-$]=80 μM, [inorganic carbon]=200 μM, [Br$^-$]=0.2 μM, TOC=0.15 mg C/L, pH=5.8, UV irradiance= 45.3 mW/cm^2, UV dosage=1178 mJ/cm^2 in 26 seconds. Dash lines are modeled results.

4.3.5 Impact of water chemical conditions on UV/AOP performance

4.3.5.1 Impact of pH

The kinetic modeling results showed that $UV/S_2O_8^{2-}$ was the most sensitive to pH (**Figure 27A**). $[HO^{\bullet}]_{ss}$ decreased by 50% as pH increased from 5 to 7, while the $[CO_3^{\bullet-}]_{ss}$ increased by 800% with the same pH increase (**Figure 27B**). As pH was increased, HCO_3^- became the predominant carbonate species ($pK_a=6.35$). This resulted in a faster transformation of $Cl^{\bullet}$ to $CO_3^{\bullet-}$ compared to the formation of $HO^{\bullet}$ via $Cl^{\bullet}$ (Reaction 14 *vs.* Reactions 7–10). $[SO_4^{\bullet-}]_{ss}$ was not sensitive to pH because the scavenging effect of $SO_4^{\bullet-}$ by HCO_3^- was negligible compared to the scavenging effect of Cl^- (Reaction 6 *vs.* Reaction 13 in **Table 8**). Therefore, a reduction of contaminant degradation with increasing pH was observed in $UV/S_2O_8^{2-}$ due to the decease of $[HO^{\bullet}]_{ss}$ (**Figure 27A**).

UV/H_2O_2 was not sensitive to pH between 5 and 7 in RO permeate chemical conditions (**Figure 28A**). As the major radical, $[HO^{\bullet}]_{ss}$ was insensitive to pH (**Figure 28B**). $HO^{\bullet}$ was predominantly scavenged by Cl^- to generate $ClOH^{\bullet-}$ (Reaction 20), but the dissociation of $ClOH^{\bullet-}$ produced $HO^{\bullet}$ (Reaction 10). Therefore, the rate of contaminant degradation remained more or less constant with pH changes (**Figure 28A**).
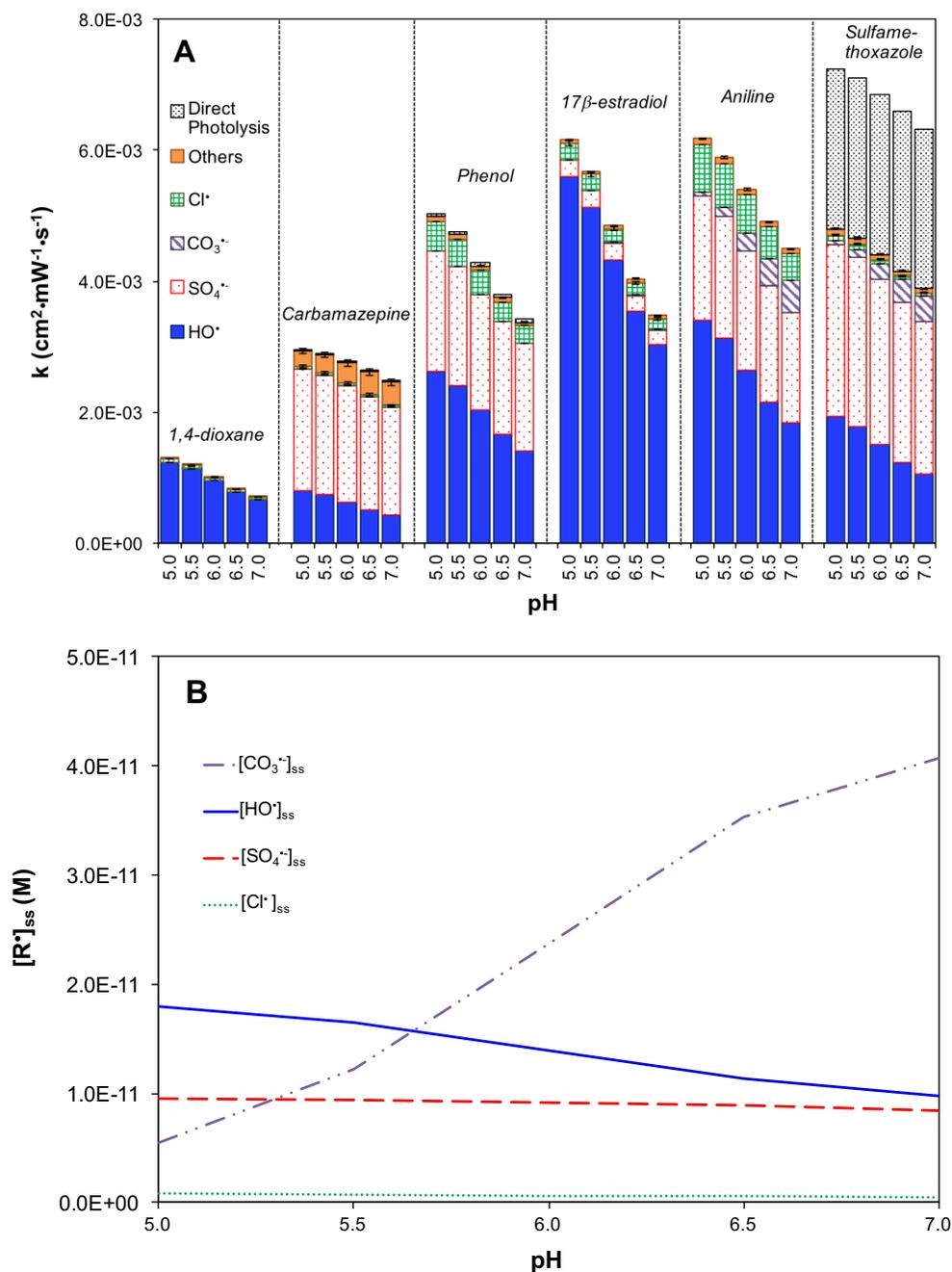
Figure 27 The effect of pH on the treatment efficiency of UV/$S_2O_8^{2-}$ based on the kinetic model. (A) first-order degradation rates of organic contaminants in treatment and (B) radical distribution. $[S_2O_8^{2-}]$=88 µM, [trace organic contaminant]=50 nM, $[Cl^-]$=80 µM, [inorganic carbon]=0.2 mM, $[Br^-]$=0.2 µM, TOC=0.15 mg C/L, UV irradiance=45 mW/cm^2.
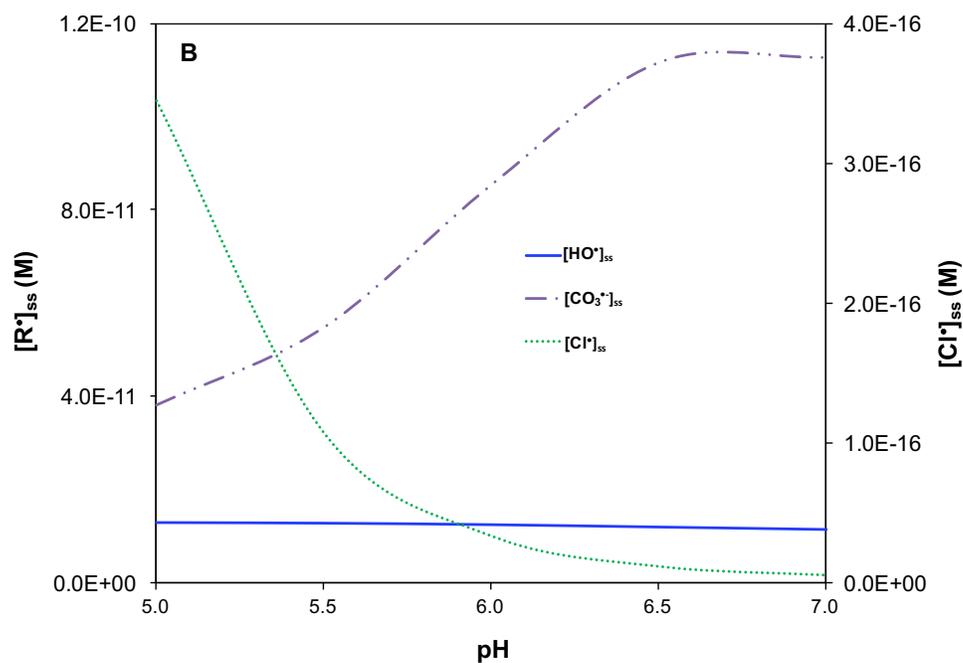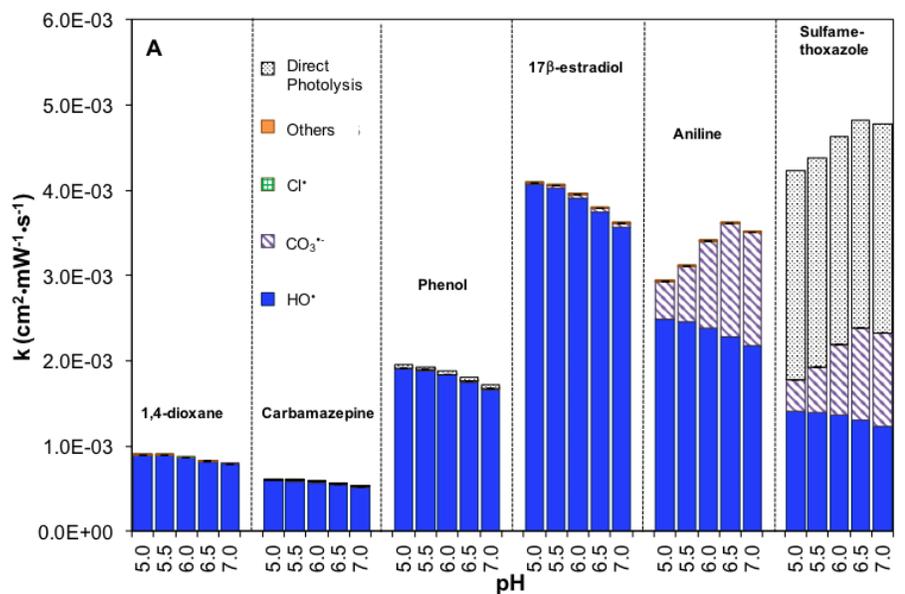
Figure 28 Effect of pH on the treatment efficiency of UV/H$_2$O$_2$ based on the kinetic model. (A) First-order degradation rates of organic contaminants in treatment. (B) Radical distribution. [H$_2$O$_2$]=88 µM, [trace organic contaminant]=50 nM, [Cl$^-$]=0.08 mM, [inorganic carbon]=0.2 mM, [Br$^-$]=0.2 µM, TOC=0.15 mg C/L, UV irradiance=45 mW/cm^2.

UV/HOCl was modestly sensitive to pH (**Figure 29A**). The steady-state concentrations of HO$^•$, Cl$^•$ and Br$^•$ decreased with increasing pH, mainly due to the scavenging effects of HCO$_3^-$ (**Figure 29B**). [HO$^•$]$_{ss}$ decreased faster than [Cl$^•$]$_{ss}$ and [Br$^•$]$_{ss}$ because of a stronger scavenging effects of HCO$_3^-$ on HO$^•$ (Reaction 12 and Reaction 21). These scavenging effects resulted in a dramatic increase of [CO$_3^{•-}$]$_{ss}$ (**Figure 29B**). Overall, the rate of contaminant decay decreased by 43% as pH increased from 5 to 7, except for aniline and sulfamethoxazole that were very reactive with CO$_3^{•-}$ (**Figure 29A**). The increase in pH also led to the conversion of HOCl to OCl$^-$ (pK=7.6), resulting in a decrease of direct oxidation of aniline by HOCl.
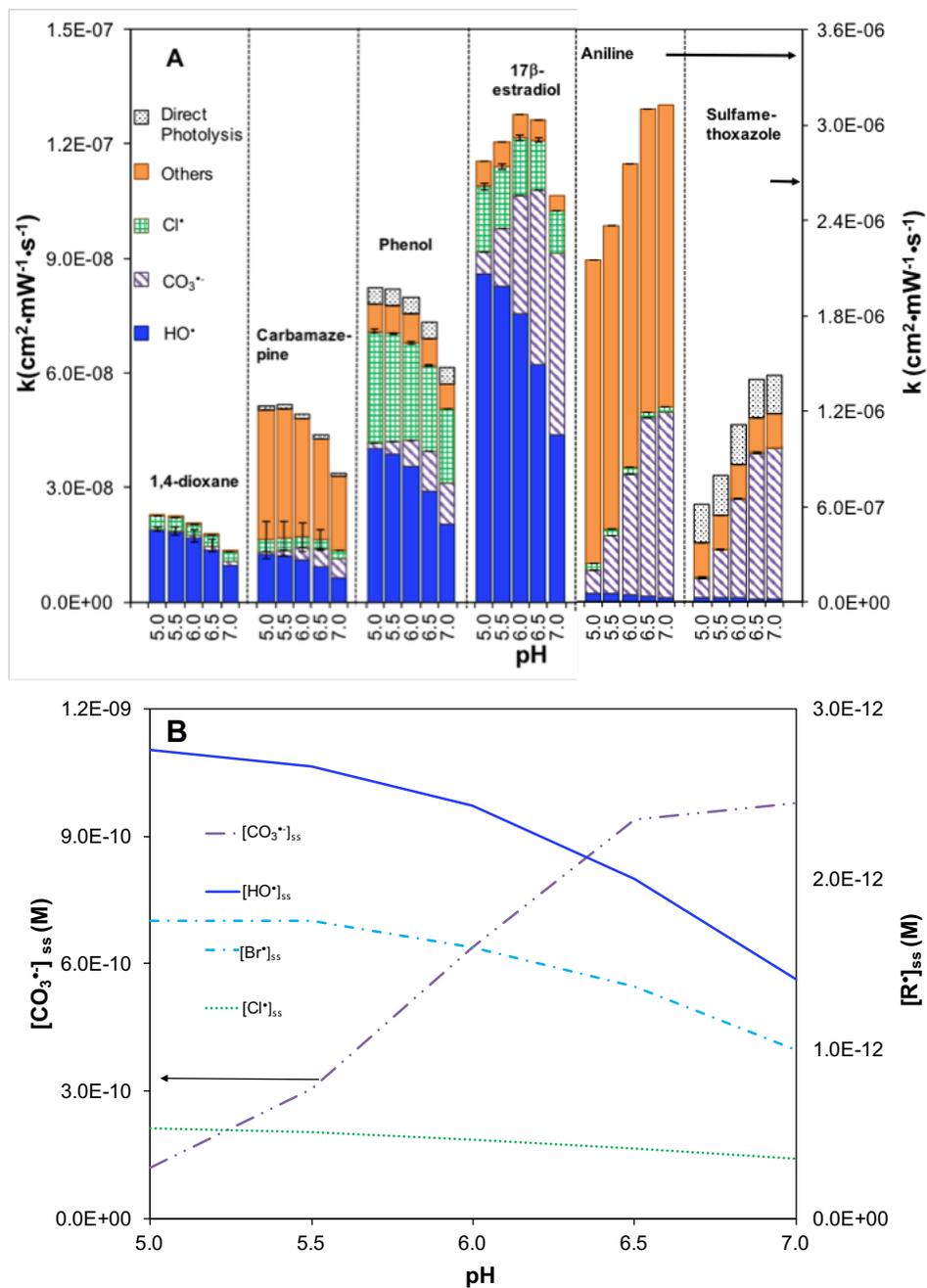
**Figure 29** Effect of pH on the treatment efficiency of UV/HOCl based on the kinetic model. (A) First-order degradation rates of organic contaminants in treatment. (B) Radical distribution. [HOCl]=88 µM, [trace organic contaminant]=50 nM, [Cl⁻]=0.08 mM, [inorganic carbon]=0.2 mM, [Br⁻]=0.2 µM, TOC=0.15 mg C/L, UV irradiance=45 mW/cm².

4.3.5.2 Impact of chloride

$UV/S_2O_8^{2-}$ was most sensitive to chloride among the three UV/AOPs (**Figure 30A**). When Cl^- concentration was increased from 10 to 280 μM, $[SO_4^{\bullet-}]_{ss}$ decreased by 94% due to the scavenging effect of Cl^-, $[HO^\bullet]_{ss}$ remained stable and $[CO_3^{\bullet-}]_{ss}$ increased by 140% (**Figure 30A**). $HO^\bullet$ initially increased with increasing chloride concentration due to the hydrolysis of $Cl^\bullet$ (Reactions 7 and 10) and generation of more $HO^\bullet$. However, when the Cl^- concentration was increased above 30 μM, $Cl_2^{\bullet-}$ formation and its transformation to $CO_3^{\bullet-}$ became the major pathway (Reactions 8 and 21). The rates of contaminant degradation generally decreased with increasing Cl^- concentrations (**Figure 30A***).*

UV/H_2O_2 was not sensitive to chloride (**Figure 31A**). Both $[HO^\bullet]_{ss}$ and $[CO_3^{\bullet-}]_{ss}$ remained stable with changing Cl^- concentration (**Figure 31B**). Although chloride can scavenge $HO^\bullet$ (Reaction 20), the dissociation of $ClOH^{\bullet-}$ quickly regenerated $HO^\bullet$, dampening the effects of chloride (Reactions 8-10). Because the formation of $CO_3^{\bullet-}$ was mainly via $HO^\bullet$ (Reaction 12), $[CO_3^{\bullet-}]_{ss}$ also remained stable.

In UV/HOCl, the change of Cl^- concentration did not strongly affect $[HO^\bullet]_{ss}$, however, decreased $[Cl^\bullet]_{ss}$ by 27% and increased $[CO_3^{\bullet-}]_{ss}$ by 400% (**Figure 32B**). This is caused by the conversion of $Cl^\bullet$ to $CO_3^{\bullet-}$ (Reaction 14). Consequently, this resulted in an enhanced degradation of 17β-estradiol, aniline and sulfamethoxazole (**Figure 32A**).
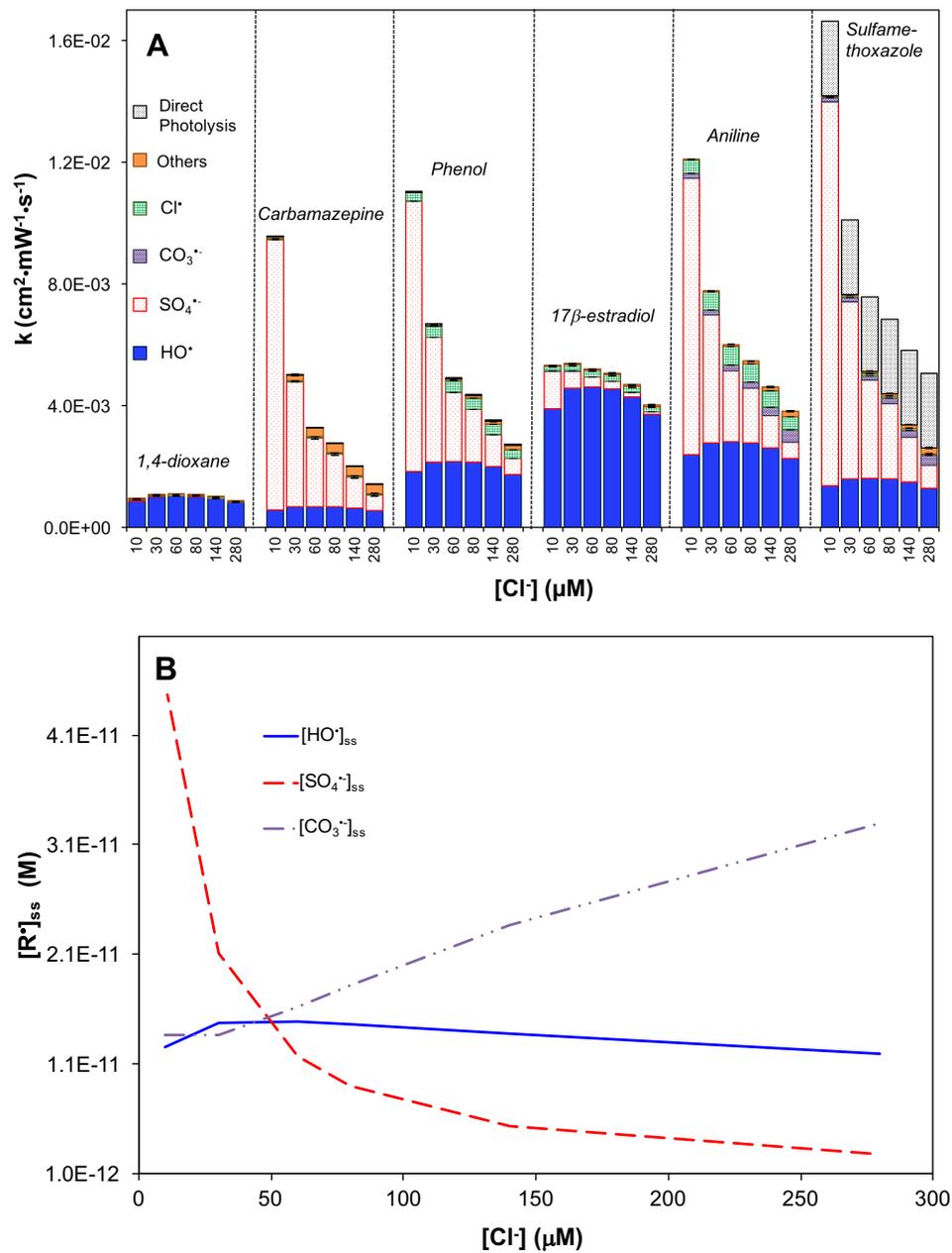
Figure 30 The effect of chloride on the treatment efficiency of UV/$S_2O_8^{2-}$ based on the kinetic model. (A) first-order degradation rates of organic contaminants in treatment and (B) radical distribution. [$S_2O_8^{2-}$]=88 μM, [trace organic contaminant]=50 nM, pH=5.8, [inorganic carbon]=0.2 mM, [Br]=0.2 μM, TOC=0.15 mg C/L, UV irradiance=45 mW/cm^2.
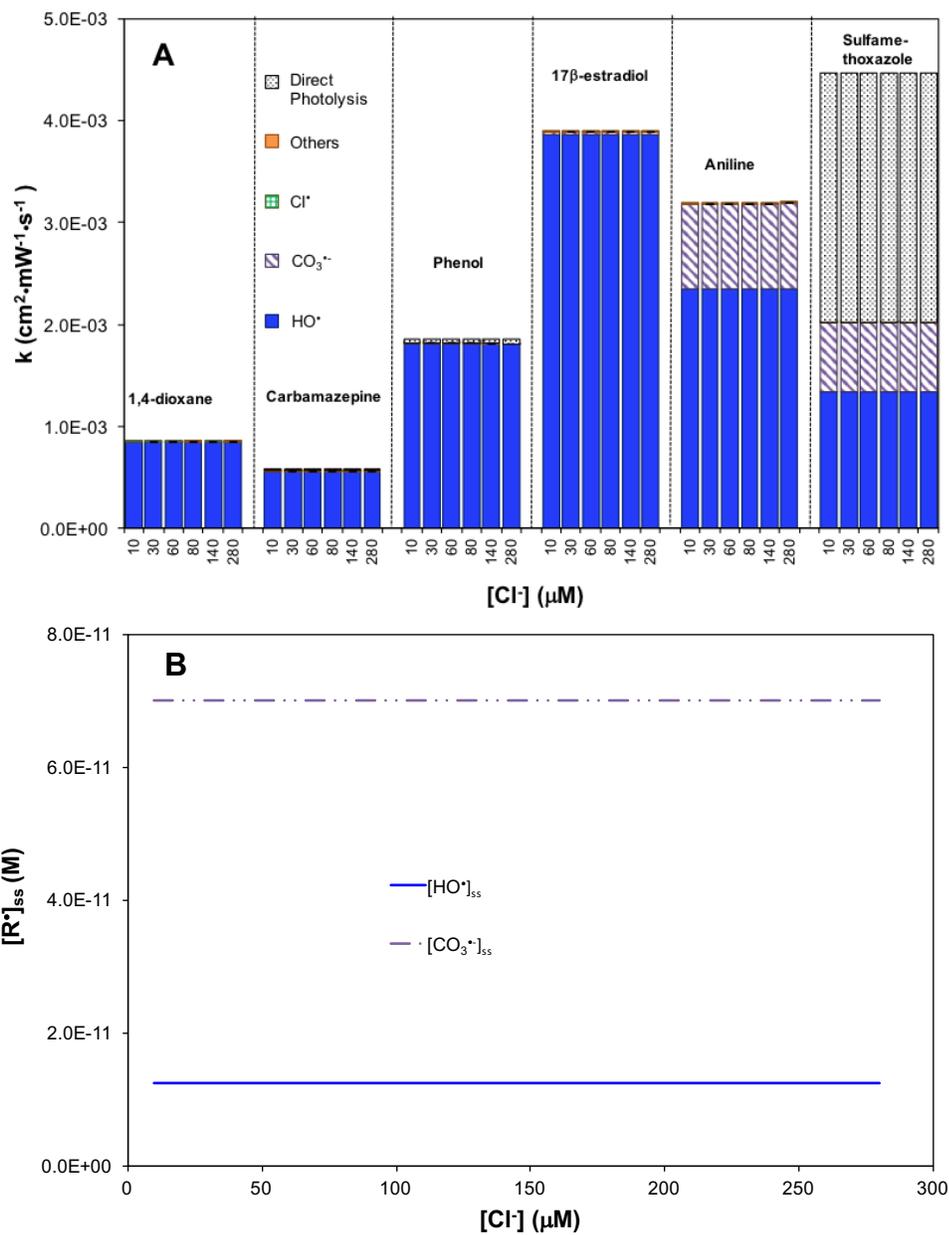
Figure 31 Effect of chloride on the treatment efficiency of UV/H_2O_2 based on the kinetic model. (A) First-order degradation rates of organic contaminants in treatment. (B) Radical distribution. [H_2O_2]=88 μM, [trace organic contaminant]=50 nM, pH=5.8, [inorganic carbon]=0.2 mM, [Br^-]=0.2 μM, TOC=0.15 mg C/L, UV irradiance=45 mW/cm^2.
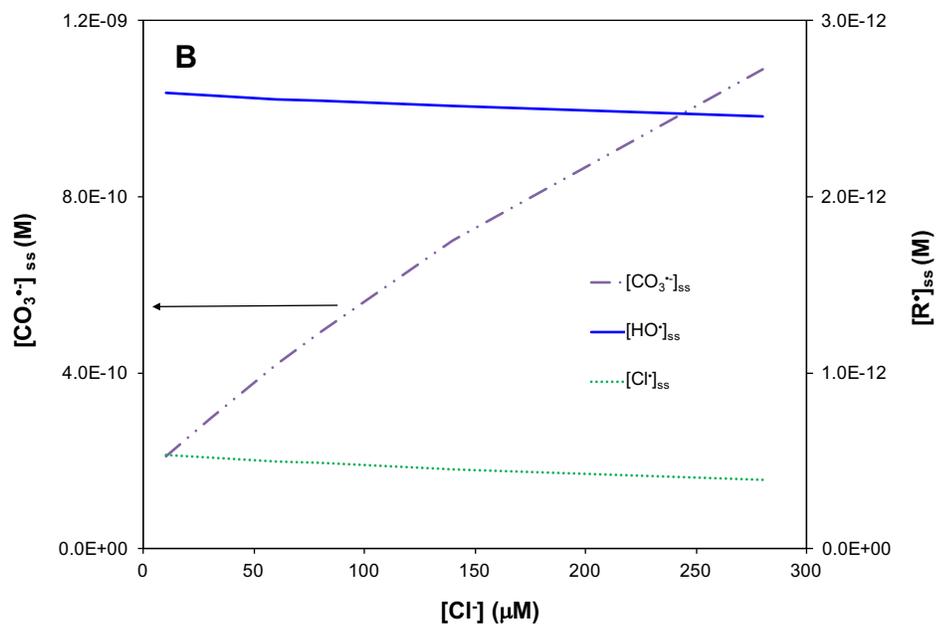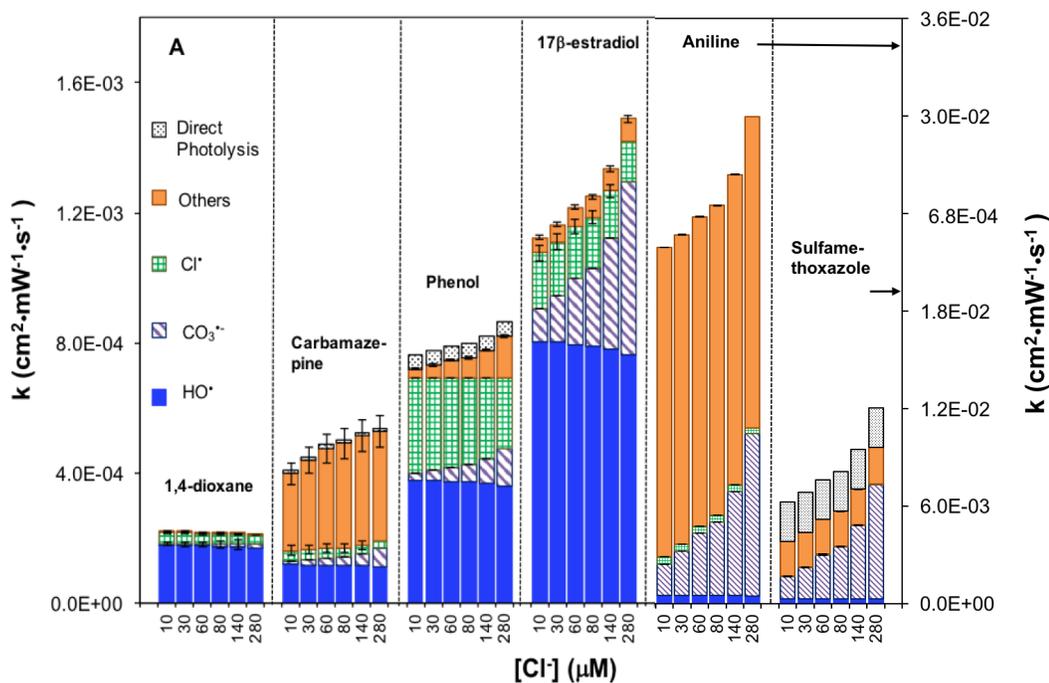
Figure 32 Effect of chloride on the treatment efficiency of UV/HOCl based on the kinetic model. (A) First-order degradation rates of organic contaminants in treatment. (B) Radical distribution. [HOCl]=88 µM, [trace organic contaminant]=50 nM, pH=5.8, [inorganic carbon]=0.2 mM, [Br$^-$]=0.2 µM, TOC=0.15 mg C/L, UV irradiance=45 mW/cm^2.

4.3.5.3 Impact of inorganic carbon

UV/$S_2O_8^{2-}$ was most sensitive to inorganic carbon (TOTCO$_3$) (**Figure 33A**). When TOTCO$_3$ increased from 40 to 400 µM, $[SO_4^{\bullet-}]_{ss}$ decreased by 5%, $[HO^\bullet]_{ss}$ decreased by 33% and $[CO_3^{\bullet-}]_{ss}$ increased by 600% (**Figure 33B**). The reduction of $[HO^\bullet]_{ss}$ was due to the scavenging effect of HCO_3^- on $Cl^\bullet$ (Reaction 14), which subsequently suppresses $HO^\bullet$ formation via $ClOH^{\bullet-}$ pathway (Reactions 8–10). Consequently, the rates of contaminant degradation decreased with increasing TOTCO$_3$ (**Figure 33A**).

In contrast, UV/H_2O_2 was not sensitive to inorganic carbon (**Figure 34A**). $[HO^\bullet]_{ss}$ remained stable with changing TOTCO$_3$ concentration (**Figure 34B**). Although $HO^\bullet$ could be scavenged by Cl^- (Reaction 20), it was quickly regenerated (Reaction 10). The scavenging effects of HCO_3^- mainly suppressed $Cl^\bullet$ and $Cl_2^{\bullet-}$ (Reactions 14 and 21) and increased $[CO_3^{\bullet-}]_{ss}$ by 9 times (**Figure 34B**). The predicted contaminant degradation rates were not sensitive to TOTCO$_3$ except for aniline and sulfamethoxazole in which rates were enhanced due to the increase of $[CO_3^{\bullet-}]_{ss}$ (**Figure 34A**).

Similarly, UV/HOCl was not sensitive to TOTCO$_3$ with respect to $[HO^\bullet]_{ss}$ and $[Cl^\bullet]_{ss}$ (**Figure 35A**). When TOTCO$_3$ increased from 40 to 400 µM, both $[HO^\bullet]_{ss}$ and $[Cl^\bullet]_{ss}$ remained relatively constant; however, $[CO_3^{\bullet-}]_{ss}$ increased dramatically due to the scavenging effect of HCO_3^- (**Figure 35B**). Therefore, contaminants that are reactive with $[CO_3^{\bullet-}]_{ss}$ exhibited an enhanced removal with increasing inorganic carbon concentration (**Figure 35A**).
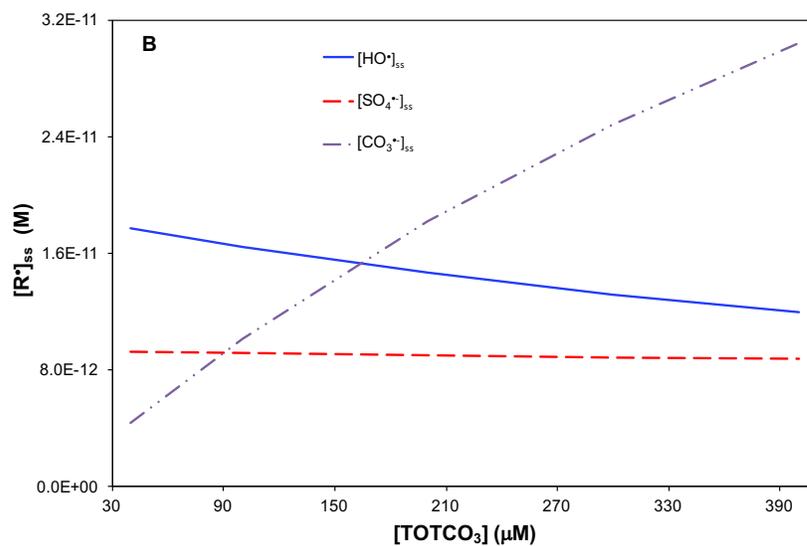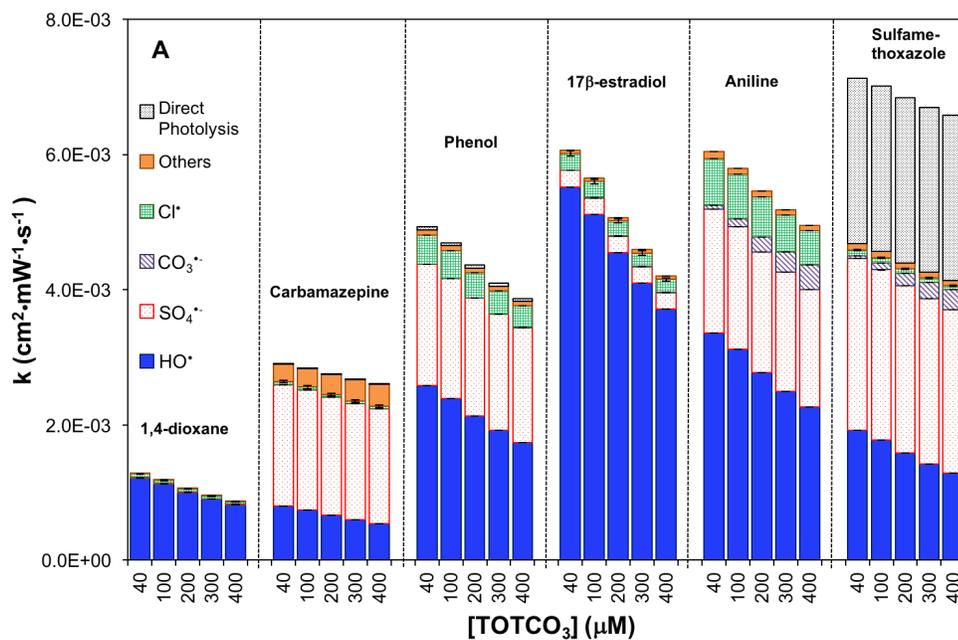
Figure 33 Effect of inorganic carbon on the treatment efficiency of UV/$S_2O_8^{2-}$ based on the kinetic model. (A) First-order degradation rates of organic contaminants in treatment. (B) Radical distribution. [$S_2O_8^{2-}$]=88 μM, [trace organic contaminant]=50 nM, pH=5.8, [Cl^-]=80 μM, [Br^-]=0.2 μM, TOC=0.15 mg C/L, UV irradiance=45 mW/cm^2.
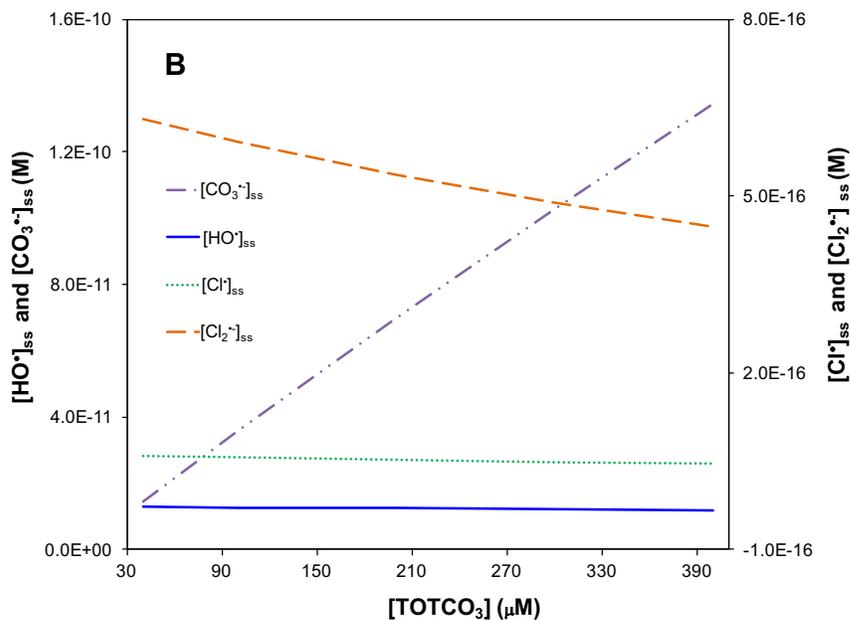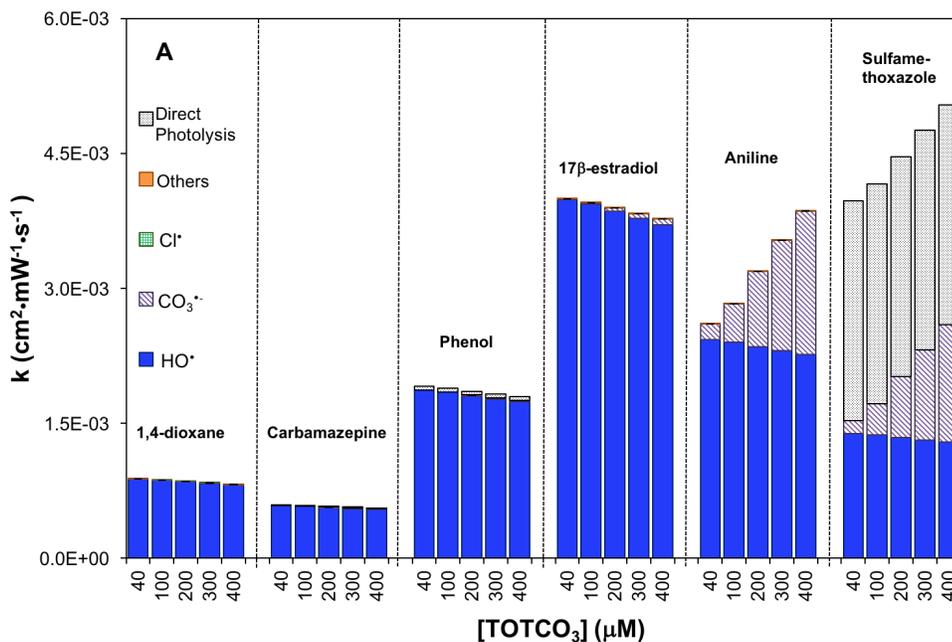
Figure 34 Effect of inorganic carbon on the treatment efficiency of UV/H_2O_2 based on the kinetic model. (A) First-order degradation rates of organic contaminants in treatment. (B) Radical distribution. [H_2O_2]=88 µM, [trace organic contaminant]=50 nM, pH=5.8, [Cl^-]=80 µM, [Br^-]=0.2 µM, TOC=0.15 mg C/L, UV irradiance=45 mW/cm^2.
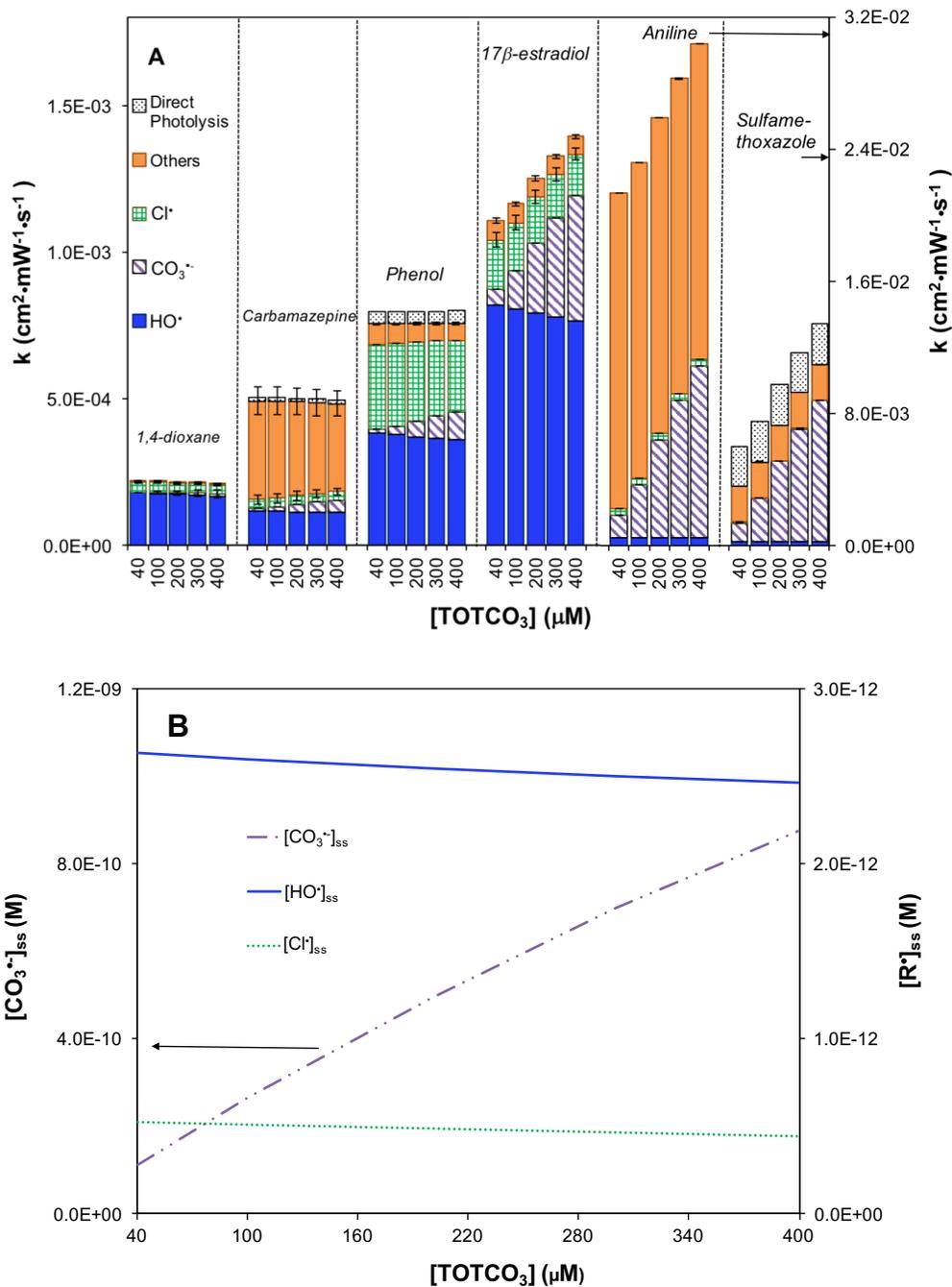
Figure 35 The effect of inorganic carbon on the treatment efficiency of UV/HOCl based on the kinetic model. (A) first-order degradation rates of organic contaminants in treatment and (B) radical distribution. [HOCl]=88 µM, [trace organic contaminant]=50 nM, pH=5.8, [Cl⁻]=80 µM, [Br⁻]=0.2 µM, TOC=0.15 mg C/L, UV irradiance=45 mW/cm².

4.4 Engineering Implications

In chemical conditions typical for potable water reuse, the kinetic modeling prediction and experimental observation showed that treatment efficiency followed the order of UV/persulfate > UV/hydrogen peroxide > UV/chlorine. This is mainly because $S_2O_8^{2-}$ photolyzes faster than H_2O_2 and generates higher levels of both $SO_4^{\bullet-}$ and $HO^{\bullet}$. Because $SO_4^{\bullet-}$ is more selective than $HO^{\bullet}$ to react with electron-rich compounds, $UV/S_2O_8^{2-}$ could potentially treat organic contaminants more efficiently than UV/H_2O_2, despite that the industrial implementation in water reuse is still in its infancy. While the application of $UV/S_2O_8^{2-}$ can increase SO_4^{2-} concentration in treated water (<10 mg/L), this level is not likely to adversely affect drinking water quality, considering the US EPA guideline standard of 250 mg/L for SO_4^{2-}.[82] However, $UV/S_2O_8^{2-}$ is more sensitive to pH, chloride, and inorganic carbon than the other two UV/AOPs. This sensitivity can impact its treatment efficiency, depending on the reactivities of radicals with individual contaminants.

UV/H_2O_2 exhibited higher treatment efficiency than UV/HOCl for some groups of contaminants. The performance of UV/H_2O_2 is limited by the rate of H_2O_2 photolysis, the strong scavenging effect of H_2O_2 on various radicals and a requirement to remove H_2O_2 residual in drinking water. However, UV/H_2O_2 is not as sensitive to changes of chemical parameters including pH, chloride, and bicarbonate as the other two UV/AOPs.

UV/HOCl is unique to the other AOPs in that it favors the generation of $CO_3^{\bullet-}$ in water reuse chemical conditions. For compounds possessing high reactivity with $CO_3^{\bullet-}$ (*e.g.*, amine-containing contaminants), UV/HOCl can be very effective. For compounds that are inert to $CO_3^{\bullet-}$, UV/HOCl is less effective than UV/H_2O_2 and $UV/S_2O_8^{2-}$. However, as a widely used disinfectant, HOCl is commonly employed in water treatment. The system can be easily upgraded to an AOP by with the addition of a UV source with less capital cost compared to other UV/AOPs.

The water chemical conditions and the targeted contaminants should be considered in the design of a UV/AOP for water reuse. For source waters containing low levels of Cl^- and HCO_3^-, $UV/S_2O_8^{2-}$ and UV/H_2O_2 work effectively. If the targeted contaminant contains amine functional groups, UV/HOCl is likely to be favored. In addition, pre-treatment steps should be carried out to minimize the presence of natural organic matter (NOM) prior to UV/AOP because NOM can significantly decrease the UV transmittance and scavenge major radicals.[83-84]

4.5 Conclusions

The performances of $UV/S_2O_8^{2-}$, UV/H_2O_2 and UV/HOCl were evaluated and compared using both comprehensive kinetic modeling and experimental investigation. The degradation of 1,4-dioxane, carbamazepine, phenol, 17β-estradiol, aniline, and sulfamethoxazole were examined in this study. The impacts of chemical conditions relevant to potable water reuse that included pH, chloride, and inorganic carbon were examined. $UV/S_2O_8^{2-}$ was predicted to be the most efficient UV/AOP when applied to RO permeate, despite that its performance is most sensitive to pH, Cl^-, and HCO_3^-. $SO_4^{\bullet-}$ is likely to be transformed through a Cl^- pathway to generate $HO^\bullet$. However, the presence of HCO_3^- also transforms $SO_4^{\bullet-}$ and $Cl^\bullet$ to less reactive $CO_3^{\bullet-}$. $HO^\bullet$ is affected less by Cl^- and HCO_3^- because the formation of $ClOH^{\bullet-}$ quickly regenerates $HO^\bullet$. An increase of pH can compromise the performance of $UV/S_2O_8^{2-}$, while pH changes have a negligible effect on UV/H_2O_2 and UV/HOCl. The presence of Cl^- and HCO_3^- transforms $SO_4^{\bullet-}$ to less reactive radicals and reduces the effectiveness of $UV/S_2O_8^{2-}$, whereas UV/H_2O_2 and UV/HOCl are less sensitive to Cl^- and HCO_3^-. The kinetic model provides a fundamental tool to examine

the mechanisms of radical photochemistry to aid in the design of UV/AOP systems and to predict the performance under different chemical conditions.

4.6 Acknowledgments

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Chapter 5

Toxicity Assessment of Benzene and 1,4-dioxane Oxidation Byproducts

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5.1 Introduction

Water shortage has become a global crisis, and our drinking water resources are limited and facing ever-increasing contamination. [1-4] Remediation of contaminated groundwater and reuse of treated wastewater effluent are promising solutions to mitigate the water crisis. Advanced Oxidation Processes (AOPs) have been widely used for many contaminated groundwater sites and water recycle treatment trains.[5-7] Persulfate ($S_2O_8^{2-}$)-based AOPs for *in situ* Chemical Oxidation (ISCO) and potable water reuse have gained increasing attention in recent years due to its capacity to degrade a variety of organic contaminants such as contaminants of emerging concerns (CECs) including hydrocarbons,[8] pharmaceuticals and personal care products (PPCPs).[9,10] Enhancement for the removal efficiency of target contaminants by $S_2O_8^{2-}$-based AOPs has taken place,[11-15] however, the formation and kinetics of oxidative byproducts (OBPs) with potentially high toxicity is of increasing concern. The formation of toxic disinfection byproducts (DBPs) in other AOPs, such as halogenated DPBs in chlorination,[16-21] bromate in ozonation[22-25] and nitrogenous DBPs in chloramination [26-30] have been reported. It is likely that $S_2O_8^{2-}$-based AOPs may also produce toxic OBPs when the parent contaminants are not fully mineralized.[31-33] Therefore, it is important to monitor the formation of oxidation byproducts, assess their toxicity, and develop new advanced oxidative treatments with minimal toxic byproduct formation.

In this study, we used benzene and 1,4-dixoane as model contaminate as they are commonly found in contaminated groundwater and wastewater effluent. Benzene is a ubiquitous contaminant and its toxicity to humans and wildlife has been well studied.

Chronic benzene exposure progressively decreases bone marrow function and increases the possibility of bone marrow cancer[34,35]. Sources of benzene contamination of soil and groundwater mainly come from the petroleum industry, and benzene has been frequently detected in soil and groundwater[36]. Benzene can be effectively oxidized by sulfate radicals to produce phenol and other organic acids, which are more easily metabolized by soil microorganisms to produce CO_2. 1,4-dioxane is listed as a class B carcinogen by the USEPA and the notification level is 1 ppb in California.[37] It is used as a surrogate for UV/AOPs efficiency validation.[38]

In this study, we compared the degradation of benzene by MnO_4^-, goethite-activated $S_2O_8^{2-}$ and H_2O_2, which were the most common AOPs used in *in situ* Chemical Oxidation. We chose goethite to activate $S_2O_8^{2-}$ and H_2O_2 because our previous studies showed that goethite exhibited the highest stoichiometric efficiency.[39] Products were identified during the treatment and toxicity of the oxidation byproducts and parent compounds were evaluated. In addition, we examined UV/H_2O_2, $UV/S_2O_8^{2-}$ and UV/NH_2Cl on 1,4-dioxane removal. UV/H_2O_2 is the most common UV/AOP utilized in potable water reuse treatment, and $UV/S_2O_8^{2-}$ and UV/NH_2Cl are also becoming popular.[40-42] NH_2Cl is frequently used as an antifoulant or disinfectant during advanced treatment trains, and it can also produce $Cl^\bullet$ radical in photolysis. The objectives of this research are to (1) identify and compare the formation and distribution of oxidation byproducts during each AOP treatment, (2) Evaluate the toxicity of the transformation products, and compare their toxicity to the parent compounds using human cell-based bioassays.

5.2. Materials and Methods

5.2.1 ISCO treatments

All chemicals used in this study were reagent grade and obtained from ACROS Organics, Sigma Aldrich or Fisher Scientific. All chemicals were used as received without further purification. Goethite was synthesized by precipitating $Fe(NO_3)_3$ with NaOH,[43] and sieved to a uniformed size (38 μm ~150μm). All cell culture supplies and chemicals were obtained from Life Technologies or Fisher Scientific and stored in appropriate conditions as instructed. Benzene was prepared one day before its use and stored in a 4^oC refrigerator. To avoid benzene evaporation, benzene was prepared daily for each experiment at final concentration (3 mM) in Milli-Q water that contained 50 mM borate buffer with minimal air space. The flask was inverted for three hours and left overnight for equilibrium to occur. Goethite was first introduced to 0.98-ml glass tubes at a final concentration of 50 g/L prior to the transfer of benzene solution. Crystal $K_2S_2O_8$, $KMnO_4$, and liquid H_2O_2 (30%) were added to the benzene solution directly at a final concentration of 150 mM. After complete mixing, the solution was quickly transferred to individual tubes. The final experimental solution consisted goethite (50g/L), 150 mM $K_2S_2O_8$, H_2O_2 or MnO_4^-, 3 mM benzene and 50 mM borate buffer. The solution was maintained at pH 8. MnO_4^- experiments did not include goethite. The tubes were then rotated and left in room temperature in the dark. One glass tube was removed for chemical analysis every five days.

5.2.2 UV/AOP treatments

A NH_2Cl stock solution (50mM) was prepared daily by adding a HOCl stock solution to $(NH_4)_2SO_4$ with a N:Cl molar ratio of 1.2:1 buffered at pH 8 using borate. The working solution contained 5 mM oxidants (*e.g.* H_2O_2, $S_2O_8^{2-}$, and NH_2Cl) and 1 mM 1,4-dioxane at pH 8. Prepared solutions were then transferred to multiple 8-mL quartz tubes and placed in a carousel in a UV chamber. The samples were illuminated with a low-pressure monochromatic UV lamp (λ=254 nm) at an intensity of 2.3 mW/cm^2 (Phillips TUV6T5) which was cooled by circulated water. Samples were collected every five minutes for chemical analysis.

5.2.3 Aldehyde preparation

The oxidation product that exhibited aldehyde-like features was prepared by UV irradiation of 15 mM benzene with 3 mM $S_2O_8^{2-}$ for two hours. The products were separated and concentrated by Solid Phase Extraction.[44] Following chromatography, the purified compound was then condensed to dryness by purging with N_2, followed by re-suspending in MQ water to a final concentration of 10 mM. The concentration of aldehyde-like compound was estimated by using DNPH derivatized glutaraldehyde followed by HPLC-UV analysis (**Figure 36**).[45]
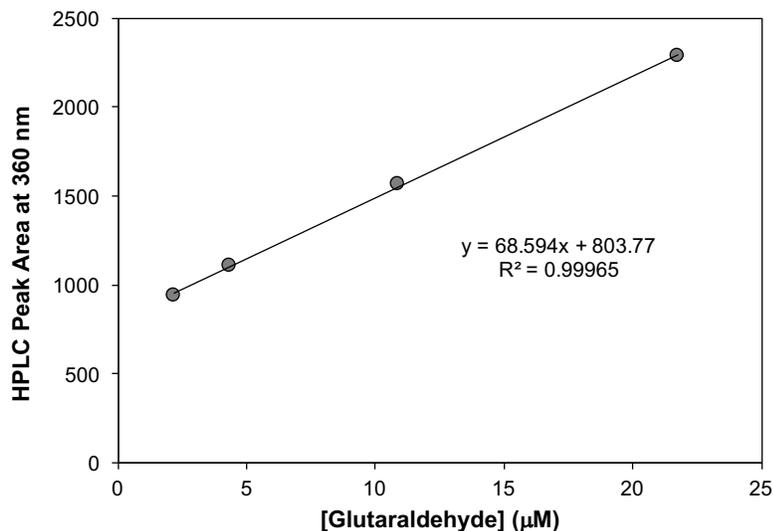
Figure 36 Calibration curve of DNPH-derivatized glutaraldehyde.

5.2.4 Analytical methods

Concentrations of H_2O_2, $S_2O_8^{2-}$, MnO_4^- and NH_2Cl were determined using potassium iodine (KI) and DPD titration, respectively.[46] Concentrations of benzene, 1,4-dioxane and EGD were directly measured with an Agilent 1200 high performance liquid chromatograph equipped with a diode array detector. A Zorbax Eclipse Deltabond column (4.6×200mm, 5.0-μm particle size). Concentrations of formaldehyde and glycolaldehyde were derivatized with 2,4-dinitrophenylhydrazine (DNPH) according to EPA Method 8315, and then analyzed by HPLC. The composition of mobile phase for benzene, phenol and aldehyde were 97% formic acid (10 mM) and 3% acetonitrile. The retention times were 7.3 minutes, 5.5 minutes and 3.5 minutes for benzene, phenol, and aldehyde, respectively. For 1,4-dioxane and ethylene glycol diformate, the composition of mobile phase was 92% H_2O and 8% acetonitrile. The retention time was 2.7 minutes and 1.9 minutes for 1,4-

Dioxane and Ethylene glycol diformate, respectively. For Formaldehyde and Glycolaldehyde, the mobile phase composition was 40% acetonitrile and 60% H_2O. The retention time was 3.5 minutes and 5.6 minutes, respectively. The sample injection volume was 100 μL and the flow rate was set at 1.0 mL/min for a total of 6 min run time. Concentrations of glycolic acid, formic acid and methoxyacetic acid were quantified by Ion Chromatography (Dionex 1000, USA).

5.2.5 Toxicity assays

HCT-116 Human colorectal carcinoma cells were cultured at 37°C in a humidified 5% CO_2 incubator, and collected after the fourth passage for the toxicity assays.[47] HCT-116 Human colorectal carcinoma cells were cultured in polystyrene culture flasks (Corning T-75) with McCoy's 5A Medium including 10% dialyzed fetal bovine serum (FBS), 100ug/ml Penicillin/Streptomycin, and 5ug/ml Blasticidin. Cells were collected before reaching 80% confluence after the fourth passage and suspended with Opti-MEM Reduced Serum Assay Medium including 0.5% dialyzed fetal bovine serum (FBS), 1% 1 mM Sodium Pyruvate, 1% 0.1mM Non-essential amino acids (NEAA) and 1% of 100u/ml Penicillin/Streptomycin at a concentration of 5,5000 cells/ml. An aliquot of 90ul of the cell suspension was added into each well of the black, clear-bottom, 96-well assay plate (Corning 3603). The cells were incubated overnight prior to sample exposures.

For cytotoxicity measurements, an 10-μl aliquot of each concentration of the test compounds was dissolved in assay medium with 5% DMSO and transferred to the assay plate. The final compound concentration in the 100-μl assay volume ranged from 0 μM to

500 uM over 8 concentrations. Three replicates were tested for each concentration. The plate was allowed to settle for 30 min at room temperature and then incubated at 37 °C, 5% CO_2 for 16 hours. After 16 hours, 10-μl of MTT reagent was added to the wells, which was incubated at 37 °C for 4 hours. The assay medium was then aspirated and 100-μl of DMSO detergent was added. Cells were then again incubated for 3 hours at room temperature in the dark. Cytotoxicity was assessed by recording the absorbance at 570 nm using the EnVision microplate reader (Perkin Elmer, Shelton, CT). Percentage reduction in cell proliferation (relative cell density) was compared to that achieved in the growth medium controls. All the readings in the test compounds were corrected with reference to the background readings. Dose response curves were plotted using GraphPad Prism 7.0, and the EC50 of each compound was calculated using the Four-Parameter Logistic nonlinear regression function.

For genotoxicity, 20 μl of LiveBLAzer™ - FRET B/G substrate mixture was added to each well after 16-hours of incubation. The substrate mixture was prepared in the absence of direct light. The plates were then incubated at room temperature for 2 hours, and fluorescence intensity was measured at 460 and 530 nm emission and with excitation at 405 nm. Readings for each well were normalized by the growth medium control. The ratio of emissions at 460nm/530 nm was calculated by Excel and dose response curves were plotted (GraphPad Prism 7.0) to compare to the positive control, Mitomycine.

The compounds used to treat the cells were prepared from known standards except that for the unsaturated aldehyde compound from benzene oxidation which was collected from HPLC eluent. For the mixture toxicity at different treatment times, the chemical

standards were combined based on the experimentally determined product compositions after treatment for 10 and 20 minutes (Table S1). After chemical exposure, fluorescesnce of the mixture was recorded using a Victor 2 plate reader (Perkin Elmer, Shelton, CT). Dose response curves were then plotted and the EC50s were calculated using GraphPad Prism 7. Both theoretical and experimentally observed genotoxicity Mitomycin equivalency quotients (MEQ) were calculated to determine the genotoxicity of 1,4-dioxane degradation during UV/AOP treatments.

5.2.4 Mitomycin Equivalency Quotient (MEQ) calculations

First, the Relative Effect Potency (REP) values were calculated as:

$REP = EC_{50(mitomycin)}/EC_{50(i)}$

where i is a specific oxidation product, the $EC_{50(mitomycin)} = 4.77$ μM.

Second, the theoretical mitomycin EQ was calculated:

$MEQ_{theoretical} = \Sigma(1000\mu M \times \%_i \times REP)$

$\%_i$ is the oxidation products composition listed in **Figure 13**

Third, the experimentally observed MEQ was calculated as:

$MEQ_{observed} = EC_{50(mitomycine)}/EC_{50(time\ 10\ min\ or\ 20\ min)}$

$EC_{50(time\ 10\ min\ or\ 20\ min)}$ was experimentally determined (**Figure 37**)

Table 13 Products distribution during UV/AOPs treatment

| Reaction Time	0 min	UV/S$_2$O$_8$$^{2-}$ 10 min	20 min	UV/H$_2$O$_2$ 10 min	20 min	UV/NH$_2$Cl 10 min	20 min
1,4-Dioxane	100%	20%	4%	51%	14%	84%	65%
Glycolaldehyde		26%	18%	24%	46%	8%	21%
Formaldehyde		4%	7%	5%	9%	1%	2%
Formic acid		13%	16%	17%	22%	0%	0%
Methoxylacetic acid		17%	28%	2%	5%	0%	0%
Glycolic acid		0%	0%	1%	4%	0%	0%
EGD		20%	27%	0%	0%	7%	12%
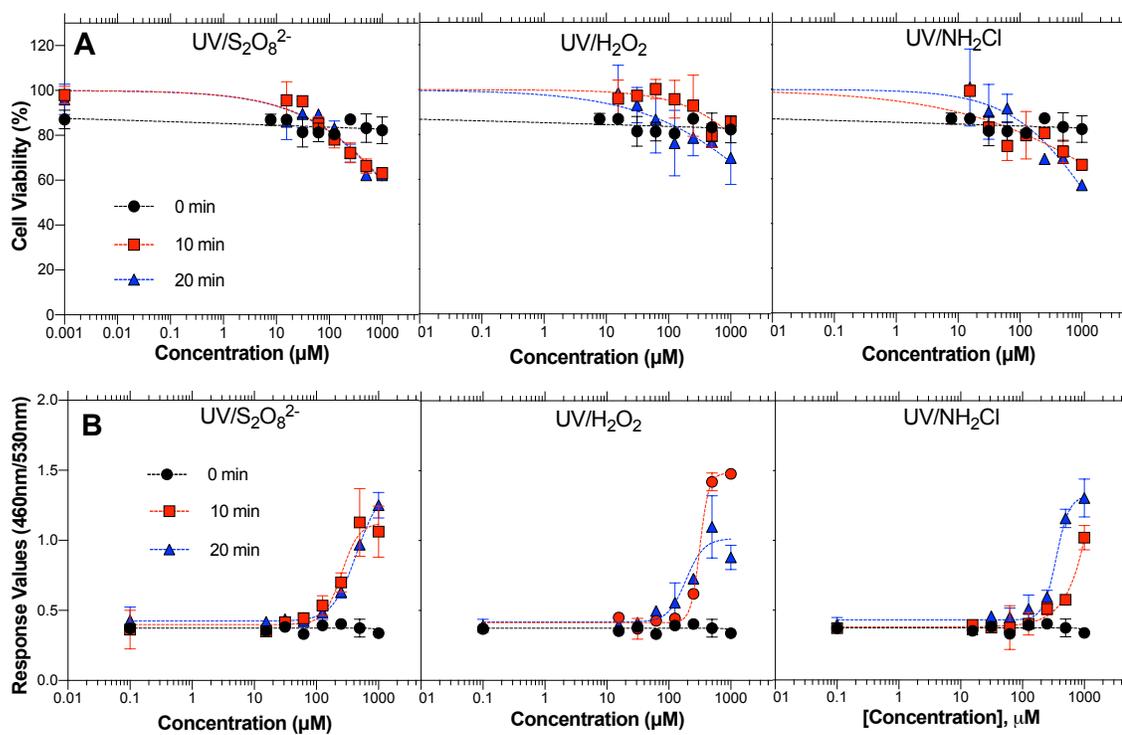
Figure 37 (A) Cytotoxicity and (B) Genotoxicity evolution of 1,4-D during UV/AOPs treatment.

5.3. Results and Discussion

5.3.1 Products distribution of benzene in treatments of MnO_4^-, goethite-activated $S_2O_8^{2-}$ and H_2O_2

The rates of oxidant disappearance followed the order of $H_2O_2 > S_2O_8^{2-} > MnO_4^-$ (**Figure 38A)**, and benzene degradation followed the same order (**Figure 38B**). Approximately 80%, 90% and less than 5% of benzene was oxidized by H_2O_2, $S_2O_8^{2-}$, and MnO_4^-, respectively. H_2O_2 was quickly activated by goethite in the first three days; hence, benzene was also quickly oxidized. After three days, all H_2O_2 was completely consumed and benzene degradation also stopped. $S_2O_8^{2-}$ was very persistente and its concentration remained stable throughout 20 days of reaction. Benzene was slowly, but continuously degraded by activated $S_2O_8^{2-}$, and achieved better removal efficiency than H_2O_2. MnO_4^- was not consumed and only less than 5% of benzene disappeared, probably due to volatilization. Goethite-activated H_2O_2 produced highly reactive $OH^\bullet$, that reacted with benzene at a diffusion-controlled rate (7.8×10^9 $M^{-1}s^{-1}$).[48] However, iron oxide could also decompose H_2O_2 without producing radicals.[49] In addition, $OH^\bullet$ also oxidized $\equiv Fe^{2+}$ to $\equiv Fe^{3+}$,[50] making H_2O_2 a less efficient process. In contrast, $S_2O_8^{2-}$ has been reported to be more persistent, which may help achieve long term remediation goals.[51] MnO_4^- was unable to oxidize benzene, which was consistent with a previous study.[52]

The distribution of benzene oxidation products was shown in **Figure 38C** and **D**. Two major products, phenol and an unsaturated aldehyde were observed in H_2O_2 and $S_2O_8^{2-}$ treatments. The mechanism of benzene degradation to phenol and the unsaturated aldehyde

was proposed by a previous study and showed that in **Scheme 10**.[43] No products were observed in the treatment with MnO_4^-. In the $S_2O_8^{2-}$ treatment, product formation reached a peak at day 3, and then were quickly oxidized by $SO_4^{\bullet-}$. At the peak, the phenol and aldehyde accounted for 60% and 15% of degraded benzene, respectively. Another 30% of undefined products were probably carboxylic acids, which were not the focus in this study. In H_2O_2 treatment, product formation peaked after 1 day of reaction with 35% of phenol and 20% of aldehyde.
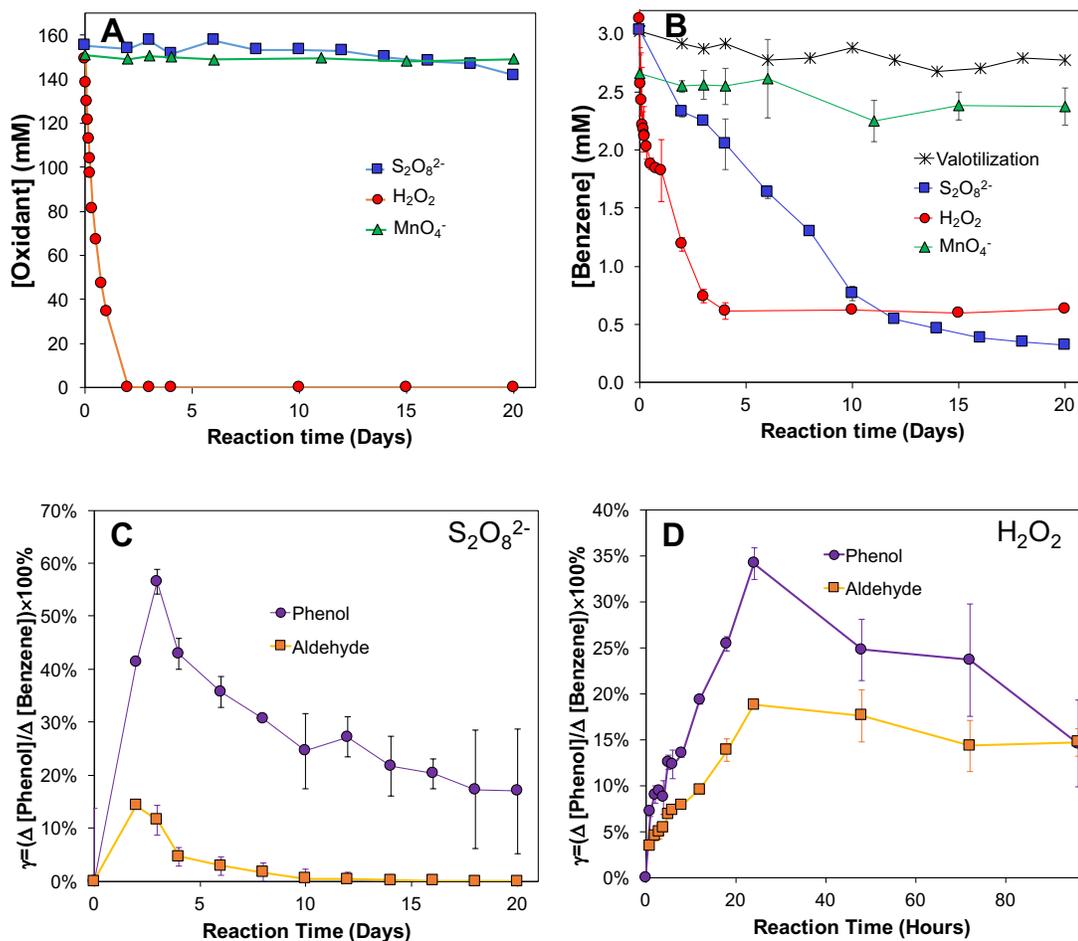
Figure 38 Benzene degradation and products evolution in $S_2O_8^{2-}$, H_2O_2 and MnO_4^-. (A) benzene degradation; (B) products formation in goethite-activated $S_2O_8^{2-}$; (C) products formation in goethite-activated H_2O_2. [Oxidants]=150mM, [Benzene]=3mM, pH=8.
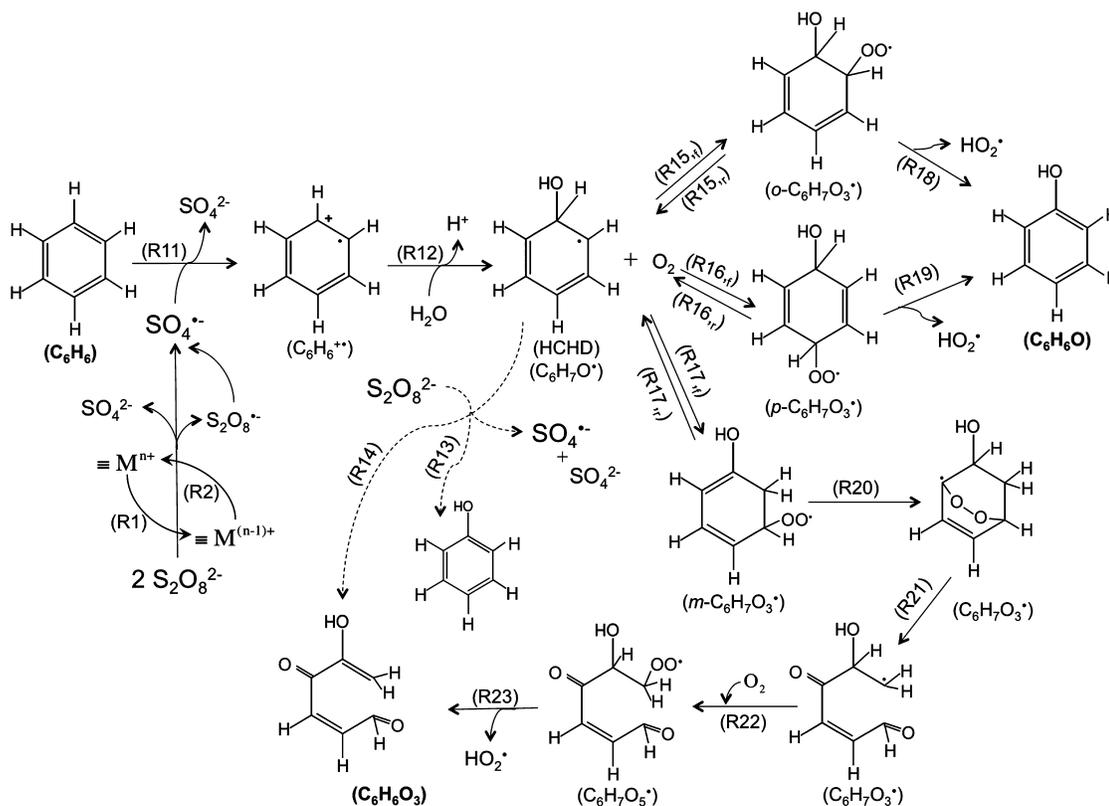
Scheme 10 Proposed benzene degradation pathway. Derived from Liu et. al. 2016.

5.3.2 Products distribution of 1,4-dioxane in UV/S$_2$O$_8^{2-}$, UV/H$_2$O$_2$, UV/NH$_2$Cl

In general, UV/S$_2$O$_8^{2-}$ had faster kinetics with respect to 1,4-dioxane removal than UV/H$_2$O$_2$ and UV/NH$_2$Cl (**Figure 39**). UV/S$_2$O$_8^{2-}$ had a higher quantum yield than UV/H$_2$O$_2$ (0.7 vs. 0.5), and produced a diverse set of radicals including both SO$_4^{\bullet-}$ and HO$^{\bullet}$.[53] UV/NH$_2$Cl produced less reactive Cl$^{\bullet}$ and Cl$_2^{\bullet-}$, which both had slow kinetics with 1,4-dioxane transformation.[54] Furthermore, the NH$_2$Cl itself was a strong scavenger and decreased radical yield.[54] Product distribution in three UV/AOPs showed similar product evolution pathways after 1,4-dioxane was oxidized (**Scheme 11**). The oxidation products

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included ethylene glycol diformate (EGD), formaldehyde (FD), glycolaldehyde (GD), glycolic acid (GA), formic acid (FA), and methoxyacetic acid (MA), which were consistent with previous observations.[55] GA was not observed in $UV/S_2O_8^{2-}$ treatments, and EGD was not observed in treatments with UV/H_2O_2. In UV/NH_2Cl treatments, only aldehyde products were observed. Both $UV/S_2O_8^{2-}$ and UV/H_2O_2 promoted further oxidation of EGD, GD, and FD to FA, GA and MA, while UV/NH_2Cl did not efficiently degrade aldehyde products.
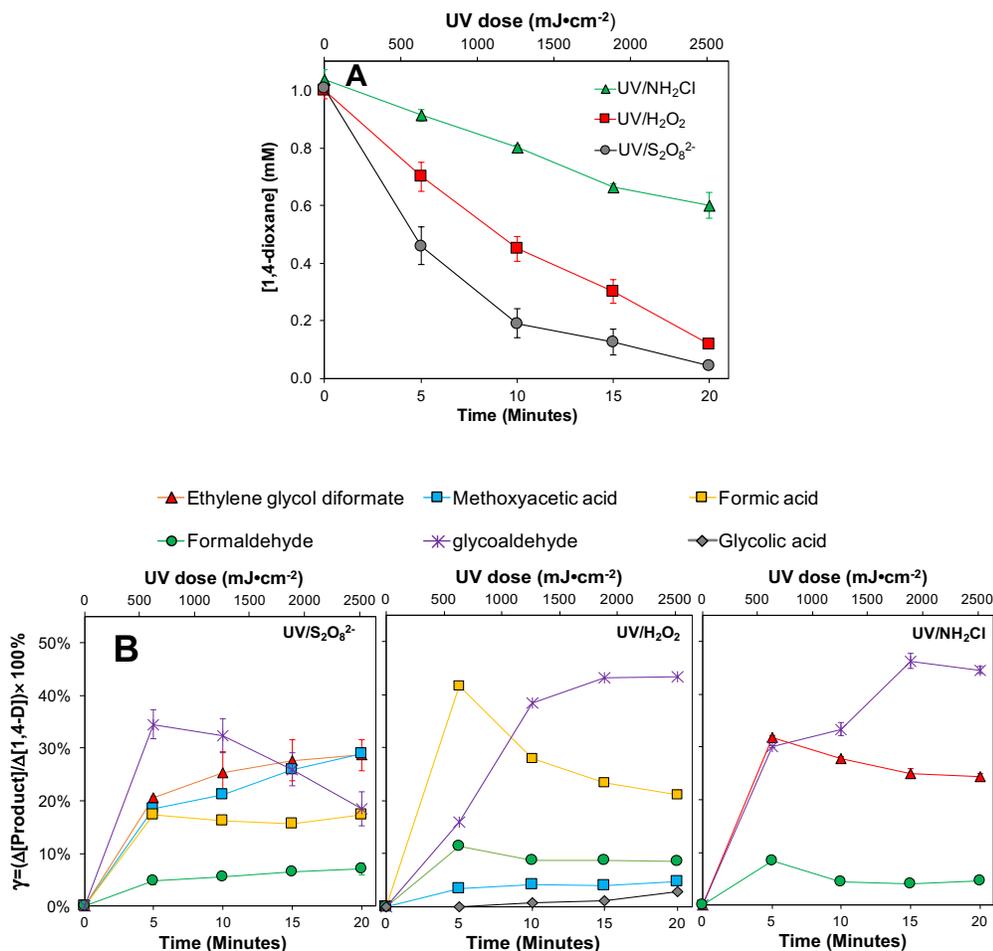
Figure 39. 1,4-D degradation and product (A) 1,4-D degradation; (B) Product form pH=8.
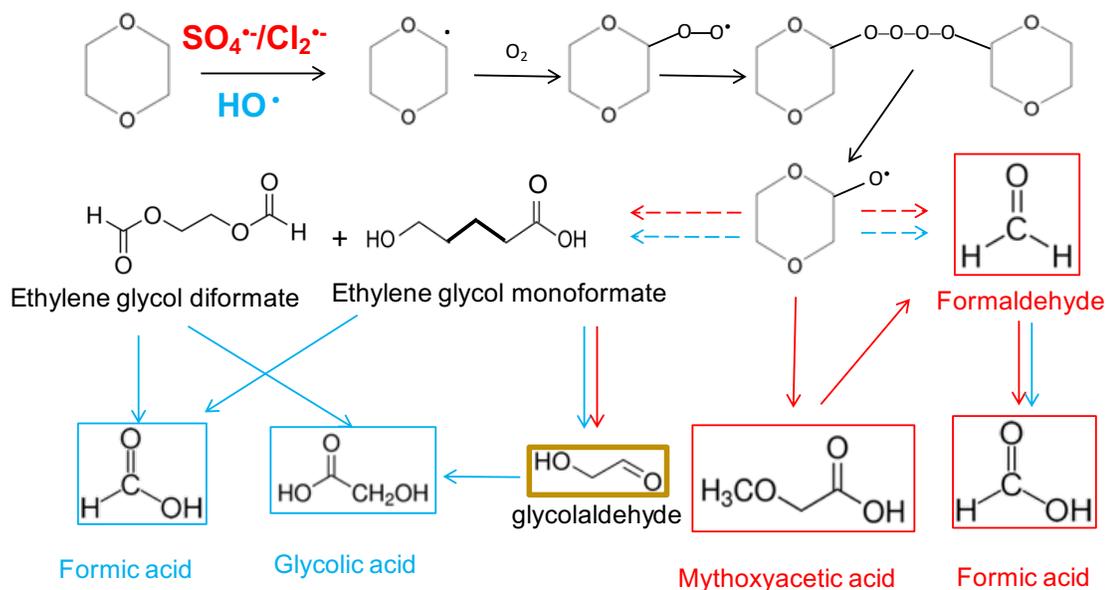
Scheme 11 Proposed 1,4-Dioxane degradation pathway in UV/$S_2O_8^{2-}$, UV/H_2O_2, and UV/NH_2Cl.

5.3.3 Cytotoxicity and genotoxicity of benzene and its OBPs

The EC_{50} of benzene and its oxidation products was derived from the concentration response curve shown in **Figure 40A** and listed in **Table 15**. The cytotoxicity rank order was: aldehyde > phenol > benzene, with aldehyde being the most cytotoxic (EC_{50}= 26 µM) followed by phenol (EC_{50}= 36 µM) and benzene (EC_{50} =292 µM). Genotoxicity also followed the same order (**Figure 40B**). The EC_{50} determined was 22 µM for aldehyde, 694 µM for phenol, and non-determinable for benzene. Unsaturated aldehydes have been reported to be 100-300-fold more cytotoxic to human bronchial fibroblasts than saturated aldehydes.[56] Unsaturated aldehydes affect cell servial and thiol levels by inhibiting the DNA repair enzyme, O^6-methylguanine-DNA methyltransferase.[56] It may also impair cellular defense mechansims such as DNA repair and detoxification, and make cells

suceptible to other toxic chemical.[56] In additon, unsaturated aldehydes are capble of inducing sister-chromatiid-exchange and production of micronuclei, which are indicators of genotoxicity.[57] Phenol has been used as positive control substance for cytotoxicity assays in Balb/c 3T3 cells and showed lineral cytotoxic responses.[58,59] Phenol induced cytotoxicity by generating phenoxyl radicals, that caused site-specific oxidative stress in the membrane phospholipids and decreased protein SH groups.[60] Phenol induced chromatid breaks and exchanges which resulted in DNA damage.[61] Benzene has also been reported to induce cytotoxicity and genotoxicity in bone marrow cells; however, the mechansim is still unclear.[62]
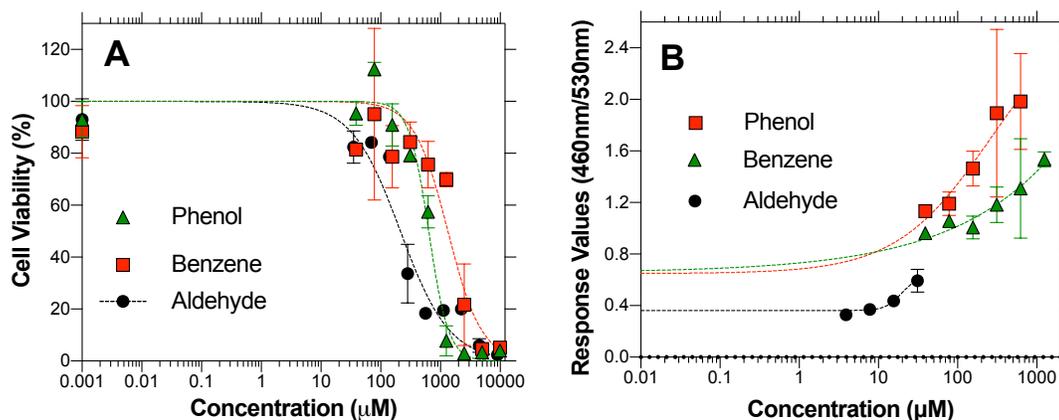
Figure 40 (A) Cytotoxicity and (B) Genotoxicity concentration response curves of benzene, phenol, and aldehyde. Each value represents the mean of three replicates ± standard deviation.

Table 14. EC_{50} values of benzene and its degradation products in P53RE-bla HCT-116 cell line after 16h exposure.

Toxic rank order	Benzene & DPs	Cytotoxicity EC_{50}(uM)	Genotoxicity EC_{50}(uM)
1	Aldehyde	$26 \pm 27\%$	$20 \pm 59\%$
2	Phenol	$36 \pm 13\%$	$256 \pm 81\%$
3	Benzene	$202 \pm 36\%$	-

5.3.4 Cytotoxicity and genotoxicity of 1,4-dioxane and its OBPs

Figure 41A presents a concentration-response curve of cell viability for 1,4-Dioxane, FD and GD in HCT-116 cells. Other compounds that had negligible cytotoxicity were shown in **Figure 42**. The EC_{50} concentrations were reported in **Table 15**, with GD being the most cytotoxic (EC_{50}= 155 µM) followed by FD (EC_{50} =613 µM). The rank order for cytotoxicity of 1,4-dioxane and its OPDs based on their LC_{50} values was: GD > FD > FA > GA > 1,4-Dioxane > EGD ≈ MA. In general, aldehyde compounds (*i.e.*, GD and FD) exhibited high cytotoxicity except EDF. GD was highly cytotoxic to HK-2 cells and caused depletion of adenosine triphosphate (ATP), release of lactate dehydrogenase (LDH), and degradation of enzymes as well as selected phospholipids. [63] GD also induced growth inhibition and oxidative stress in human breast cancer cells.[64] FD is a known carcinogen and highly reactive with proteins and DNA. [65] FD-induced cytotoxicity inhibited mitochondrial respiration, decreased ATP depletion, and generated reactive oxygen species which contributed to oxidative stress and cell lysis in isolated rat hepatocytes.[66] EGD has two carbonyl groups; however, when applied to HCT-116 cells, cell viability was not reduced in the present study. Although studies on the toxicity of EGD have not been

reported, our data suggests EGD might be quickly metabolized to downstream products that are not cytotoxic.
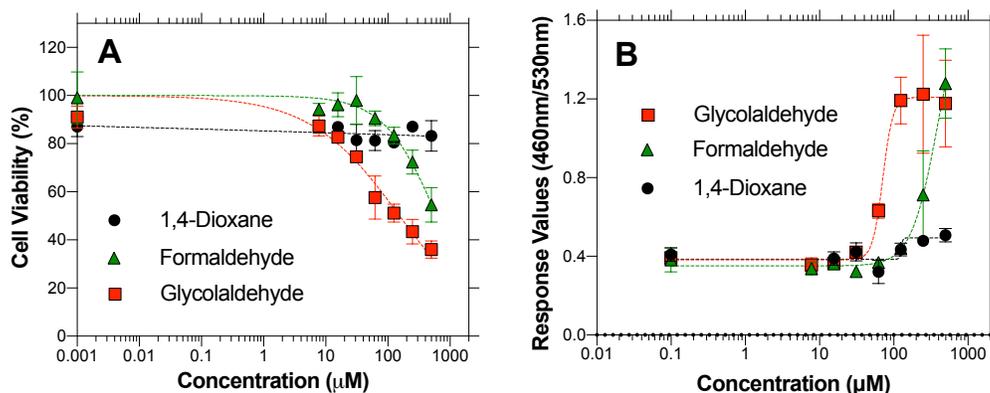
Figure 41. (A) Cytotoxicity and (B) Genotoxicity dose response curves of 1,4-dioxane, Formaldehyde, and glycolaldehyde. Each value represents the mean of three replicates ± standard deviation.

Table 15. LC_{50}, EC_{50} and relative effect potency (REP) values of 1,4-dioxane and its degradation products in P53RE-bla HCT-116 cell line after 16h exposure.

Toxicity-level Ranking	Chemicals	Cytotoxicity $EC_{50}(uM)$	Genotoxicity $EC_{50}(uM)$	REP*
1	Glycolaldehyde	$(1.6\pm0.2)\times10^2$	$(7.1\pm1.0)\times10^1$	6.7×10^{-2}
2	Formaldehyde	$(6.1\pm0.9)\times10^2$	$(4.0\pm2.5)\times10^2$	1.2×10^{-2}
3	Formic acid	$(1.3\pm30)\times10^{14}$	-	-
4	Glycolic acid	$(7.8\pm31)\times10^{15}$	-	-
5	1,4-dioxane	$(1.1\pm5.2)\times10^{29}$	$>(2.0\pm7.9)\times10^4$	2.4×10^{-4}

* Relative genotoxicity effect potency values, $REP=EC_{50(mitomycine)}/EC_{50(i)}$, where *i* is a specific degradation product.

Aldehydes are highly reactive electrophilic molecules that damage DNA through formation of aldehyde-derived DNA adducts. [67,68] The genotoxicity assay using P53-GeneBLAzer Assay indicated that aldehyde compounds were highly genotoxic (**Figure 41B**) compared to 1,4-dioxane and its carboxylic acid degradates (**Figure 42B**). The EC_{50}

concentrations were 71 μM for GD and 395 μM for FD (**Table 15**). 1,4-dioxane showed

relatively low genotoxicity with an EC50>20000 μM. GD has been reported to cause DNA-

protein crosslinks and DNA single-strand breaks in human peripheral ononulcear blood

cells.[69] Similarly, FD formed adducts with DNA and proteins,[70] and resulted in

chromosome loss due to formaldehyde-induced defects in the mitotic apparatus.[71] In

agreement with our observation, 1,4-dioxane produced negative genotoxicity responses in

several in vitro assays.[72,73] A few studies reported that 1,4-dioxane elevated chromosamal

breaks and DNA repairs in rats or mice with chronical injection of 1,4-dioxane.[74,75] Our

results indicated that 1,4-dioxane is a weak geno-toxinant to human cells. In contrast, its

aldehyde OBPs were extreamtly toxic to human cells.
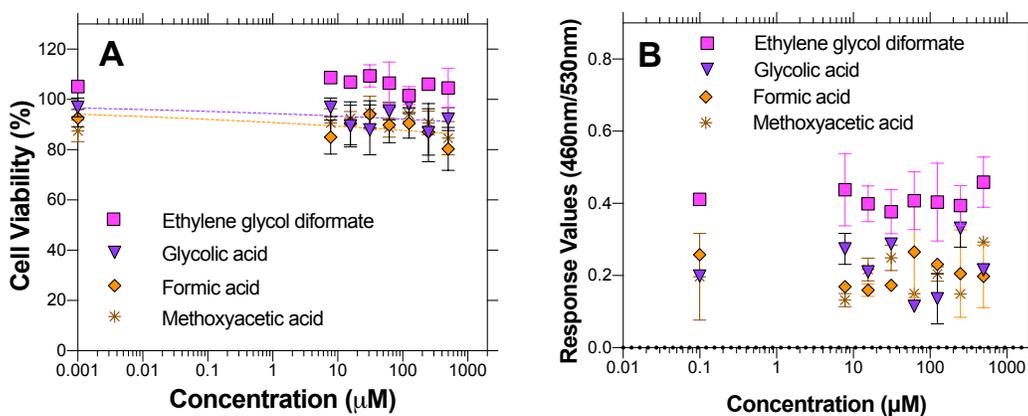
Figure 42 (A) Cytotoxicity and (B) Genotoxicity dose response curves of Ethylenen glycol diformate, glycolic acid, formic acid and methoxyacetic acid. Each value represents the mean of three replicates ± standard deviation.

5.3.5 Genotoxicity comparison among $UV/S_2O_8^{2-}$, UV/H_2O_2, and UV/NH_2Cl treatments

The mitomycin equivalency quotient (MEQ) at the beginning (0 minute), middle

(10 minutes), and end (20 minutes) of the UV treatment was compared for the three

UV/AOP treatments (**Figure 43**). At the beginning of the treatment, 1,4-dioxane was only chemical present in the system with a mitomycin EQ of 2.4×10^{-4}. After 10 minutes of UV irradiation, $UV/S_2O_8^{2-}$, UV/H_2O_2, and UV/NH_2Cl treatments increased the mitomycin EQs from 2.4×10^{-4} to 1.9×10^{-2}, 1.6×10^{-2}, and 4.0×10^{-3}, respectively (Figure 3). Glycolaldehyde was consistently the major contributor to the mitomycin EQs in the three AOP treatments (**Table 15** and **Figure 13**). After 20 min $UV/S_2O_8^{2-}$ treatment, the mitomycin EQ was decreased from 1.9×10^{-2} to 1.2×10^{-2}, due to the oxidation of glycolaldehyde to non-toxic carboxylic acids (**Figure 13**). In contrast, UV/H_2O_2, and UV/NH_2Cl treatments further increased the mitomycin EQs 2 to 3 folds after 20 minutes (Figure 3), which was consistant with the 2-3-fold increase of glycolaldehyde concentrations. The results suggest that $UV/S_2O_8^{2-}$ can quickly oxidize 1,4-dioxane and further degrade its products; while UV/H_2O_2 and UV/NH_2Cl degraded 1,4-dioxane at slower rates, resulting in an accumulation of toxic glycolaldehyde during the treatment. In comparison with UV/H_2O_2, UV/NH_2Cl exhibited lower TEQ because UV/NH_2Cl was inefficient to degrade 1,4-Dioxane, as evidenced by the large portion of 1,4-dioxane remaining after 20-minutes of treatment.
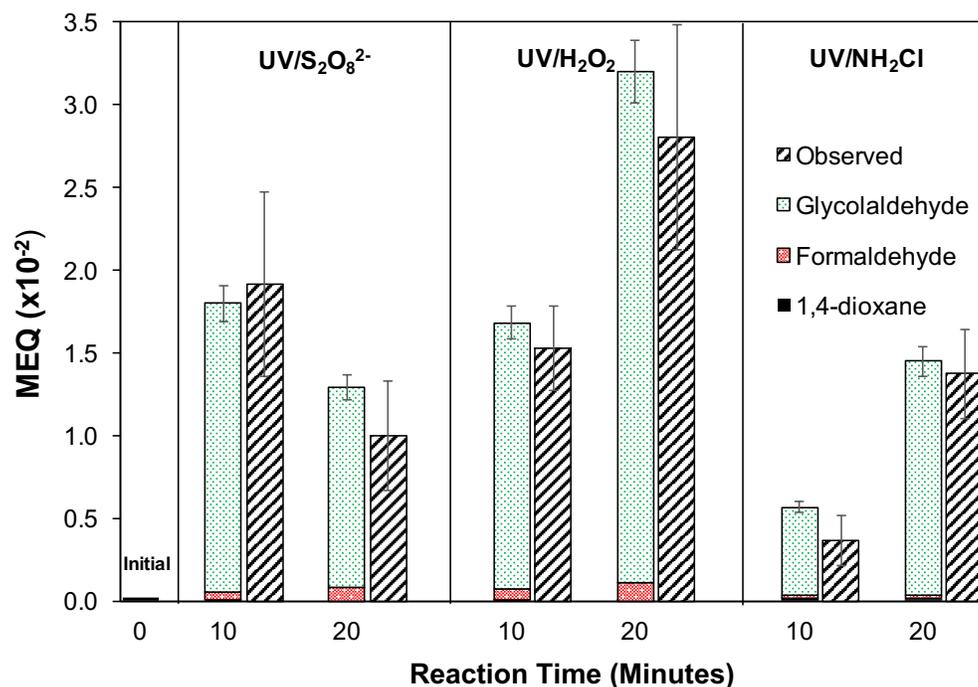
Figure 43. Mitomycin Equivalent of genotoxicity evolution during UV/AOPs treatment. Observed Mitomycin Equivalent was the calculated based on experimentally obtained EC_{50} (Details please refer to Text S5). Error bars represent SQRT. UV/$S_2O_8^{2-}$: two-way ANOVA test showed no difference between calculated and observed MEQ (P=0.677); and a significant difference between MEQ at time 0, 10 and 20 (P=0.014). UV/H_2O_2: calculated vs. Observed (P=0.254); time factor (P=0.0043). UV/NH2Cl: calculated vs. Observed (P=0.250); time factor (P=0.005).

5.4 Engineering Implications

AOPs are usually implemented in ISCO and water reuse treatment processes due to their ability to degrade contaminants. However, our study brought up the concerns of the formation of more toxic OBPs during AOP treatments while treating toxic contaminants in groundwater or recycled wastewater. Oxidizing benzene by mineral-activated $S_2O_8^{2-}$ and H_2O_2 generated more toxic phenol and an unsaturated aldehyde. In the case of 1,4-dioxane degradation by UV/$S_2O_8^{2-}$, UV/H_2O_2, and UV/NH$_2$Cl, the oxidation

generates glycolaldehyde and formaldehyde that are 100 times more toxic than 1,4-dioxane. For many aromatic compounds, the initial oxidation steps usually leads to the formation of aldehydes as intermediates with high geno- and cyto- toxicity. Despite the low-level existence of OBPs in highly treated water, the risk of long term exposure warrants great attention. Our results also demonstrate that $S_2O_8^{2-}$ is a much more stable oxidant than H_2O_2 when applied to ISCO treatment, and can completely remove parent compound and oxidation products with extended treatment. UV/ $S_2O_8^{2-}$ is also superior to UV/H_2O_2 and UV/NH_2Cl in terms of minimizing the formation of more toxic OBPs. For instance, UV/$S_2O_8^{2-}$ showed a better efficiency in degrading both 1,4-dioxane and its OBPs t nontoxic derivatives than UV/H_2O_2, and UV/NH_2Cl.

5.5 Acknowledgments

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Chapter 6

Summary and Conclusions

Activated $S_2O_8^{2-}$ has recently gained popularity in ISCO applications. Alternatively, $S_2O_8^{2-}$ would be applied in advanced treatment train for portable water reuse. However, the underlying activation mechanism is not fully understood. Hence, the goal of this dissertation was to investigate and better understand the kinetics and mechanism of $S_2O_8^{2-}$ -based AOPs in ISCO and UV/AOP applications. To that end, we explored how common chemical constituents, such as carbonate, chloride, and pH can impact benzene degradation by mineral-activated $S_2O_8^{2-}$ when applied to ISCO (Chapter 2); how the presence of NH_2Cl, chloride, pH and oxygen levels impacted 1,4-dioxane removal when $S_2O_8^{2-}$ was used as oxidant in UV/AOPs for treating RO permeate (Chapter 3); How to develop a kinetic model to predict the large scale UV/AOP treatment efficiency and elucidate underlying chemical mechanism (Chapter 4); and what oxidation byproducts could be formed during the $S_2O_8^{2-}$ -based AOPs, and how the toxicity potency of the degradation products were compared to the parent compounds (Chapter 5).

6.1 Persulfate-Based ISCO for Groundwater Remediation: Impacts of Alkalinity, pH and Chloride

In Chapter 2, we examined the impacts of alkalinity, pH and chloride on benzene degradation by heterogeneously activated $S_2O_8^{2-}$. $S_2O_8^{2-}$ was activated by ferrihydrite, goethite and pyrolusite to generate $SO_4^{\cdot-}$. Benzene was used as a model aquifer contaminant. A comprehensive kinetic model was established to elucidate the mechanisms of radical generation, mineral surface complexation and radical distribution. A few key findings were derived from this study.

First, the surface area-normalized rates of $S_2O_8^{2-}$ decomposition and benzene degradation followed the order of pyrolusite > goethite > ferrihydrite. The $S_2O_8^{2-}$ decomposition was mainly due to Fenton-like reactions involving oxidized and reduced surfaces sites of metal oxides reacting with $S_2O_8^{2-}$. Benzene degradation was primary due to $SO_4^{\bullet-}$. However, $SO_4^{\bullet-}$ was also scavenged by reactive mineral surface complexes such as ferrihydrite, which lowers the radical yield.

Second, an increase of alkalinity from 0 to 10 meq/L decreased the rates of $S_2O_8^{2-}$ decomposition and benzene degradation. Carbonate species, especially CO_3^{2-} are strong chelating agents that form carbonano-complexes with mineral surfaces and decreases the reactivity of the surfaces. The presence of alkalinity also transformed reactive $SO_4^{\bullet-}$ and $HO^{\bullet}$ to non-reactive $CO_3^{\bullet-}$, which hindered benzene degradation.

Third, an increase in pH from 8 to 12 generally accelerated $S_2O_8^{2-}$ decomposition and benzene degradation due to enhanced formation of reactive surface hydroxo complexes. However, a further pH increase from 12 to 13 decreased the reaction rate because the concentrations of reactive hydroxo surface complex decreased by 10 times from pH 12 to 13 due to hydroxo surface equilibrium.

Forth, a change in the chloride level up to 5 mM had a negligible effect on the reaction kinetics because chloride did not strongly impact mineral surface complexes. Although, the presence of chloride accelerated the transformation of $SO_4^{\bullet-}$ to $CO_3^{\bullet-}$, it also prevented the formation of carbonato complexes, hence, the overall rates of $S_2O_8^{2-}$ decomposition and benzene degradation were not affected.

Finally, both phenol and aldehyde were identified as the major transformation products of benzene degradation. The yields of phenol and aldehyde were positively correlated with the branching ratio of $SO_4^{\bullet-}$ reacting with benzene, but inversely correlated with that of $HO^{\bullet}$ or $CO_3^{\bullet-}$, indicating that $SO_4^{\bullet-}$ preferentially oxidized benzene via pathways involving fewer hydroxylation steps compared to $HO^{\bullet}$ or $CO_3^{\bullet-}$.

This study demonstrated that $S_2O_8^{2-}$-based ISCO is applicable to groundwater remediation with elevated salinity, however, the remediation efforts need to pay special attention to native alkalinity and pH levels. These factors can alter the redox reactivity in the aquifer and the effectiveness on persulfate activation. Results also suggest that aquifers with abundant goethite can increase the persistence of persulfate and increase remediation efficiency. Although aquifer minerals with higher abundance of ferrihydrite and pyrolusite can accelerate persulfate decomposition, these minerals tend to have lower stoichiometric efficiency of radical yields.

6.2 $S_2O_8^{2-}$-Based AOPs for Potable Water Reuse

In Chapter 3, we studied the application of $S_2O_8^{2-}$ as an alternative oxidant to replace H_2O_2 in UV/AOPs for treating 1,4-dioxane, a contaminant that readily passes through RO membranes. The impact of antifouling agent, NH_2Cl, chloride, pH and oxygen were examined. The results presented in Chapter 3 contain four key findings.

First, the results suggested that NH_2Cl-to-$S_2O_8^{2-}$ molar ratio of 0.1 exhibited the highest treatment efficiency. Beyond this ratio, NH_2Cl has a photon filtering effect that competed with $S_2O_8^{2-}$ for UV light. NH_2Cl photolysis rate increased with increasing dosage,

while $S_2O_8^{2-}$ photolysis was suppressed. Although, NH_2Cl was quickly photolyzed, it produced less reactive $Cl^{\bullet}$ and $NH_2^{\bullet}$. Furthermore, high NH_2Cl dosage significantly scavenged $HO^{\bullet}$, $SO_4^{\bullet-}$, and $Cl_2^{\bullet-}$ radicals and decreased 1,4-dioxane degradation rate.

Second, at the optimal ratio, the degradation rate of 1,4-dioxane increased linearly with the increasing total oxidant dose up to 6 mM. When the total oxidant dosage exceeded 6 mM, major scavenging by $S_2O_8^{2-}$ reduced the$[HO^{\bullet}]_{ss}$, thus 1,4-dioxane degradation rate also reduced. In contrast, at 1:1-ratio, 1,4-dioxane degradation rate was 33 to 240% lower compared to that at 0.1:1 ratio, and the optimal condition was observed at 4 mM. At 1:1-ratio, the high NH_2Cl dosage decreased the yield of $HO^{\bullet}$ and $SO_4^{\bullet-}$.

Third, the major products of NH_2Cl photolysis were NH_4^+, nitrate, gaseous nitrogen and organic nitrogen, and products of $S_2O_8^{2-}$ photolysis was sulfate (SO_4^{2-}), with a 2:1 stoichiometry. In addition, $UV/S_2O_8^{2-}$ promoted gaseous nitrogen formation and decreases the formation of undesired NH_2Cl decay products, NH_4^+ and organic nitrogen.

Fourth, the presence of chloride hindered 1,4-dioxane degradation rate in $UV/S_2O_8^{2-}$ due to the transformation of reactive $HO^{\bullet}$ and $SO_4^{\bullet-}$ to less reactive $Cl_2^{\bullet-}$. Furthermore, the simultaneous photolysis of NH_2Cl and $S_2O_8^{2-}$ was sensitive to the solution pH, due to a disproportionation of NH_2Cl into less photo-reactive dichloramine ($NHCl_2$) and radical scavenger NH_4^+ at pH lower than 6. Presence of dissolved O_2 also promoted 1,4-dixoane degradation by participating in the 1,4-dioxane and NH_4^+ oxidation steps.

Results from this study suggested that the presence of NH_2Cl can be beneficial to $UV/S_2O_8^{2-}$ to remove 1,4-dioxane, however, the treatment efficiency depends on a careful

control of an optimal NH_2Cl dosage and a minimal chloride residue. Results from this study assist in the development of more efficient UV/AOP technologies for potable water reuse.

6.3 Modeling Approach for Simulating and Comparing Full Scale UV/H_2O_2, UV/$S_2O_8^{2-}$, and UV/HOCl

In chapter 4, we developed a kinetic model using open source software, Kintecus, to compare the treatment efficiency of UV/H_2O_2, UV/$S_2O_8^{2-}$, and UV/HOCl on the degradation of six representative trace organic contaminants namely 1,4-dioxane, carbamazepine, phenol, 17β-estradiol, aniline, and sulfamethoxazole. The fundamental mechanisms of radical generation, radical distribution, and contaminant degradation in three UV/AOPs were investigated. The impacts of RO permeate chemical constituents including pH, chloride and inorganic carbon were examined. The analysis of the results in Chapter 4 revealed four key findings.

First, results showed that the treatment efficiency of contaminants generally followed the order of UV/$S_2O_8^{2-}$ > UV/H_2O_2 > UV/HOCl，because $S_2O_8^{2-}$ photolyzed faster than H_2O_2 and generated higher levels of both $SO_4^{\bullet-}$ and $HO^{\bullet}$. In UV/$S_2O_8^{2-}$ treatment, both $SO_4^{\bullet-}$ and $HO^{\bullet}$ were important for contaminant degradation. In UV/H_2O_2 treatment, $HO^{\bullet}$ contributed the most to the contaminant degradation with the exception that $CO_3^{\bullet-}$ was important for aniline and sulfamethoxazole degradation. Interestingly, $CO_3^{\bullet-}$ was predominate in UV/HOCl due to fast kinetics of the reaction between chloride and carbonates.

Second, the model results suggested that $UV/S_2O_8^{2-}$ was most sensitive to pH, $UV/HOCl$ was modestly sensitive to pH, and UV/H_2O_2 was insensitive to pH. This was because at pH 7, HCO_3^- was the dominant carbonate species. In $UV/S_2O_8^{2-}$ and $UV/HOCl$ treatments, both $SO_4^{\bullet-}$ and $Cl^\bullet$ could be quickly transformed into $CO_3^{\bullet-}$ by HCO_3^- at pH 7, which had lower reactivity with contaminants. While in UV/H_2O_2 treatment, $HO^\bullet$ equilibrated with chloride and not significantly impacted by HCO_3^- with increasing pH.

Third, the sensitivity to chloride follows the following order: $UV/S_2O_8^{2-}$ > $UV/HOCl$ > UV/H_2O_2. In $UV/S_2O_8^{2-}$, the presence of chloride accelerated the transformation of $SO_4^{\bullet-}$ to $Cl^\bullet$, which quickly reacting with HCO_3^- to generate $CO_3^{\bullet-}$. The same mechanism was also observed in $UV/HOCl$. However, UV/H_2O_2 was not sensitive to chloride because it reacted with chloride to generate of $ClOH^{\bullet-}$, but the dissociation of $ClOH^{\bullet-}$ quickly regenerated $HO^\bullet$.

Forth, carbonates also exhibited higher influence in treatments of $UV/S_2O_8^{2-}$ and $UV/HOCl$ than in UV/H_2O_2, mainly because both $SO_4^{\bullet-}$ and $Cl^\bullet$ reacted quickly with carbonates to form non-reactive $CO_3^{\bullet-}$. In contrast, UV/H_2O_2 was not sensitive to carbonates because it reacted faster with chloride than with carbonates.

Overall in Chapter 4, the combined experimental and modeling approach provided fundamental chemistry understanding on different UV/AOPs and guidance on the design and optimization of UV/AOP systems for water reuse under diverse chemical conditions. Among three UV/AOPs, $UV/S_2O_8^{2-}$ demonstrated the highest treatment performance. However, it was more sensitive to pH, chloride, and inorganic carbon than the other two

UV/AOPs. UV/H_2O_2 exhibited higher treatment efficiency than UV/HOCl for some groups of contaminants, but its performance is limited by the rate of H_2O_2 photolysis. UV/HOCl is unique to the other AOPs in that it favors the generation of $CO_3^{\cdot-}$, and very effective in degrading amine-containing contaminants.

6.4 Toxicity Assessment of Benzene and 1,4-dioxane Oxidation Byproducts

In chapter 5, the formation and distribution of oxidation byproducts of benzene and 1,4-dioxane during various AOPs were compared. The cytotoxicity and genotoxicity of the individual byproducts and the toxicity evolution of 1,4-dioxzne during the AOP treatments were evaluated using HCT-116 Human colorectal carcinoma cells. Three key findings were observed in this study.

First, results showed that benzene was transformed to phenol and unsaturated aldehyde products in both goethite-activated $S_2O_8^{2-}$ and H_2O_2 treatments, and no products were observed in MnO_4^- treatment because benzene was not oxidized by MnO_4^- in the experimental period examined in this study (*e.g.* 14 days). 1,4-dioxane was transformed to six major intermediates after UV/$S_2O_8^{2-}$ and UV/H_2O_2 treatments including ethylene glycol diformate, formaldehyde, glycolaldehyde, glycolic acid, formic acid, and methoxyacetic acid. Only aldehyde products were observed in UV/NH_2Cl treatment.

Second, both genotoxicity and cytotoxicity studies indicated that aldehyde byproducts were way more toxic than benzene or 1,4-dioxane. Aldehyde and phenol from benzene oxidation was 10 times more toxic than benzene. Similarly, formaldehyde and glycolaldehyde were a few folds more toxic than 1,4-dioxane. The rank order for

cytotoxicity of benzene and its oxidation byproducts based on their LC50 values was: aldehyde > phenol > benzene. The rank order for 1,4-dioxane and OBPs was: GD > FD > FA > GA > 1,4-Dioxane > EGD ≈ MA. Unsaturated aldehyde, phenol, GD and FD induced strong genotoxicity, whereas benzene and 1,4-dioxane exhibited weak genotoxicity.

Third, 1,4-dioxane oxidation increased total toxicity during the three UV/AOPs, mainly because of the formation of glycolaldehyde. Fortunately, $UV/S_2O_8^{2-}$ could further reduce the toxicity with extended treatment time due to the transformation of toxic aldehydes to less toxic organic acids.

This study suggests UV/AOP treatments could produce OBPs with higher geno- and cyto- toxicity than their parent compounds, which calls for new treatment strategies to minimize the formation of more toxic oxidation byproducts when applying AOP treatments to remove CECs. For many aromatic compounds, the initial oxidation steps usually lead to the formation of aldehydes as intermediates with high geno- and cyto- toxicity. Despite the low-level existence of OBPs in highly treated water, the risk of long term exposure warrants great attention. Our results also suggested that there would be strategies for minimizing the formation of more toxic OBPs. For instance, $S_2O_8^{2-}$-based AOP can significantly decrease the formation of toxic byproducts with extend treatment time. In both ISCO and wastewater recycle scenario, $UV/S_2O_8^{2-}$ showed a better efficiency in degrading benzene, 1,4-dioxane and their OBPs than other AOPs.

Appendix A

Supplemental Information for Chapter 2

Appendix A-1 Surface site concentration of ferrihydrite, goethite and pyrolusite.

The surface site concentrations were calculated based on prior literature values of surface density and the surface area of each mineral measured in this study. Based on prior literature, the surface density of ferrihydrite, goethite and pyrolusite was 2.0×10^{-1} mole site/mole Fe(III), 1.6×10^{-2} mole site/mole Fe(III) and 8.7×10^{-2} mole site /mole Mn(IV), respectively.[1-3] These literature values were reported for minerals with a particular surface area. The surface area of each mineral used in this study was directly measured and listed in Table S1. Accordingly, the actual surface site concentrations of each mineral in this study was calculated based on the prior literature values and adjusted with the experimentally measured surface area.

The surface site concentration of ferrihydrite was calculated as:

$$C_{surface\ sites} = \frac{100\ g\ ferrihydrite}{L} \times \frac{180\ m^2}{g} \times \frac{g}{600\ m^2} \times \frac{1\ mole}{88.9g} \times \frac{2.0 \times 10^{-1}\ mole\ sites}{mole\ ferrihydrite}$$

$$= 6.7 \times 10^{-2}\ M\ sites$$

The surface site concentration of goethite was calculated as:

$$C_{surface\ sites} = \frac{100\ g\ goethite}{L} \times \frac{1\ mole}{88.9g} \times \frac{21\ m^2}{g} \times \frac{g}{79\ m^2} \times \frac{1.6 \times 10^{-2}\ mole\ sites}{mole\ goethite}$$

$$= 4.8 \times 10^{-3}\ M\ sites$$

The surface site concentration of pyrolusite was calculated as:

$$C_{surface\ sites} = \frac{100\ g\ pyrolusite}{L} \times \frac{1\ mole}{86.9g} \times \frac{1.1 \times 10^{-1}\ m^2}{g} \times \frac{g}{188\ m^2} \times \frac{8.7 \times 10^{-2}\ mole\ sites}{mole\ pyrolusite}$$

$$= 5.9 \times 10^{-5} M\ sites$$

Appendix A- 2 High performance liquid chromatography and its operating conditions.

Chromatographic separation of benzene and its products was achieved using an Agilent 1200 high performance liquid chromatography equipped with a Diode array detector. A Zorbax Eclipse XDB-C18 column (4.6×50mm, 1.8 μm particle size) equipped with a guard column (Eclipse XDB-C18, 4.6×12.5mm) was used. 10 mM formic acid and pure acetonitrile were used as eluents. The composition of eluents was optimized and changed with elution time for better peak separations. Specifically, between 0 and 4.5 minutes of elution, the eluent was 97% formic acid and 3% acetonitrile. Between 4.5 and 7 minutes, the eluent was 30% formic acid and 70% acetonitrile. Between 7 and 10 minutes, the eluent was 97% formic acid and 3% acetonitrile. The sample injection volume was 100μL and the flow rate was set at 1.0 mL/min. The calibration curves of benzene and phenol were first established under the conditions described above and the concentration of benzene and phenol were quantified based on the peak areas recorded.

Appendix A-3 Details on the comprehensive kinetic modeling

The kinetic model on persulfate decomposition and benzene degradation was built on the platform of Kintecus 4.55 software. A total of 77 and 56 elemental reactions were established to model persulfate decomposition and benzene degradation in the presence of Fe(III) oxide and Mn(IV) oxide, respectively. All reactions incorporated in the kinetic model were summarized in Table S2. Of 77 reactions for Fe(III) oxides, 67 rate constants were directly obtained from radiolysis literature. For the rest of the reactions with unknown rate constants, four reactions involving homogeneous persulfate activation by soluble Fe(III) were optimized using experimental data from persulfate activation by soluble Fe(III), and rate constants of six reactions involving heterogeneous persulfate activation by ferrihydrite and goethite were optimized using experimental data at different alkalinity, pH, and chloride levels. Of 56 reactions involving Mn(IV) oxide, 53 rate constants were directly obtained from radiolysis literature. The remaining three unknown rate constants involving heterogeneous persulfate activation by pyrolusite was also model-derived based on the experimental data. Soluble Mn(IV) activation of persulfate was not considered due to the extremely low solubility of pyrolusite.

Specifically, among reactions with known rate constants, rate constants of eight reactions for each mineral involving hydroxo and carbonato surface complexation were derived based on the published values of equilibrium constants (Reactions 25-40 in Table 1 of the main text and Reactions 46-53 and 60-67 in Table S2 of the SI).

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Using ferrihydrite as an example, three hydroxo surface complexes exist at the pH ranging between 8 and 13: $\equiv Fe(III)\text{-}OH_2^+$, $\equiv Fe(III)\text{-}OH^0$ and $\equiv Fe(III)\text{-}O^-$ (pK_1=7.29; pK_2=8.93).[1] The first step of protonation/deprotonation between $\equiv Fe(III)\text{-}OH_2^+$ and $\equiv Fe(III)\text{-}OH^0$ involves the forward reaction (R1) and the reverse reaction (R2) as follows:

$$\equiv Fe(III) - OH_2^+ \rightarrow \equiv Fe(III) - OH + H^+ \qquad \text{(R1)}$$

$$\equiv Fe(III) - OH + H^+ \rightarrow \equiv Fe(III) - OH_2^+ \qquad \text{(R2)}$$
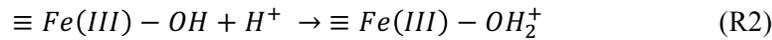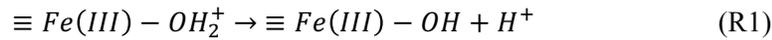
The rate constant of the reverse reaction (k_2) was fixed at 1×10^{11} M^{-1}s^{-1} (*i.e.*, the maximal diffusion-limited rate constant for a second-order reaction). The choice of a very large value of rate constants ensured an instantaneous equilibrium of metal hydroxo surface complexes. The rate constant of the forward reaction (k_1) was calculated as:

$$k_1 = K_1 \times k_2$$

K_1 is the equilibrium constant between $\equiv Fe(III)\text{-}OH_2^+$ and $\equiv Fe(III)\text{-}OH^0$ for the following equilibrium reaction:

$$\equiv Fe(III) - OH_2^+ \rightleftharpoons \equiv Fe(III) - OH + H^+ \qquad K_1 = 10^{-7.29}$$
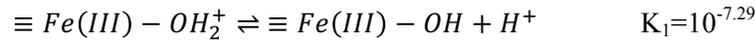
The ratio of k_1 to k_2 is always equal to the known equilibrium constant K_1.

Similar approaches were applied to the kinetic modeling of surface carbonato complexation reactions. Using ferrihydrite as an example, surface carbonato complexes are generated via $\equiv Fe(III)\text{-}OH^0$ in the presence of carbonate:

$$\equiv Fe(III) - OH + CO_3^{2-} + H^+ \rightarrow \equiv Fe(III) - OCO_2^- + H_2O \qquad \text{(R3)}$$

$$\equiv Fe(III) - OCO_2^- + H_2O \rightarrow \equiv Fe(III) - OH + CO_3^{2-} + H^+ \qquad \text{(R4)}$$
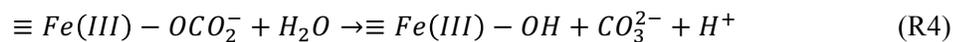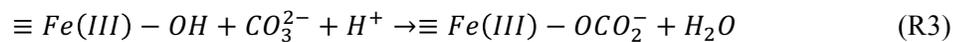
The rate constant of the forward reaction (k_3) was set at 1×10^{15} $M^{-2}s^{-1}$, *i.e.*, the maximal diffusion-limited rate constant for a third-order reaction. The choice of a very large value of rate constants ensured an instantaneous equilibrium of metal hydroxo surface complexes. and the rate constant of the reverse reaction (k_4) was calculated as:

$$k_4 = \frac{k_3}{\beta_2}$$

β_2 (log β_2=12.78)[4] is the equilibrium constant between $\equiv Fe(III)-OH$ and $\equiv Fe(III)-OCO_2^-$ for the following equilibrium:

$$\equiv Fe(III) - OH + CO_3^{2-} + H^+ \rightleftharpoons \equiv Fe(III) - OCO_2^- + H_2O \qquad \beta_2 = 10^{12.78}$$
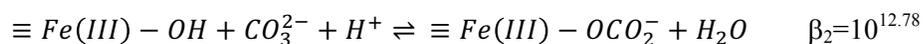
The ratio of k_3 to k_4 is always equal to the known equilibrium constant β_2.

Using this approach, the equilibria of all metal surface hydroxo and carbonato complexes were established in the Kintecus software platform as a series of fast forward and reverse reactions (Reactions 25-40 in Table 1 of the main text and Reactions 46-53 and 60-67 in Table S2 of the SI).

In addition, rate constants of four reactions (Reactions 2, 7, 22 and 42 in Table S2) involving homogeneous persulfate decomposition by soluble Fe(III) were optimized using the experimental data of persulfate activation by soluble Fe(III).

Rate constants of six reactions involving heterogeneous persulfate decomposition by ferrihydrite and goethite and rate constants of three reactions involving persulfate decomposition by pyrolusite were optimized using experimental data at different alkalinity, pH and chloride levels (Reactions 1-6 and 14-16 in Table 1 of the main text and Reactions

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54-59 and 68-70 in Table S2 of the SI). Using ferrihydrite as an example, firstly, persulfate activation by the surface hydroxo complexes of $\equiv$Fe(III)-O$^-$ (Reaction 3-4 in Table 1) and SO$_4$$^{\bullet-}$ scavenging reaction by $\equiv$Fe(III)-O$^-$ (Reaction 15 in Table 1) were fitted using the experimental dataset at pH 12 and 13 (Figure 3A-3B). Because the pK value of $\equiv$Fe(III)-OH/$\equiv$Fe(III)-O$^-$ deprotonation is 8.93,[1] $\equiv$Fe(III)-O$^-$ is the predominant hydroxo surface complex at pH 12 and 13, and Reactions 1-2 and 14 involving the surface complexes of Fe(III)-OH were negligible at pH 12 and 13. Accordingly, Reactions 1-2 and 14 were not considered during this first step of modeling.

The best model fitting of the rate constants for Reactions 3-4 and 15 were achieved by applying Powell non-restricted algorithms to minimize the root mean squares (RMS) between the model prediction and experimental observation based on the kinetics of persulfate decomposition and benzene degradation. Following that, two sets of rate constants were obtained at pH 12 and 13. The average values of the rate constants with standard deviations were calculated based on the fitting results at these two pHs.

Secondly, the rate constants of Reactions 1-2 and 14 in Table 1 were modelled using nine sets of experimental data, including experiments conducted at pH 8 and 10 (two sets of data shown in Figures 3A and 3B), three alkalinity levels (three sets of data shown in Figures 2A and 2B) and four chloride levels (four sets of data shown in Figures S4A and S4B). The rate constants of Reactions 1-2 and 14 were modelled independently for nine times, using one set of data each time. The average values of the rate constants with standard deviations were calculated from these nine sets of data accordingly.

Same procedures were applied to model the rate constants of persulfate activation by surface complexes of goethite (Reactions 54-59 in Table S2), which were fitted using the experimental data set at different levels of pH (dataset from Figure 3C-3D), alkalinity (dataset from Figure 2C-D), and chloride (dataset from Figure S4C-4D). Persulfate activation by the surface complexes of pyrolusite (Reaction 5-6 in Table 1, also shown as Reactions 68-69 in Table S2) and $SO_4^{\bullet-}$ scavenging reaction by surface complex of pyrolusite (Reaction 16 in Table 1, also shown as Reaction 70 in Table S2) were fitted using the experimental data set at different levels of pH (dataset from Figure 3E-3F), alkalinity (dataset from Figure 2E-F) and chloride (dataset from Figure S4E-4F).

Finally, the uncertainty analysis for the predicted steady-state concentrations of surface complexes was conducted using Kintecus software, which calculated the average values and standard deviations of each predicted parameter. Specifically, the modelled rate constants were randomized within the predicted rate constants ± standard deviations. The model ran one hundred simulations with varied rate constants using Gaussian distributed random numbers to calculate the confidence band at 95% confidence level.

Appendix A-4 Calculations on the contribution of each reaction to the total persulfate decomposition and the radical contribution to benzene degradation

Persulfate decomposition was contributed by Fenton-like reactions, surface reactions and radical reactions. Taking goethite as an example, the rate of persulfate decomposition by goethite was calculated as follows:

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_{obs}[S_2O_8^{2-}]$$

$$= (k_1 + k_2[Fe^{3+}]_{ss} + k_3[Fe^{2+}]_{ss} + k_{54}[\equiv Fe(III) - OH]_{ss} + k_{55}[\equiv Fe(II) - OH]_{ss} +$$

$$k_{56}[\equiv Fe(III) - O^-]_{ss} + k_{57}[\equiv Fe(II) - O^-]_{ss} + k_{20}[HO^\cdot]_{ss} +$$

$$k_{21}[SO_4^{\cdot-}]_{ss} + k_{22}[CO_3^{\cdot-}]_{ss} + k_{71}[Cl^\cdot]_{ss}) [S_2O_8^{2-}]$$

Where k_{obs} is the observed first-order rate constant of persulfate decomposition obtained from the experiments. All other k_i values (except for k_1) are the second-order rate constants corresponding to the reactions listed in **Appendix A-5**, where i stands for the number of reaction in **Appendix A-5**. For example, k_1 is the first-order rate constant for Reaction 1 in **Appendix A-5**, k_2 is the second-order rate constant for Reaction 2 in **Appendix A-5**. The same calculation was applied to ferrihydrite and pyrolusite. Reaction 2 and 3 were not included for pyrolusite because Mn(IV) and Mn(III) species were not soluble.

The percentile contribution of each reaction to the total rate of persulfate decomposition was calculated as the branching ratio of each reaction to the overall observed first-order rate constant.

The rate of benzene degradation was calculated as:

$$-\frac{d[benzene]}{dt} = k_{obs-benzene}[benzene]$$

$$= (k_{39}[SO_4^{\cdot-}]_{ss} + k_{40}[HO^{\cdot}]_{ss} + k_{41}[CO_3^{\cdot-}]_{ss} + k_{88}[Cl^{\cdot}]_{ss})[benzene]$$

Where $k_{obs-benzene}$ is the observed first-order rate constant of benzene degradation obtained from the experiments. All other k_i values are the second-order rate constants corresponding to the reactions listed in **Appendix A-5**, where i stands for the number of reaction in **Appendix A-5**. For example, k_{39} is the first-order rate constant for Reaction 39 in **Appendix A-5**.

The percentile contribution of $SO_4^{\cdot-}$ to benzene degradation was calculated as:

$$\%_{SO_4^-} = \frac{k_{39}[SO_4^{\cdot-}]_{ss}}{k_{obs-benzene}} \times 100\%$$

Similar calculations were conducted to quantify the contributions of $HO^{\cdot}$, $Cl^{\cdot}$ and $CO_3^{\cdot-}$ to benzene degradation.

Appendix A-5 Table of reactions and their rate constants used in the kinetic model.

No.	Reaction	Rate Constant (M^{-1} s^{-1})	Reference [*]
	Homogeneous Reactions		
1	$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$ (25 °C)	1.7×10^{-8}	5 [a]
2	$S_2O_8^{2-} + Fe^{3+} \rightarrow S_2O_8^{\cdot-} + Fe^{2+}$	$(6.6\pm1.2)\times10^{-2}$	
3	$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\cdot-} + SO_4^{2-} + Fe^{3+}$	2.7×10^{1}	6
4	$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$	7.2×10^{3}	7 [a,d]
5	$Fe^{2+} + SO_4^{\cdot-} \rightarrow SO_4^{2-} + Fe^{3+}$	9.9×10^{8}	8
6	$Fe^{2+} + HO^{\cdot} \rightarrow OH^- + Fe^{3+}$	3.5×10^{8}	9
7	$Fe^{2+} + CO_3^{\cdot-} \rightarrow CO_3^{2-} + Fe^{3+}$	$(4.7\pm0.8)\times10^{5}$	
8	$Fe^{2+} + HCO_3^- \rightarrow FeHCO_3^+$	9.3×10^{6}	10
9	$FeHCO_3^+ \rightarrow Fe^{2+} + HCO_3^-$	1.0×10^{5}	10 [a]
10	$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3$	1.0×10^{9}	10
11	$FeCO_3 \rightarrow Fe^{2+} + CO_3^{2-}$	4.7×10^{4}	10 [a]
12	$Fe^{2+} + 2CO_3^{2-} \rightarrow Fe(CO_3)_2^{2-}$	1.2×10^{11}	10 [b]
13	$Fe(CO_3)_2^{2-} \rightarrow Fe^{2+} + 2CO_3^{2-}$	1.0×10^{5}	10 [a]
14	$Fe^{2+} + CO_3^{2-} + OH^- \rightarrow Fe(CO_3)(OH)^-$	7.9×10^{13}	10 [b]
15	$Fe(CO_3)(OH)^- \rightarrow Fe^{2+} + CO_3^{2-} + OH^-$	1.0×10^{5}	10 [a]
16	$Fe^{3+} + SO_4^{2-} \rightarrow FeSO_4^+$	3.9×10^{7}	11
17	$FeSO_4^+ \rightarrow Fe^{3+} + SO_4^{2-}$	1.0×10^{5}	11 [a]
18	$Fe^{2+} + SO_4^{2-} \rightarrow FeSO_4^0$	2.3×10^{6}	11
19	$FeSO_4^0 \rightarrow Fe^{2+} + SO_4^{2-}$	1.0×10^{5}	11 [a]
20	$S_2O_8^{2-} + HO^{\cdot} \rightarrow S_2O_8^{\cdot-} + OH^-$	1.4×10^{7}	12
21	$S_2O_8^{2-} + SO_4^{\cdot-} \rightarrow S_2O_8^{\cdot-} + SO_4^{2-}$	6.5×10^{5}	13
22	$S_2O_8^{2-} + CO_3^{\cdot-} \rightarrow S_2O_8^{\cdot-} + CO_3^{2-}$	$(1.6\pm0.2)\times10^{3}$	
23	$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^- + HO^{\cdot}$	1.2×10^{1}	14
24	$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + HO^{\cdot}$	7.0×10^{7}	15

25	$HO^{\cdot} + OH^- \rightarrow O^{\cdot-} + H_2O$	1.3×10^{10}	16
26	$O^{\cdot-} + H_2O \rightarrow HO^{\cdot} + OH^-$	3.3×10^3	16
27	$O^{\cdot-} + O_2 \rightarrow O_3^{\cdot-}$	3.6×10^9	16
28	$O_3^{\cdot-} \rightarrow O_2 + O^{\cdot-}$	2.6×10^3	17 [a]
29	$H_2CO_3 \rightarrow HCO_3^- + H^+$	2.5×10^4	18 [a]
30	$HCO_3^- + H^+ \rightarrow H_2CO_3$	5.0×10^{10}	18
31	$HCO_3^- \rightarrow CO_3^{2-} + H^+$	2.5×10^0	19 [a]
32	$HCO_3^- + HO^{\cdot} \rightarrow CO_3^{\cdot-} + H_2O$	8.6×10^6	16
33	$HCO_3^- + Cl^{\cdot} \rightarrow CO_3^{\cdot-} + HCl$	2.2×10^8	20
34	$HCO_3^- + Cl_2^{\cdot-} \rightarrow 2\,Cl^- + H^+ + CO_3^{\cdot-}$	8.0×10^7	18
35	$HCO_3^- + SO_4^{\cdot-} \rightarrow CO_3^{\cdot-} + SO_4^{2-} + H^+$	9.1×10^6	21
36	$CO_3^{2-} + H^+ \rightarrow HCO_3^-$	5.0×10^{10}	18
37	$CO_3^{2-} + HO^{\cdot} \rightarrow CO_3^{\cdot-} + OH^-$	3.9×10^8	16
38	$CO_3^{2-} + SO_4^{\cdot-} \rightarrow CO_3^{\cdot-} + SO_4^{2-}$	2.5×10^6	22
39	$C_6H_6 + SO_4^{\cdot-} \rightarrow C_6H_6^{\cdot+} + SO_4^{2-}$	3.0×10^9	23
40	$C_6H_6 + HO^{\cdot} \rightarrow C_6H_7O^{\cdot}$	7.8×10^9	24
41	$C_6H_6 + CO_3^{\cdot-} + H_2O \rightarrow C_6H_7O^{\cdot} + HCO_3^-$	5.0×10^4	25
42	$C_6H_6^{\cdot+} + H_2O \rightarrow C_6H_7O^{\cdot} + H^+$	$(3.2\pm0.6) \times 10^5$	[a]
43	$C_6H_7O^{\cdot} + O_2 \rightarrow C_6H_7O_3^{\cdot}$	1.5×10^9	26
44	$C_6H_7O_3^{\cdot} \rightarrow C_6H_7O^{\cdot} + O_2$	8.0×10^5	25 [a]
45	$C_6H_7O_3^{\cdot} \rightarrow phenol$	2.0×10^4	25 [a]

Heterogeneous Reactions

46	$\equiv Fe(III) - OH_2 \rightarrow \equiv Fe(III) - OH + H^+$	4.0×10^1	27 [a]
47	$\equiv Fe(III) - OH + H^+ \rightarrow \equiv Fe(III) - OH_2$	5.0×10^9	27
48	$\equiv Fe(III) - OH \rightarrow \equiv Fe(III) - O^- + H^+$	4.0×10^{-1}	27 [a]
49	$\equiv Fe(III) - O^- + H^+ \rightarrow \equiv Fe(III) - OH$	5.0×10^9	27

50	$\equiv Fe(III) - OH + CO_3^{2-} + H^+ \rightarrow\equiv Fe(III) - OCO_2^- + H_2O$	1.0×10^{15}	27 [b]
51	$\equiv Fe(III) - OHCO_2^- \rightarrow\equiv Fe(III) - OH + CO_3^{2-}$	1.7×10^2	27 [a]
52	$\equiv Fe(III) - OH + CO_3^{2-} + 2H^+ \rightarrow\equiv Fe(III) - OCO_2H^0 + H_2O$	1.0×10^{20}	27 [c]
53	$\equiv Fe(III) - OCO_2H^0 + H_2O \rightarrow\equiv Fe(III) - OH + CO_3^{2-} + 2H^+$	5.0×10^1	27 [a]
54	$\equiv Fe(III) - OH + S_2O_8^{2-} \rightarrow\equiv Fe(II) - OH + S_2O_8^{\cdot-}$	$(1.9 \pm 0.3) \times 10^{-5}$	
55	$\equiv Fe(II) - OH + S_2O_8^{2-} \rightarrow\equiv Fe(III) - OH + SO_4^{\cdot-} + SO_4^{2-}$	$(2.8 \pm 0.3) \times 10^{-5}$	
56	$\equiv Fe(III) - O^- + S_2O_8^{2-} \rightarrow\equiv Fe(II) - O^- + S_2O_8^{\cdot-}$	$(1.2 \pm 0.3) \times 10^{-5}$	
57	$\equiv Fe(II) - O^- + S_2O_8^{2-} \rightarrow\equiv Fe(III) - O^- + SO_4^{\cdot-} + SO_4^{2-}$	$(2.8 \pm 0.5) \times 10^{-5}$	
58	$0.5 S_2O_8^{\cdot-} +\equiv Fe(III) - OH \rightarrow SO_4^{\cdot-} +\equiv Fe(II) - OH$	$(4.0 \pm 0.9) \times 10^{-6}$	
59	$0.5 S_2O_8^{\cdot-} +\equiv Fe(III) - O^- \rightarrow SO_4^{\cdot-} +\equiv Fe(II) - O^-$	$(1.8 \pm 0.2) \times 10^{-6}$	
60	$\equiv Mn(IV) - OH_2 \rightarrow\equiv Mn(IV) - OH + H^+$	1.3×10^9	3 [a]
61	$\equiv Mn(IV) - OH + H^+ \rightarrow \equiv Mn(IV) - OH_2$	5.0×10^9	3
62	$\equiv Mn(IV) - OH \rightarrow\equiv Mn(IV) - O^- + H^+$	1.3×10^7	3 [a]
63	$\equiv Mn(IV) - O^- + H^+ \rightarrow \equiv Mn(IV) - OH$	5.0×10^9	3
64	$\equiv Mn(IV) - OH + CO_3^{2-} + H^+ \rightarrow\equiv Mn(IV) - OCO_2^- + H_2O$	1.0×10^{15}	28 [b]
65	$\equiv Mn(IV) - OCO_2^- + H_2O \rightarrow \equiv Mn(IV) - OH + CO_3^{2-} + H^+$	7.1×10^0	28 [a]
66	$\equiv Mn(IV) - OH + CO_3^{2-} + 2H^+ \rightarrow\equiv Mn(IV) - OCO_2H^0 + H_2O$	1.0×10^{20}	28 [c]
67	$\equiv Mn(IV) - OCO_2H^0 + H_2O \rightarrow\equiv Mn(IV) - OH + CO_3^{2-} + 2H^+$	2.2×10^{-3}	28 [a]
68	$\equiv Mn(IV) - O^- + S_2O_8^{2-} \rightarrow\equiv Mn(III) - O^- + S_2O_8^{\cdot-}$	$(2.2 \pm 0.4) \times 10^{-3}$	
69	$\equiv Mn(III) - O^- + S_2O_8^{2-} \rightarrow\equiv Mn(IV) - O^- + SO_4^{\cdot-} + SO_4^{2-}$	$(4.9 \pm 1.3) \times 10^{-3}$	
70	$\equiv Mn(III) - O^- + SO_4^{\cdot-} \rightarrow\equiv Mn(IV) - O^- + SO_4^{2-}$	$(5.6 \pm 1.5) \times 10^{10}$	
71	$S_2O_8^{2-} + Cl^{\cdot} \rightarrow S_2O_8^{\cdot-} + Cl^-$	8.8×10^6	29
72	$SO_4^{2-} + Cl^{\cdot} \rightarrow SO_4^{\cdot-} + Cl^-$	2.5×10^8	30
73	$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\cdot}$	6.6×10^8	31
74	$HO^{\cdot} + Cl^- \rightarrow ClOH^{\cdot-}$	4.3×10^9	32
75	$ClOH^{\cdot-} \rightarrow Cl^- + HO^{\cdot}$	6.1×10^9	32 [a]

#	Reaction	Rate constant	Ref
76	$ClOH^{\cdot-} + Cl^- \rightarrow OH^- + Cl_2^{\cdot-}$	1.0×10^4	33
77	$ClOH^{\cdot-} + H^+ \rightarrow Cl^\cdot + H_2O$	2.1×10^{10}	33
78	$Cl^\cdot + H_2O \rightarrow ClOH^{\cdot-} + H^+$	4.5×10^3	33
79	$Cl^\cdot + OH^- \rightarrow ClOH^{\cdot-}$	1.8×10^{10}	34
80	$Cl^\cdot + Cl^- \rightarrow Cl_2^{\cdot-}$	8.5×10^9	35
81	$Cl_2^{\cdot-} + OH^- \rightarrow Cl^- + ClOH^{\cdot-}$	4.5×10^7	35
82	$Cl_2^{\cdot-} + H_2O \rightarrow Cl^- + HClOH^\cdot$	2.4×10^0	36
83	$HClOH^\cdot \rightarrow H^+ + ClOH^{\cdot-}$	1.0×10^8	36 [a]
84	$H^+ + Cl^- \rightarrow HCl$	5.0×10^{10}	18
85	$HCl \rightarrow H^+ + Cl^-$	8.6×10^{16}	18 [a]
86	$CO_3^{2-} + Cl^\cdot \rightarrow CO_3^{\cdot-} + Cl^-$	5.0×10^8	20
87	$CO_3^{2-} + Cl_2^{\cdot-} \rightarrow CO_3^{\cdot-} + 2\,Cl^-$	1.6×10^8	20
88	$C_6H_6 + Cl^\cdot + H_2O \rightarrow C_6H_7O^\cdot + HCl$	6.0×10^9	37

[*] Reaction rate constants without references were obtained in this study from the kinetic model. All rate constants on Fe(III) in this table are for goethite. Rate constants for ferrihydrite are listed in Table 1 of the main text.

[a] rate constants are in unit of s^{-1}

[b] rate constants are in unit of $M^{-2}\,s^{-1}$

[c] rate constants are in unit of $M^{-3}\,s^{-1}$

[d] Reaction is a first-order reaction and independent of pH when pH > 8.

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Appendix B

Supplemental Information for Chapter 3

Appendix B-1 Calculation of direct photolysis rates

The photolysis rate (r_p) of $S_2O_8^{2-}$ and NH_2Cl with monochromatic low-pressure mercury vapor UV lamp (λ=254nm) was calculated as:

$$r_p = -\, \Phi \times I_0 \times f_{oxidant} \times f_{solution} \qquad\qquad (Eq.\ S1)$$

where Φ is the primary quantum yield of the oxidant ($\Phi_{S_2O_8^{2-}}$=1.4 mole/Einstein, Φ_{NH_2Cl}=0.54 mole/Einstein),[1,2] I_0 is volume-normalized surface irradiance of the UV lamp (Einsteins·L^{-1}·s^{-1}) that was calculated as 7.1×10^{-6} Einstein·L^{-1}·s^{-1}, $f_{oxidant}$ is the fraction of incident light absorbed by the oxidant and $f_{solution}$ is the fraction absorbed by the total solution.

$$f_{oxidant} = \frac{\varepsilon_p c_p}{\sum \varepsilon_i c_i} \qquad\qquad (Eq.S2)$$

$$f_{solution} = 1 - 10^{-(\alpha + \sum \varepsilon_i c_i)l} \qquad\qquad (Eq.\ S3)$$

α is the absorption coefficient of the solution at the wavelength of 254 nm, ε_p and c_p are the molar extinction coefficient (M^{-1}·cm^{-1}) and the concentration (M) of the oxidant, respectively ($\varepsilon_{S_2O_8^{2-}}$=21.1 M^{-1}·cm^{-1}, ε_{NH_2Cl} =371 M^{-1}·cm^{-1}),[3,4] ε_i and c_i are the molar extinction coefficient and concentration of solution constituents, and l is the effective light path of the reactor (l=0.49cm).

Appendix B-2 Table of Rate constants and elemental reactions for kinetics modeling

No.	Reaction	Rate Constant (M^{-1} s^{-1})	Reference [*]
	Photolysis of $S_2O_8^{2-}$ and relevant reactions		
1	$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^{\cdot-}$	See Appendix B-1	Calculated
2	$S_2O_8^{2-} + OH\cdot \rightarrow S_2O_8^{\cdot-}$	1.4×10^7	5
3	$S_2O_8^{2-} + SO_4^{\cdot-} \rightarrow S_2O_8^{\cdot-} + SO_4^{2-}$	6.6×10^5	6
4	$S_2O_8^{2-} + Cl\cdot \rightarrow S_2O_8^{\cdot-} + Cl$	8.8×10^6	7
5	$S_2O_8^{2-} + Cl_2^{\cdot-} \rightarrow S_2O_8^{\cdot-} + 2Cl^-$	$(6.0 \pm 2.3)\times10^5$	Modelled
6	$S_2O_8^{2-} + S_2O_8^{\cdot-} \rightarrow product$	$(4.0 \pm 0.8)\times10^{-1}$	Modelled
7	$SO_5^{2-} + H^+ \rightarrow HSO_5^-$	5.0×10^{10}	3
8	$SO_5^{2-} + SO_4^{\cdot-} \rightarrow SO_5^{\cdot} + SO_4^{2-}$	1.0×10^8	8
9	$HSO_5^- \rightarrow H^+ + SO_5^{2-}$	2.0×10^{1} [a]	3
10	$HSO_5^- + OH\cdot \rightarrow H_2O + SO_5^{\cdot-}$	1.7×10^7	9
11	$HSO_4^{2-} \rightarrow H^+ + SO_4^{2-}$	6.3×10^8 [a]	Calculated based on pka
12	$H^+ + SO_4^{2-} \rightarrow HSO_4^{2-}$	5.0×10^{10}	Calculated based on pka
13	$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^{2-} + OH\cdot$	6.6×10^2 [a]	10
14	$SO_4^{2-} + Cl\cdot \rightarrow SO_4^{\cdot-} + Cl^-$	2.5×10^8	8
15	$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + OH\cdot$	7.0×10^7	11
16	$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl\cdot$	3.0×10^8	8
17	$SO_4^{\cdot-} + OH\cdot \rightarrow HSO_5^-$	1.0×10^{10}	8
18	$SO_4^{\cdot-} + HSO_5^- \rightarrow SO_5^{\cdot-} + SO_4^{2-} + H^+$	1.0×10^6	8
19	$SO_4^{\cdot-} + S_2O_8^{\cdot-} \rightarrow S_2O_8^{2-} + SO_2 + O_2$	9.9×10^5	12
20	$SO_4^{\cdot-} + SO_5^{\cdot-} \rightarrow S_2O_8^{2-} + 0.5O_2$	9.0×10^9	12
21	$SO_4^{\cdot-} + SO_4^{\cdot-} \rightarrow S_2O_8^{2-}$	7.0×10^8	8
22	$SO_4^{\cdot-} + HO_2^{\cdot} \rightarrow HSO_4^- + O_2$	3.5×10^9	6
23	$SO_5^{\cdot-} + SO_5^{\cdot-} \rightarrow S_2O_8^{2-} + O_2$	2.2×10^8	8
24	$SO_5^{\cdot-} + SO_5^{\cdot-} \rightarrow SO_4^{\cdot-} + SO_4^{\cdot-} + O_2$	2.1×10^8	8
25	$SO_5^{\cdot-} + HO_2^{\cdot} \rightarrow O_2 + HSO_5^-$	5.0×10^7	13
26	$H_2O \rightarrow H^+ + OH^-$	1.0×10^{-3} [a]	14
27	$H^+ + OH^- \rightarrow H_2O$	1.0×10^{11}	14
28	$H^+ + O_2^{\cdot-} \rightarrow HO_2^{\cdot}$	5.0×10^{10}	15
29	$OH\cdot + OH^- \rightarrow O^{\cdot-} + H_2O$	1.2×10^{10}	16
30	$O^{\cdot-} + H_2O \rightarrow OH\cdot + OH^-$	1.8×10^5 [a]	16
31	$O^{\cdot-} + HO_2^- \rightarrow O_2^{\cdot-} + OH^-$	4.0×10^8	16
32	$O^{\cdot-} + O_2 \rightarrow O_3^{\cdot-}$	3.6×10^9	16
34	$O_3^{\cdot-} \rightarrow O_2 + O^{\cdot-}$	2.6×10^3 [a]	17
35	$OH\cdot + O^{\cdot-} \rightarrow HO_2^-$	1.0×10^{10}	16
36	$OH\cdot + HO_2^- \rightarrow HO_2^{\cdot} + OH^-$	7.5×10^9	18
37	$OH\cdot + HO_2^{\cdot} \rightarrow H_2O + O_2$	6.6×10^9	19
38	$OH\cdot + O_2^{\cdot-} \rightarrow OH^- + O_2$	7.0×10^9	20
39	$OH\cdot + OH\cdot \rightarrow H_2O_2$	5.5×10^9	17
40	$OH\cdot + Cl^- \rightarrow ClOH^{\cdot-}$	4.3×10^9	21
41	$OH\cdot + HSO_4^- \rightarrow H_2O + SO_4^{\cdot-}$	1.7×10^6	22
42	$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$	8.3×10^5	23
43	$HO_2^{\cdot} + O_2^{\cdot-} \rightarrow HO_2^- + O_2$	9.7×10^7	23

44	$HO_2^{\cdot} \rightarrow H^+ + O_2^{\cdot-}$	1.6×10^5 [a]	23
	Photolysis of NH$_2$Cl and relevant reactions		
45	$NH_2Cl \overset{h\nu}{\rightarrow} NH_2^{\cdot} + Cl^{\cdot}$	See Text S3	Calculated
46	$NH_2Cl + OH^{\cdot} \rightarrow NHCl^{\cdot} + H_2O$	5.1×10^8	24
47	$NH_2Cl + SO_4^{\cdot-} \rightarrow NHCl^{\cdot} + HSO_4^-$	$(2.4 \pm 0.2) \times 10^7$	This study
48	$NH_2Cl + Cl^{\cdot} \rightarrow NHCl^{\cdot} + HCl$	2.4×10^7	This study
49	$NH_2Cl + Cl_2^{\cdot-} \rightarrow NHCl^{\cdot} + H^+ + 2Cl^-$	$(6.5 \pm 3.5) \times 10^6$	Modeled
50	$NH_2Cl + NH_2^{\cdot} \rightarrow NHCl^{\cdot} + NH_3$	$(1.0 \pm 0.8) \times 10^5$	Modeled
51	$NH_2Cl + H^{\cdot} \rightarrow NHCl^{\cdot} + HCl$	1.2×10^9	
52	$NH_2Cl + ClO^{\cdot} \rightarrow NHCl^{\cdot} + HOCl$	1.0×10^5	
53	$NH_2Cl + H_2O \rightarrow HOCl + NH_3$	2.8×10^{-5} [a]	25
54	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	4.2×10^6	25
55	$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$	k_d [b]	26
56	$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$	6.1×10^4	27
57	$NH_2Cl + NHCl_2 \rightarrow 3HCl + N_2$	1.5×10^{-2}	26
58	$NH_4^+ \rightarrow NH_3 + H^+$	4.2×10^1 [a]	Calculated based on pka
59	$NH_3 + H^+ \rightarrow NH_4^+$	8.4×10^{10}	Calculated based on pka
60	$NH_3 + OH^{\cdot} \rightarrow NH_2^{\cdot} + H_2O$	9.7×10^7	28
61	$NH_3 + SO_4^{\cdot-} \rightarrow NH_2^{\cdot} + HSO_4^-$	1.4×10^7	29
62	$NH_3 + Cl^{\cdot} \rightarrow NH_2^{\cdot} + HCl$	1.0×10^7	assumed
63	$NH_3 + Cl_2^{\cdot-} \rightarrow NH_2^{\cdot} + HCl + Cl^-$	1.0×10^7	assumed
64	$NH_3 + O^{\cdot-} \rightarrow NH_2^{\cdot} + OH^-$	3.0×10^7	30
65	$NH_4^+ + H^{\cdot} \rightarrow product$	4.0×10^4	31
66	$NH_4^+ + SO_4^{\cdot-} \rightarrow NH_2^{\cdot} + HSO_4^-$	3.0×10^5	29
67	$NH_4^+ + Cl^{\cdot} \rightarrow NH_2^{\cdot} + HCl$	$(1.3 \pm 0.5) \times 10^5$	modeled
68	$NH_4^+ + Cl_2^{\cdot-} \rightarrow NH_2^{\cdot} + HCl + Cl^-$	$(1.3 \pm 0.5) \times 10^5$	modeled
69	$NH_2^{\cdot} + H^+ \rightarrow NH_3^{\cdot+}$	5.0×10^9	Calculated based on pka
70	$NH_3^{\cdot+} \rightarrow NH_2^{\cdot} + H^+$	1.0×10^3 [a]	Calculated based on pka
71	$NH_3^{\cdot+} + NH_2Cl \rightarrow NH_3 + NHCl^{\cdot} + H^+$	1.0×10^5	assumed
72	$NH_2^{\cdot} + O_2 \rightarrow NH_2O_2^{\cdot}$	1.0×10^7	29
73	$NH_2^{\cdot} + NH_2^{\cdot} \rightarrow H_2NNH_2$	2.2×10^9	32
74	$NH_2^{\cdot} + OH^{\cdot} \rightarrow H_2NOH$	9.5×10^9	32
75	$NH_2O_2^{\cdot} + O_2^{\cdot-} \rightarrow ONO_2^- + H_2O$	2.3×10^7	32
76	$NH_2O_2^{\cdot} + O_2^{\cdot-} \rightarrow H_2NO_2^- + O_2$	6.6×10^8	32
77	$NHCl^{\cdot} + O_2 \rightarrow NHCl.$	1.0×10^7	assumed
78	$NHCl^{\cdot} + NHCl^{\cdot} \rightarrow N_2 + 2HCl$	1.0×10^9	assumed
79	$NHCl_2 \overset{h\nu}{\rightarrow} NHCl^{\cdot} + Cl^{\cdot}$	See Text S3	Calculated
80	$NHCl_2 + OH^{\cdot} \rightarrow NHCl^{\cdot} + H_2O$	8.0×10^8	This study
81	$NHCl_2 + SO_4^{\cdot-} \rightarrow NHCl^{\cdot} + HSO_4^-$	$(1.0 \pm 0.2) \times 10^8$	This study
82	$NHCl_2 + Cl^{\cdot} \rightarrow NHCl^{\cdot} + HCl$	$(3.2 \pm 0.4) \times 10^7$	This study
83	$NHCl_2 + Cl_2^{\cdot-} \rightarrow NHCl^{\cdot} + H^+ + 2Cl^-$	$(4.4 \pm 1.2) \times 10^6$	This study
84	$NHCl_2 + NH_2^{\cdot} \rightarrow NHCl^{\cdot} + NH_3$	1.0×10^5	assumed
85	$NHCl_2 + HOCl \rightarrow NHCl_2 + H_2O$	3.5×10^2	26
86	$NHCl_2 + H_2O \rightarrow NHCl_2 + HOCl$	6.4×10^{-7}	33
87	$NHCl_2 + H_2O \rightarrow NOH + 2HCl$	1.7×10^2	26
88	$NOH + NHCl_2 \rightarrow N_2 + HOCl + HCl$	2.8×10^4	26

89	$NOH + NH_2Cl \rightarrow N_2 + H_2O + HCl$	8.3×10^3	26
	Reactive chlorine species reactions		
90	$ClOH^{\cdot-} \rightarrow Cl^- + OH^{\cdot}$	6.1×10^9 [a]	21
91	$ClOH^{\cdot-} + Cl^- \rightarrow OH^- + Cl_2^{\cdot-}$	1.0×10^4	34
92	$ClOH^{\cdot-} + H^+ \rightarrow Cl^{\cdot} + H_2O$	2.1×10^{10}	21
93	$Cl^{\cdot} + H_2O \rightarrow ClOH^{\cdot-} + H^+$	2.5×10^5 [a]	21
94	$Cl^{\cdot} + OH^- \rightarrow ClOH^{\cdot-}$	1.8×10^{10}	35
95	$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot-}$	8.5×10^9	36
96	$Cl^{\cdot} + Cl_2 \rightarrow Cl_3$	5.3×10^8	37
97	$Cl^{\cdot} + ClO^- \rightarrow ClO^{\cdot} + Cl^-$	8.3×10^9	35
98	$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$	8.8×10^7	38
99	$Cl_2^{\cdot-} + Cl^{\cdot} \rightarrow Cl_2 + Cl^-$	2.1×10^9	36
100	$Cl_2^{\cdot-} + OH^- \rightarrow Cl^- + ClOH^{\cdot-}$	4.5×10^7	34
101	$Cl_2^{\cdot-} \rightarrow Cl^{\cdot} + Cl^-$	6.0×10^4 [a]	36
102	$Cl_2^{\cdot-} + Cl_2^{\cdot-} \rightarrow 2\ Cl^- + Cl_2$	9.0×10^8	36
103	$Cl_2^{\cdot-} + H_2O \rightarrow Cl^- + HClOH^{\cdot}$	1.3×10^3 [a]	37
104	$Cl_2^{\cdot-} + OH^{\cdot} \rightarrow HOCl + Cl^-$	1.0×10^9	39
105	$Cl_2^{\cdot-} + HO_2^{\cdot} \rightarrow O_2 + H^+ + 2Cl^-$	3.0×10^9	40
106	$Cl_2^{\cdot-} + O_2^{\cdot-} \rightarrow O_2 + 2Cl^-$	2.0×10^9	41
107	$HClOH^{\cdot} \rightarrow H^+ + ClOH^{\cdot-}$	1.0×10^8 [a]	37
108	$HClOH^{\cdot} \rightarrow Cl^{\cdot} + H_2O$	1.0×10^2 [a]	37
109	$HClOH^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot-} + H_2O$	5.0×10^9	37
110	$H^+ + Cl^- \rightarrow HCl$	5.0×10^{10}	14
111	$HCl \rightarrow H^+ + Cl^-$	8.6×10^{16} [a]	14
112	$ClO^- + OH^{\cdot} \rightarrow ClO^{\cdot} + OH^-$	8.8×10^9	42
113	$ClO^- + O_2^{\cdot-} + H_2O \rightarrow Cl^{\cdot} + 2\ OH^- + O_2$	2.0×10^8	43
114	$ClO^{\cdot} + ClO^{\cdot} \rightarrow product$	2.5×10^9	35
115	$Cl_2 + Cl^- \rightarrow Cl_3^-$	2.0×10^4	44
116	$Cl_2 + O_2^{\cdot-} \rightarrow O_2 + Cl_2^{\cdot-}$	1.0×10^9	43
117	$Cl_2 + HO_2^{\cdot} \rightarrow H^+ + O_2 + Cl_2^{\cdot-}$	1.0×10^9	45
118	$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$	2.2×10^0 [a]	46
119	$Cl_2OH^- \rightarrow HOCl + Cl^-$	5.5×10^9 [a]	46
120	$Cl_3^- \rightarrow Cl_2 + Cl^-$	1.1×10^5 [a]	44
121	$Cl_3^- + HO_2^{\cdot} \rightarrow Cl_2^{\cdot-} + HCl + O_2$	1.0×10^9	45
122	$Cl_3^- + O_2^{\cdot-} \rightarrow Cl_2^{\cdot-} + Cl^- + O_2$	3.8×10^9	43
	Phosphate relevant reactions		
123	$H_3PO_4 \rightarrow H_2PO_4^- + H^+$	4.0×10^8 [a]	14
124	$H_2PO_4^- + H^+ \rightarrow H_3PO_4$	5.0×10^{10}	14
125	$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$	3.2×10^3 [a]	14
126	$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$	5.0×10^{10}	14
127	$HPO_4^{2-} \rightarrow PO_4^{3-} + H^+$	2.5×10^{-2} [a]	14
128	$PO_4^{3-} + H^+ \rightarrow HPO_4^{2-}$	5.0×10^{10}	14
129	$H_3PO_4 + OH^{\cdot} \rightarrow H_2PO_4 + H_2O$	4.2×10^4	6
130	$H_2PO_4^- + OH^{\cdot} \rightarrow HPO_4^{\cdot-} + H_2O$	4.2×10^4	29
131	$HPO_4^{2-} + OH^{\cdot} \rightarrow HPO_4^{\cdot-} - + OH^-$	1.5×10^5	29
132	$PO_4^{3-} + OH^{\cdot} \rightarrow product$	1.0×10^7	47
133	$H_2PO_4^- + SO_4^{\cdot-} \rightarrow HPO_4^{\cdot-} + HSO_4^-$	7.0×10^4	29
134	$HPO_4^{2-} + SO_4^{\cdot-} \rightarrow HPO_4^{\cdot-} + SO_4^{2-}$	1.2×10^6	29

135	$HPO_4^{\cdot-} + Cl^- \rightarrow HPO_4^{2-} + Cl^{\cdot}$	1.0×10^4	29
136	$HPO_4^{\cdot-} + HPO_4^{\cdot-} \rightarrow P_2O_8^{4-} + 2H^+$	4.5×10^8	47
137	$HPO_4^{\cdot-} + SO_4^{2-} \rightarrow product$	1.0×10^4	48
	Organics reactions		
138	$1,4 - D + OH^{\cdot} \rightarrow product$	3.1×10^9	41
139	$1,4 - D + SO_4^{\cdot-} \rightarrow product$	4.1×10^7	42
140	$1,4 - D + Cl^{\cdot} \rightarrow product$	4.4×10^6	36
141	$1,4 - D + Cl_2^{\cdot-} \rightarrow product$	3.3×10^6	36
142	$BA + OH^{\cdot} \rightarrow product$	6.0×10^9	34
143	$BA + SO_4^{\cdot-} \rightarrow product$	1.2×10^9	38
144	$BA + Cl^{\cdot} \rightarrow product$	1.8×10^{10}	49
145	$BA + Cl_2^{\cdot-} \rightarrow product$	2.0×10^6	35
146	$BA + ClO^{\cdot} \rightarrow product$	3.0×10^6	50
147	$BA + O^{\cdot-} \rightarrow product$	4.0×10^7	51
148	$BA + NH_2^{\cdot} \rightarrow product$	4.0×10^5	39
149	$NB + OH^{\cdot} \rightarrow product$	4.7×10^9	34
150	$NB + H^{\cdot} \rightarrow product$	2.3×10^9	34

[a] rate constants are in unit of s^{-1}

[b] $k_d = k_{H+}[\text{H}^+] + k_{H_3PO_4}[\text{H}_3\text{PO}_4] + k_{\text{H}_2\text{PO}_4^{2-}}[\text{H}_2\text{PO}_4^{2-}]$, $k_{H+} = 7 \times 10^3 \, \text{M}^{-2}\text{s}^{-1}$,[26] $k_{H_3PO_4} = 8.9 \times 10^2 \, \text{M}^{-2}\text{s}^{-1}$,[52] $k_{\text{H}_2\text{PO}_4^{2-}} = 3.9 \times 10^{-1} \, \text{M}^{-2}\text{s}^{-1}$ [52]

Appendix B-3 Details on the comprehensive kinetic modeling

The kinetic model was built on the platform of Kintecus 4.55 software. A total of 150 elemental reactions were established to predict $S_2O_8^{2-}$ and NH_2Cl photolysis rates and calculate steady-state concentrations of radical species. All reactions incorporated in the kinetic model were summarized in Table S1. Of 150 reactions, 130 rate constants were directly obtained from radiolysis literature, and 6 rate constants were optimized using data fitting into the model. First, the rate constants for Reactions 67-68 were optimized using the data sets from 1,4-D degradation by $UV/S_2O_8^{2-}$ at different NH_4^+ dosages. Then the rate constants for Reactions 5-6 and 49-50 were optimized using experimental data from 1,4-D degradation by $UV/S_2O_8^{2-}$ at different NH_2Cl dosages. The best model fittings were achieved by applying Powell non-restricted algorithms to minimize the root mean squares (RMS) between the model prediction and experimental observation based on the kinetics of oxidant photolysis rates and 1,4-dioxane degradation rates. One rate constant was optimized at each concentration, and the average values of the rate constants with standard deviations were then calculated. The rate constants for Reactions 62-63, 71, 77-78, and 84 were assumed based on the reactivity of similar compounds. Rate constants for Reaction 47-48, 80-83 were obtained through Pulse-radiolysis studies (**Appendix B-5**). Finally, the modelled rate constants were randomized within the predicted rate constants $\pm$ standard deviations, and calculated the confidence band at 95% confidence level.

Appendix B-4 Calculation of theoretical additive degradation rate of 1,4-D by UV/S$_2$O$_8$$^{2-}$ and UV/NH$_2$Cl

The theoretical additive degradation kinetics of 1,4-D by UV/S$_2$O$_8$$^{2-}$ and UV/NH$_2$Cl was calculated based on equation S4:

$$k_{1,4-D} = k_{S_2O_8^{2-}} \times f_{S_2O_8^{2-}} + k_{NH_2Cl} \times f_{NH_2Cl}$$ (Eq. S4)

Where k$_{1,4-D}$ is the total degradation rate of 1,4-D, $k_{S_2O_8^{2-}}$ is the observed 1,4-D degradation rate by UV/S$_2$O$_8$$^{2-}$ ([S$_2$O$_8$$^{2-}$]=2mM), $f_{S_2O_8^{2-}}$ is the fraction of UV light absorbed by 2 mM S$_2$O$_8$$^{2-}$ in the mix system, k_{NH_2Cl} is the rate of 1,4-D degradation by UV/NH$_2$Cl at a specific concentration (0.1-4 mM), and f_{NH_2Cl} is the fraction of light absorbed by NH$_2$Cl at the specific concentration (0.1-4 mM) in the mix system.

$f_{S_2O_8^{2-}}$ is calculated as:

$$f_{S_2O_8^{2-}} = \frac{\varepsilon_{S_2O_8^{2-}} \times [S_2O_8^{2-}]}{\varepsilon_{S_2O_8^{2-}} \times [S_2O_8^{2-}]}$$ (Eq. S5)

$\varepsilon_{S_2O_8^{2-}}$ and ε_{NH_2Cl} are the molar extinction coefficients of S$_2$O$_8$$^{2-}$ and NH$_2$Cl, respectively (M^{-1}·cm^{-1}). [S$_2$O$_8$$^{2-}$] and [NH$_2$Cl] are the concentrations of the S$_2$O$_8$$^{2-}$ NH$_2$Cl, respectively (M).

Similarly, f_{NH_2Cl} is calculated as:

$$f_{NH_2Cl} = \frac{\varepsilon_{NH_2Cl} \times [NH_2Cl]}{\varepsilon_{S_2O_8^{2-}} \times [S_2O_8^{2-}]}$$ (Eq. S6)

Appendix B-5 Calculation of fate of each reactive radical species.

B-5.1 Fate of HO$^\bullet$ in UV/S$_2$O$_8^{2-}$ and NH$_2$Cl:

Once HO$^\bullet$ was generated, it participated in the following four reactions: [5,24,34]

$$HO\cdot + Cl^- \rightarrow ClOH\cdot^- \qquad\qquad k_1=3.0\times10^9 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Reaction S1)}$$

$$HO\cdot + NH_2Cl \rightarrow NHCl\cdot + H_2O \quad k_2=5.1\times10^8 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Reaction S2)}$$

$$HO\cdot + 1,4-dioxane \rightarrow product \ k_3=3.1\times10^9 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Reaction S3)}$$

$$HO\cdot + S_2O_8^{2-} \rightarrow product \qquad\qquad k_4=1.4\times10^7 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Reaction S4)}$$

Under the experimental condition with 2 mM of S$_2$O$_8^{2-}$, 0-4 mM of NH$_2$Cl and 250 μM of 1,4-dioxane, HO$^\bullet$ branching ratio was calculated as:

$$\%_{HO\cdot-Cl^-} = \frac{k_1[Cl^-]}{k_1[Cl^-]+k_2[NH_2Cl]+k_3[1,4D]+k_4[S_2O_8^{2-}]}\times100\% = 1-81\% \qquad \text{(Eq. S7)}$$

$$\%_{HO\cdot-NH_2Cl} = \frac{k_2[NH_2Cl]}{k_1[Cl^-]+k_2[NH_2Cl]+k_3[1,4D]+k_4[S_2O_8^{2-}]}\times100\% = 0-14\% \qquad \text{(Eq. S8)}$$

$$\%_{HO\cdot-1,4D} = \frac{k_3[1,4D]}{k_1[Cl^-]+k_2[NH_2Cl]+k_3[1,4D]+k_4[S_2O_8^{2-}]}\times100\% = 5-96\% \qquad \text{(Eq. S9)}$$

$$\%_{HO\cdot-S_2O_8^{2-}} = \frac{k_4[S_2O_8^{2-}]}{k_1[Cl^-]+k_2[NH_2Cl]+k_3[1,4D]+k_4[S_2O_8^{2-}]}\times100\% = 0-4\% \qquad \text{(Eq. S10)}$$

Branching ratios of HO$^\bullet$ with different species were summarized:

[NH2Cl] (mM)	0	0.1	0.2	0.4	1	2	3	4
%HO$^\bullet$-Cl$^-$	1%	26%	40%	55%	70%	77%	79%	81%
%HO$^\bullet$-NH$_2$Cl	0%	4%	7%	9%	12%	13%	14%	14%
%HO$^\bullet$-1,4-D	96%	67%	51%	35%	18%	10%	7%	5%
%HO$^\bullet$-S$_2$O$_8^{2-}$	4%	2%	2%	1%	1%	0%	0%	0%

B-5.2 Fate of $SO_4^{\bullet-}$ in $UV/S_2O_8^{2-}$ and NH_2Cl:

Once $SO_4^{\bullet-}$ was generated, five reactions could act as sinks for $SO_4^{\bullet-}$:[37,36]

$$SO_4^- + 1,4-dioxane \rightarrow product \qquad k_5=4.1\times10^7 \text{ M}^{-1}\text{s}^{-1} \qquad \text{(Reaction S5)}$$

$$SO_4^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^- \qquad k_6=6.5\times10^5 \text{ M}^{-1}\text{s}^{-1} \qquad \text{(Reaction S6)}$$

$$SO_4^- + H_2O \rightarrow OH^\cdot + HSO_4^- \qquad k_7= 6.6\times10^2 \text{ s}^{-1} \qquad \text{(Reaction S7)}$$

$$SO_4^- + Cl^- \rightarrow Cl^\cdot \qquad k_8=3.0\times10^8 \text{ M}^{-1}\text{s}^{-1} \qquad \text{(Reaction S8)}$$

$$SO_4^- + NH_2Cl \rightarrow product \qquad k_9=2.4\pm0.1\times10^7 \text{ M}^{-1}\text{s}^{-1}\text{(Reaction S9)}$$

The rate constant for $SO_4^{\bullet-}$ with NH_2Cl was obtained from the model.

Under the experimental condition of 2 mM $S_2O_8^{2-}$, 250 mM 1,4-D and 0-4 mM NH_2Cl, the branching ratio of $SO_4^{\bullet-}$ with each species in $UV/S_2O_8^{2-}/NH_2Cl$ were calculated:

$$\%_{SO_4^- -1,4D} = \frac{k_5[1,4D]}{k_5[1,4D]+k_6[S_2O_8^{2-}]+k_7+k_8[Cl^-]+k_9[NH_2Cl]}\times100\% = 1-80\% \quad \text{(Eq. S11)}$$

$$\%_{SO_4^- -S_2O_8^{2-}} = \frac{k_6[S_2O_8^{2-}]}{k_5[1,4D]+k_6[S_2O_8^{2-}]+k_7+k_8[Cl^-]+k_9[NH_2Cl]}\times100\% = 0-10\% \quad \text{(Eq. S12)}$$

$$\%_{SO_4^- -H_2O} = \frac{k_7}{k_5[1,4D]+k_6[S_2O_8^{2-}]+k_7+k_8[Cl^-]+k_9[NH_2Cl]}\times100\% = 0-5\% \quad \text{(Eq. S13)}$$

$$\%_{SO_4^- -Cl^-} = \frac{k_8[Cl^-]}{k_5[1,4D]+k_6[S_2O_8^{2-}]+k_7+k_8[Cl^-]+k_9[NH_2Cl]}\times100\% = 5-91\% \quad \text{(Eq. S14)}$$

$$\%_{SO_4^- -NH_2Cl^-} = \frac{k_9[NH_2Cl]}{k_5[1,4D]+k_6[S_2O_8^{2-}]+k_7+k_8[Cl^-]+k_9[NH_2Cl]}\times100\% = 0-8\% \quad \text{(Eq. S15)}$$

Branching ratios of $SO_4^{\bullet-}$ with different species were summarized:

[NH2Cl] (mM)	0	0.1	0.2	0.4	1	2	3	4
%SO$_4^{\bullet-}$-1,4-D	80%	23%	13%	7%	4%	2%	2%	1%
%SO$_4^{\bullet-}$-S$_2$O$_8^{2-}$	10%	3%	2%	1%	0%	0%	0%	0%
%SO$_4^{\bullet-}$-H$_2$O	5%	1%	1%	0%	0%	0%	0%	0%
%SO$_4^{\bullet-}$-Cl$^-$	5%	68%	78%	85%	89%	91%	91%	91%
%SO$_4^{\bullet-}$-NH$_2$Cl	0%	5%	6%	7%	7%	7%	7%	8%

B-5.3 Fate of $Cl^\bullet$ in $UV/S_2O_8^{2-}$ and NH_2Cl:

$Cl^\bullet$ also has multiple sinks, including Cl^-, $S_2O_8^{2-}$, H_2O, 1,4-dioxane and NH_2Cl: [36,8,34,54]

$$Cl\cdot + Cl^- \rightarrow Cl_2^- \qquad\qquad k_{10}=8.5\times10^9 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Reaction S10)}$$

$$Cl\cdot + S_2O_8^{2-} \rightarrow S_2O_8^- + Cl^- \qquad k_{11}=8.8\times10^6 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Reaction S11)}$$

$$Cl\cdot + H_2O \rightarrow ClOH^{\cdot-} + H^+ \qquad k_{12}= 2.5\times10^5 \text{ s}^{-1} \qquad \text{(Reaction S12)}$$

$$Cl\cdot + 1,4-dioxane \rightarrow product \quad k_{13}=4.4\times10^6 \text{ M}^{-1}\text{s}^{-1} \qquad \text{(Reaction S13)}$$

$$Cl\cdot + NH_2Cl \rightarrow product \qquad\qquad k_{14}=3.5\pm0.2\times10^7 \text{ M}^{-1}\text{s}^{-1} \text{ (Reaction S14)}$$

The rate of $Cl^\bullet$ reacting NH_2Cl was obtained from the model.

Under the experimental condition of 2 mM $S_2O_8^{2-}$, 250 mM 1,4-dioxane and 0-4 mM NH_2Cl, the branching ratio of $Cl^\bullet$ with each species was then calculated as:

$$\%_{Cl\cdot-Cl^-} = \frac{k_{10}[Cl^-]}{k_{10}[Cl^-]+k_{11}[S_2O_8^{2-}]+k_{12}+k_{13}[1,4D]+k_{14}[NH_2Cl]}\times100\% = 6-99\% \quad \text{(Eq. S16)}$$

$$\%_{Cl\cdot-S_2O_8^{2-}} = \frac{k_{11}[S_2O_8^{2-}]}{k_{10}[Cl^-]+k_{11}[S_2O_8^{2-}]+k_{12}+k_{13}[1,4D]+k_{14}[NH_2Cl]}\times100\% = 0-6\% \quad \text{(Eq. S17)}$$

$$\%_{Cl\cdot-H_2O} = \frac{k_{12}}{k_{10}[Cl^-]+k_{11}[S_2O_8^{2-}]+k_{12}+k_{13}[1,4D]+k_{14}[NH_2Cl]}\times100\% = 1-87\% \quad \text{(Eq. S18)}$$

$$\%_{Cl\cdot-1,4D} = \frac{k_{13}[1,4D]}{k_{10}[Cl^-]+k_{11}[S_2O_8^{2-}]+k_{12}+k_{13}[1,4D]+k_{14}[NH_2Cl]}\times100\% =< 0.4\% \quad \text{(Eq. S19)}$$

$$\%_{Cl\cdot-NH_2Cl} = \frac{k_{14}[NH_2Cl]}{k_{10}[Cl^-]+k_{11}[S_2O_8^{2-}]+k_{12}+k_{13}[1,4D]+k_{14}[NH_2Cl]}\times100 =< 1\% \quad \text{(Eq. S20)}$$

Branching ratios of $Cl^\bullet$ with different species were summarized:

[NH2Cl] (mM)	0	0.1	0.2	0.4	1	2	3	4
%Cl⁻-Cl⁻	6%	76%	86%	92%	97%	98%	99%	99%
%Cl⁻-S₂O₈²⁻	6%	2%	1%	0%	0%	0%	0%	0%
%Cl⁻-H₂O	87%	22%	13%	7%	3%	1%	1%	1%
%Cl⁻-1,4-D	0%	0%	0%	0%	0%	0%	0%	0%
%Cl⁻-NH₂Cl	0%	0%	0%	0%	0%	0%	0%	0%

B-5.4 Fate of $Cl_2^{\bullet-}$ in UV/$S_2O_8^{2-}$ and NH_2Cl:

$Cl_2^{\bullet-}$ also has multiple sinks, including NH_2Cl, $S_2O_8^{2}$, H_2O, and 1,4-dioxane:

$$Cl_2^- + NH_2Cl \rightarrow NHCl^{\cdot} + H^+ + 2Cl^- \quad k_{15}=(5\text{-}9)\times10^6 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Reaction S15)}$$

$$Cl_2^- + S_2O_8^{2-} \rightarrow NHCl^{\cdot} + H^+ + 2Cl^- \quad k_{16}=10^2\text{-}10^6 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Reaction S16)}$$

$$Cl_2^- + H_2O \rightarrow HClOH^{\cdot} + Cl^- \quad k_{17}=1.3\times10^3 \text{ s}^{-1} \quad \text{(Reaction S17)}$$

$$Cl_2^- + 1,4-dioxane \rightarrow product \quad k_{18}=3.3\times10^6 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Reaction S18)}$$

The rate constant of $Cl_2^{\bullet-}$ with NH_2Cl was obtained from the model.

Under the experimental condition with 2 mM of $S_2O_8^{2-}$, 0-4 mM of NH_2Cl and 250 μM of 1,4-dioxane, $Cl_2^{\bullet-}$ branching ratio was calculated as:

$$\%_{Cl_2^- - NH_2Cl} = \frac{k_{15}[NH_2Cl]}{k_{15}[NH_2Cl]+k_{16}[S_2O_8^{2-}]+k_{17}+k_{18}[1,4D]} \times 100\% = 0-86\% \quad \text{(Eq. S21)}$$

$$\%_{Cl_2^- - S_2O_8^{2-}} = \frac{k_{16}[S_2O_8^{2-}]}{k_{15}[NH_2Cl]+k_{16}[S_2O_8^{2-}]+k_{17}+k_{18}[1,4D]} \times 100\% = 5-36\% \quad \text{(Eq. S22)}$$

$$\%_{Cl_2^- - H_2O} = \frac{k_{17}}{k_{15}[NH_2Cl]+k_{16}[S_2O_8^{2-}]+k_{17}+k_{18}[1,4D]} \times 100\% = 6-39\% \quad \text{(Eq. S23)}$$

$$\%_{Cl_2^- - 1,4D} = \frac{k_{18}[1,4D]}{k_{15}[NH_2Cl]+k_{16}[S_2O_8^{2-}]+k_{17}+k_{18}[1,4D]} \times 100\% = 3-25\% \quad \text{(Eq. S24)}$$

Branching ratios of $Cl_2^{\bullet-}$ with different species were summarized:

[NH2Cl] (mM)	0	0.1	0.2	0.4	1	2	3	4
%$Cl_2^{\bullet-}$-NH_2Cl	0%	23%	35%	49%	68%	78%	82%	86%
%$Cl_2^{\bullet-}$-$S_2O_8^{2-}$	36%	28%	23%	18%	12%	8%	7%	5%
%$Cl_2^{\bullet-}$-H_2O	39%	30%	25%	20%	13%	9%	7%	6%
%$Cl_2^{\bullet-}$-1,4-D	25%	19%	16%	13%	8%	5%	4%	3%

Appendix B-6 Electron pulse radiolysis for determining second-order rate constants of $SO_4^{•-}$, $Cl^•$ and $Cl_2^{•-}$ with NH_2Cl and $NHCl_2$.

Detailed radical generation and experimental procedures would be found in our previous publication. [36]

$$y = 23,571,911.81x + 223,499.74$$
$$R^2 = 0.95$$

$$y = 23,710,814.41x + 198,871.10$$
$$R^2 = 1.00$$

Figure B1 Variation in NH_2Cl growth kinetics from data in Table S5 were used to determine second order rate constants for (A) NH_2Cl reaction with $SO_4^{•-}$ and (B) NH_2Cl reaction with $Cl^•$. Based on the slope of the correlation, the second-order rate constants between NH_2Cl reaction with $SO_4^{•-}$, $(2.4 \pm 0.2) \times 10^7$ $M^{-1}s^{-1}$ and between NH_2Cl reaction with $Cl^•$, 2.4×10^7 $M^{-1}s^{-1}$.

Figure B2 Variation in NH_2Cl growth kinetics from top data used to determine second order rate constants for (A) $NHCl_2$ reaction with $SO_4^{•-}$; (B) $NHCl_2$ reaction with $Cl^{•}$; (C) $NHCl_2$ reaction with $Cl_2^{•-}$. Based on the slope of the correlation, the second-order rate constant between $NHCl_2$ reaction with $SO_4^{•-}=(1.0 \pm 0.15) \times 10^8$ $M^{-1}s^{-1}$, the second-order rate constant between $NHCl_2$ reaction with $Cl^{•}=(3.2 \pm 0.38) \times 10^7$ $M^{-1}s^{-1}$, the second-order rate constant between $NHCl_2$ reaction with $Cl_2^{•-}=(4.4 \pm 1.2) \times 10^6$ $M^{-1}s^{-1}$.

Appendix B-7 Calculation of HClOH$^\bullet$ scavenging by chloride

HClOH$^\bullet$ reacts with chloride through the following equation:

$$HClOH^\bullet + Cl^- \rightarrow Cl_2^{\bullet-} + H_2O \quad k_{Cl}=5\times10^9 \text{ M}^{-1}\text{s}^{-1} \qquad \text{(Reaction S18)}$$

Therefore, HClOH$^\bullet$ scavenging by chloride is calculated as:

$$\%_{HClOH^\bullet-Cl^-} = \frac{k_{Cl^-}[Cl^-]}{k_{HClOH^\bullet} + k_{Cl^-}[Cl^-]}\times100\% = 9\%$$

[ClOH$^{\bullet-}$]$_{ss}$ also decreased by 9%, because $[ClOH^{\bullet-}]_{ss} = \frac{k_{HClOH^\bullet}[HClOH^\bullet]_{ss}}{k_{ClOH^{\bullet-}}}$

The branching ratio of HO$^\bullet$ reacting with 2 mM chloride and 0.2 mM is calculated as:

$Branching\ ratio_{HO^\bullet-Cl^\bullet}$

$$= \frac{k_{Cl^-}[0.002M] + k_{NH_2Cl}[NH_2Cl] + k_{1,4D}[1,4-dioxane]+k_{S_2O_8^{2-}}[S_2O_8^{2-}]}{k_{Cl^-}[0.0002M] + k_{NH_2Cl}[NH_2Cl] + k_{1,4D}[1,4-dioxane]+k_{S_2O_8^{2-}}[S_2O_8^{2-}]}\times100\% = 217\%$$

Reference:

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Appendix C

Supplemental Information for Chapter 4

Appendix C-1 Calculation of photolysis rates

The photolysis rate (r_p) of H_2O_2, $S_2O_8^{2-}$ and HOCl by low-pressure high-output (LPHO) mercury vapor UV lamp (λ=254nm) was calculated based on the following equation:

$$r_p = -2 \times \Phi \times I_0 \times f_{oxidant} \times f_{solution} \qquad (1)$$

Φ is the extinction coefficient of the oxidation, *i.e.*, Φ_{H2O2}=0.5 (Baxendale and Wilson, 1957), $\Phi_{persulfate}$=0.7 (Mark et al., 1990), Φ_{HOCl}=0.7 (Watts and Linden, 2007), Φ_{OCl^-}=0.52 (Nowell and Hoigne, 1992). I_o is volume-normalized UV irradiance from the flow-through UV reactor (Scheme S1).

$f_{oxidant}$ is the fraction of incident light absorbed by the oxidant. $f_{solution}$ is the fraction of light absorbed by the total solution, which were calculated as:

$$f_{oxidant} = \frac{\varepsilon_p c_p}{\sum \varepsilon_i c_i} \qquad (2)$$

$$f_{solution} = 1 - 10^{-(\alpha + \sum \varepsilon_i c_i)l} \qquad (3)$$

ε_p is the molar extinction coefficient of the oxidant ($M^{-1} \cdot cm^{-1}$), c_p is the concentration of the oxidant (M). ε_i and c_i are the molar extinction coefficient and concentration for NOM and a particular contaminant selected. α is the absorption coefficient of the solution at the wavelength of 254 nm and l is the path length of the reactor (cm). The direct photolysis rate for NOM and a particular contaminant is also calculated based on the same equations except $f_{contaminant}$ is calculated based on the ε_i and c_i of the particular contaminant.

The volume-normalized surface irradiance from a flow-through UV reactor (I_o) was calculated as follows:

$$I_0 = \frac{W_{UV} \times S_{UV}}{E_{254nm} \times V \times t} \tag{4}$$

The flow-through UV reactor was based on a configuration widely applied in water reuse facilities (Scheme S1). The hydraulic retention time of the UV reactor (t) is 26 second. The energy output of the low-pressure high-output mercury vapor UV lamp (W_{uv}) during the hydraulic retention time of the UV reactor is 1179 mJ (Trojan Technology, London, ON). The UV lamp surface area (S_{uv}) is 1302 cm^2. E is the energy of one mole of photons at the wavelength of 254 nm (4.72×10^8 mJ), V is the volume of the UV reactor (9.8 L). Consequently, I_o was calculated as 1.27×10^{-5} L^{-1}s^{-1}.

Appendix C-2 Table of rate constants and elemental reactions for kinetics modeling

No.	Reaction	Rate Constant	Reference
1	$H_2O_2 \xrightarrow{h\nu} 2OH^{\cdot}$	1.0×10^{-3} s^{-1}	Calculated
2	$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^{\cdot-}$	1.4×10^{-3} s^{-1}	Calculated
3	$HOCl \xrightarrow{h\nu} OH^{\cdot} + Cl^{\cdot}$	3.9×10^{-3} s^{-1}	Calculated
4	$ClO^- \xrightarrow{h\nu} Cl^{\cdot} + O^{\cdot-}$	3.2×10^{-3} s^{-1}	Calculated
5	$NOM \xrightarrow{h\nu} OH^{\cdot} + products$	1.8×10^{-10} s^{-1}	Calculated
6	$S_2O_8^{2-} + OH^{\cdot} \rightarrow S_2O_8^{\cdot-}$	1.4×10^7 M^{-1}s^{-1}	1
7	$S_2O_8^{2-} + SO_4^{\cdot-} \rightarrow S_2O_8^{\cdot-} + SO_4^{2-}$	6.6×10^5 M^{-1}s^{-1}	2
8	$S_2O_8^{2-} + Cl^{\cdot} \rightarrow S_2O_8^{\cdot-} + Cl$	8.8×10^6 M^{-1}s^{-1}	3
9	$S_2O_8^{2-} + CO_3^{\cdot-} \rightarrow S_2O_8^{\cdot-} + CO_3^{2-}$	3.0×10^7 M^{-1}s^{-1}	4
10	$S_2O_8^{2-} + SO_5^{\cdot-} \rightarrow S_2O_8^{\cdot-} + SO_5^{2-}$	1.0×10^5 M^{-1}s^{-1}	Assumed
11	$SO_5^{2-} + H^+ \rightarrow HSO_5^-$	5.0×10^{10} M^{-1}s^{-1}	4
12	$SO_5^{2-} + SO_4^{\cdot-} \rightarrow SO_5^{\cdot} + SO_4^{2-}$	1.0×10^8 M^{-1}s^{-1}	5
13	$HSO_5^- \rightarrow H^+ + SO_5^{2-}$	2.0×10^1 s^{-1}	4
14	$HSO_5^- + OH^{\cdot} \rightarrow H_2O + SO_5^{\cdot-}$	1.7×10^7 M^{-1}s^{-1}	6
15	$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^{2-} + OH^{\cdot}$	6.6×10^2 s^{-1}	7
16	$SO_4^{2-} + Cl^{\cdot} \rightarrow SO_4^{\cdot-} + Cl^-$	2.5×10^8 M^{-1}s^{-1}	5
17	$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + OH^{\cdot}$	7.0×10^7 M^{-1}s^{-1}	8
18	$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\cdot}$	3.0×10^8 M^{-1}s^{-1}	5
19	$SO_4^{\cdot-} + OH^{\cdot} \rightarrow HSO_5^-$	1.0×10^{10} M^{-1}s^{-1}	5
20	$SO_4^{\cdot-} + HSO_5^- \rightarrow SO_5^{\cdot-} + SO_4^{2-} + H^+$	1.0×10^6 M^{-1}s^{-1}	5
21	$HSO_4^- \rightarrow H^+ + SO_4^{2-}$	1.2×10^{-2} s^{-1}	Calculated
22	$SO_4^{\cdot-} + SO_4^{\cdot-} \rightarrow S_2O_8^{2-}$	7.0×10^8 M^{-1}s^{-1}	5
23	$SO_5^{\cdot-} + SO_5^{\cdot-} \rightarrow S_2O_8^{2-} + O_2$	2.2×10^8 M^{-1}s^{-1}	5
24	$SO_5^{\cdot-} + SO_5^{\cdot-} \rightarrow SO_4^{\cdot-} + SO_4^{\cdot-} + O_2$	2.1×10^8 M^{-1}s^{-1}	5
25	$SO_5^{\cdot-} + HO_2^{\cdot} \rightarrow O_2 + HSO_5^-$	5.0×10^7 M^{-1}s^{-1}	9
26	$H_2O_2 \rightarrow H^+ + HO_2^-$	1.3×10^{-1} s^{-1}	4
27	$H^+ + HO_2^- \rightarrow H_2O_2$	5.0×10^{10} M^{-1}s^{-1}	4
28	$H_2O_2 + SO_4^{\cdot-} \rightarrow HO_2^{\cdot} + HSO_4^-$	1.2×10^7 M^{-1}s^{-1}	10
29	$H_2O_2 + SO_4^{\cdot-} \rightarrow HO_2^{\cdot} + SO_4^{2-} + H^+$	1.2×10^7 M^{-1}s^{-1}	11
30	$H_2O_2 + O_2^{\cdot-} \rightarrow OH^{\cdot} + OH^- + O_2$	1.3×10^{-1} M^{-1}s^{-1}	12
31	$H_2O_2 + O^{\cdot-} \rightarrow O_2^{\cdot-} + H_2O$	4.0×10^8 M^{-1}s^{-1}	13
32	$H_2O \rightarrow H^+ + OH^-$	1.0×10^{-3} s^{-1}	4
33	$H^+ + OH^- \rightarrow H_2O$	1.0×10^{11} M^{-1}s^{-1}	4
34	$H^+ + O_2^{\cdot-} \rightarrow HO_2^{\cdot}$	5.0×10^{10} M^{-1}s^{-1}	14
35	$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O$	2.7×10^7 M^{-1}s^{-1}	13
36	$OH^{\cdot} + OH^- \rightarrow O^{\cdot-} + H_2O$	1.2×10^{10} M^{-1}s^{-1}	13
37	$O^{\cdot-} + H_2O \rightarrow OH^{\cdot} + OH^-$	1.8×10^5 s^{-1}	13
38	$O^{\cdot-} + HO_2^- \rightarrow O_2^{\cdot-} + OH^-$	4.0×10^8 M^{-1}s^{-1}	13
39	$O^{\cdot-} + O_2 \rightarrow O_3^{\cdot-}$	3.6×10^9 M^{-1}s^{-1}	13
40	$O^{\cdot-} + O_2^{\cdot-} + H^+ \rightarrow OH^- + O_2$	6.0×10^8 M^{-1}s^{-1}	15
41	$O_3^{\cdot-} \rightarrow O_2 + O^{\cdot-}$	2.6×10^3 s^{-1}	16
42	$OH^{\cdot} + O^{\cdot-} \rightarrow HO_2^-$	1.0×10^{10} M^{-1}s^{-1}	13
43	$OH^{\cdot} + HO_2^- \rightarrow HO_2^{\cdot} + OH^-$	7.5×10^9 M^{-1}s^{-1}	17
44	$OH^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2$	6.6×10^9 M^{-1}s^{-1}	18

45	$OH^{\cdot} + O_2^{\cdot-} \rightarrow OH^- + O_2$	7.0×10^9 M^{-1}s^{-1}	19
46	$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$	3.6×10^9 M^{-1}s^{-1}	20
47	$OH^{\cdot} + Cl^- \rightarrow ClOH^{\cdot-}$	4.3×10^9 M^{-1}s^{-1}	21
48	$OH^{\cdot} + HSO_4^- \rightarrow H_2O + SO_4^{\cdot-}$	1.7×10^6 M^{-1}s^{-1}	22
49	$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$	8.3×10^5 M^{-1}s^{-1}	23
50	$HO_2^{\cdot} + H_2O_2 \rightarrow OH^{\cdot} + H_2O + O_2$	3.0×10^0 M^{-1}s^{-1}	24
51	$HO_2^{\cdot} + O_2^{\cdot-} \rightarrow HO_2^- + O_2$	9.7×10^7 M^{-1}s^{-1}	23
52	$HO_2^{\cdot} \rightarrow H^+ + O_2^{\cdot-}$	1.6×10^5 s^{-1}	23
53	$ClOH^{\cdot-} \rightarrow Cl^- + OH^{\cdot}$	6.1×10^9 s^{-1}	21
54	$ClOH^{\cdot-} + Cl^- \rightarrow OH^- + Cl_2^{\cdot-}$	1.0×10^4 M^{-1}s^{-1}	25
55	$ClOH^{\cdot-} + H^+ \rightarrow Cl^{\cdot} + H_2O$	2.1×10^{10} M^{-1}s^{-1}	21
56	$HOCl + H_2O_2 \rightarrow HCl + H_2O + O_2$	1.1×10^4 M^{-1}s^{-1}	26
57	$HOCl + OH^{\cdot} \rightarrow ClO^{\cdot} + H_2O$	2.0×10^9 M^{-1}s^{-1}	27
58	$HOCl + O_2^{\cdot-} \rightarrow Cl^{\cdot} + OH^- + O_2$	7.5×10^6 M^{-1}s^{-1}	27
59	$HOCl + HO_2^{\cdot} \rightarrow Cl^{\cdot} + OH^- + O_2 + H$	7.5×10^6 M^{-1}s^{-1}	27
60	$HOCl + Cl^{\cdot} \rightarrow ClO^{\cdot} + H^+ + Cl^-$	3.0×10^9 M^{-1}s^{-1}	28
61	$HOCl + Cl^- \rightarrow Cl_2OH^-$	1.5×10^4 M^{-1}s^{-1}	29
62	$Cl^{\cdot} + H_2O_2 \rightarrow H^+ + Cl^- + HO_2^{\cdot}$	2.0×10^9 M^{-1}s^{-1}	30
63	$Cl^{\cdot} + H_2O \rightarrow ClOH^{\cdot-} + H^+$	2.5×10^5 s^{-1}	21
64	$Cl^{\cdot} + OH^- \rightarrow ClOH^{\cdot-}$	1.8×10^{10} M^{-1}s^{-1}	28
65	$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot-}$	8.5×10^9 M^{-1}s^{-1}	30
66	$Cl^{\cdot} + Cl_2 \rightarrow Cl_3$	5.3×10^8 M^{-1}s^{-1}	31
67	$Cl^{\cdot} + ClO^- \rightarrow ClO^{\cdot} + Cl^-$	8.3×10^9 M^{-1}s^{-1}	28
68	$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$	8.8×10^7 M^{-1}s^{-1}	32
69	$Cl_2^{\cdot-} + Cl^{\cdot} \rightarrow Cl_2 + Cl^-$	2.1×10^9 M^{-1}s^{-1}	30
70	$Cl_2^{\cdot-} + OH^- \rightarrow Cl^- + ClOH^{\cdot-}$	4.5×10^7 M^{-1}s^{-1}	25
71	$Cl_2^{\cdot-} \rightarrow Cl^{\cdot} + Cl^-$	6.0×10^4 s^{-1}	30
72	$Cl_2^{\cdot-} + Cl_2^{\cdot-} \rightarrow 2\,Cl^- + Cl_2$	9.0×10^8 M^{-1}s^{-1}	30
73	$Cl_2^{\cdot-} + H_2O \rightarrow Cl^- + HClOH$	1.3×10^3 s^{-1}	33
74	$Cl_2^{\cdot-} + OH^{\cdot} \rightarrow HOCl + Cl^-$	1.0×10^9 M^{-1}s^{-1}	34
75	$Cl_2^{\cdot-} + H_2O_2 \rightarrow HO_2^{\cdot} + H^+ + 2\,Cl^-$	1.4×10^5 M^{-1}s^{-1}	27
76	$Cl_2^{\cdot-} + HO_2^{\cdot} \rightarrow O_2 + H^+ + 2\,Cl^-$	3.1×10^9 M^{-1}s^{-1}	27
77	$Cl_2^{\cdot-} + O_2^{\cdot-} \rightarrow O_2 + 2\,Cl^-$	2.0×10^9 M^{-1}s^{-1}	27
78	$HClOH \rightarrow H^+ + ClOH^{\cdot-}$	1.0×10^8 s^{-1}	33
79	$HClOH \rightarrow Cl^{\cdot} + H_2O$	1.0×10^2 s^{-1}	33
80	$HClOH + Cl^- \rightarrow Cl_2^{\cdot-} + H_2O$	5.0×10^9 M^{-1}s^{-1}	33
81	$H^+ + Cl^- \rightarrow HCl$	5.0×10^{10} M^{-1}s^{-1}	4
82	$HCl \rightarrow H^+ + Cl^-$	8.6×10^{16} s^{-1}	4
83	$ClO^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2$	1.7×10^5 M^{-1}s^{-1}	26
84	$ClO^- + OH^{\cdot} \rightarrow ClO^{\cdot} + OH^-$	8.8×10^9 M^{-1}s^{-1}	27
85	$ClO^- + O_2^{\cdot-} + H_2O \rightarrow Cl^{\cdot} + 2\,OH^- + O_2$	2.0×10^8 M^{-1}s^{-1}	27
86	$Cl_2 + Cl^- \rightarrow Cl_3^-$	2.0×10^4 M^{-1}s^{-1}	35
87	$Cl_2 + O_2^{\cdot-} \rightarrow O_2 + Cl_2^{\cdot-}$	1.0×10^9 M^{-1}s^{-1}	27
88	$Cl_2 + HO_2^{\cdot} \rightarrow H^+ + O_2 + Cl_2^{\cdot-}$	1.0×10^9 M^{-1}s^{-1}	36
89	$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$	2.2×10^0 s^{-1}	29
90	$Cl_2 + H_2O_2 \rightarrow 2\,HCl + O_2$	1.3×10^4 M^{-1}s^{-1}	27
91	$Cl_2OH^- \rightarrow HOCl + Cl^-$	5.5×10^9 s^{-1}	29
92	$Cl_3^- \rightarrow Cl_2 + Cl^-$	1.1×10^5 s^{-1}	35
93	$Cl_3^- + HO_2^{\cdot} \rightarrow Cl_2^{\cdot-} + HCl + O_2$	1.0×10^9 M^{-1}s^{-1}	36
94	$Cl_3^- + O_2^{\cdot-} \rightarrow Cl_2^{\cdot-} + Cl^- + O_2$	3.8×10^9 M^{-1}s^{-1}	27
95	$H_2CO_3 \rightarrow HCO_3^- + H^+$	2.5×10^4 s^{-1}	4

96	$H_2CO_3 + OH^. \rightarrow CO_3^{.-} + H_2O + H^+$	1.0×10^6 M⁻¹s⁻¹	37
97	$HCO_3^- + H^+ \rightarrow H_2CO_3$	5.0×10^{10} M⁻¹s⁻¹	4
98	$HCO_3^- \rightarrow CO_3^{2-} + H^+$	2.5×10^0 s⁻¹	27
99	$HCO_3^- + OH^. \rightarrow CO_3^{.-} + H_2O$	8.6×10^6 M⁻¹s⁻¹	13
100	$HCO_3^- + Cl^. \rightarrow CO_3^{.-} + HCl$	2.2×10^8 M⁻¹s⁻¹	38
101	$HCO_3^- + Cl_2^{.-} \rightarrow 2\,Cl^- + H^+ + CO_3^{.-}$	8.0×10^7 M⁻¹s⁻¹	27
102	$HCO_3^- + SO_4^{.-} \rightarrow CO_3^{.-} + SO_4^{2-} + H^+$	9.1×10^6 M⁻¹s⁻¹	39
103	$CO_3^{2-} + H^+ \rightarrow HCO_3^-$	5.0×10^{10} M⁻¹s⁻¹	27
104	$CO_3^{2-} + OH^. \rightarrow CO_3^{.-} + OH^-$	3.9×10^8 M⁻¹s⁻¹	13
105	$CO_3^{2-} + Cl^. \rightarrow CO_3^{.-} + Cl^-$	5.0×10^8 M⁻¹s⁻¹	38
106	$CO_3^{2-} + Cl_2^{.-} \rightarrow CO_3^{.-} + 2\,Cl^-$	1.6×10^8 M⁻¹s⁻¹	27
107	$CO_3^{2-} + ClO^. \rightarrow CO_3^{.-} + ClO^-$	6.0×10^2 M⁻¹s⁻¹	40
108	$CO_3^{2-} + SO_4^{.-} \rightarrow CO_3^{.-} + SO_4^{2-}$	2.5×10^6 M⁻¹s⁻¹	41
109	$CO_3^{.-} + H_2O_2 \rightarrow HCO_3^- + HO_2^.$	4.3×10^5 M⁻¹s⁻¹	42
110	$CO_3^{.-} + HO_2^- \rightarrow CO_3^{2-} + HO_2^.$	3.0×10^7 M⁻¹s⁻¹	42
111	$CO_3^{.-} + HO_2^- \rightarrow HCO_3^- + O_2^{.-}$	3.0×10^7 M⁻¹s⁻¹	1
112	$CO_3^{.-} + OH^. \rightarrow product$	3.0×10^9 M⁻¹s⁻¹	43
113	$CO_3^{.-} + CO_3^{.-} \rightarrow product$	3.0×10^7 M⁻¹s⁻¹	43
114	$CO_3^{.-} + O_2^{.-} \rightarrow CO_3^{2-} + O_2$	6.0×10^8 M⁻¹s⁻¹	43
115	$CO_3^{.-} + 2Br^- \rightarrow CO_3^{2-} + Br_2^-$	3.4×10^4 M⁻¹s⁻¹	40
116	$CO_3^{.-} + ClO^- \rightarrow CO_3^{2-} + ClO^.$	5.1×10^5 M⁻¹s⁻¹	44
117	$Br^- + OH^. \rightarrow BrOH^{.-}$	1.1×10^{10} M⁻¹s⁻¹	27
118	$Br^- + SO_4^- \rightarrow Br^. + SO_4^{2-}$	3.5×10^9 M⁻¹s⁻¹	45
119	$Br^- + H^+ \rightarrow + HBr$	5.0×10^{10} M⁻¹s⁻¹	4
120	$Br^- + HOCl \rightarrow BrCl + OH^-$	1.3×10^{-1} M⁻¹s⁻¹	46
121	$Br^- + Cl_2 \rightarrow BrCl_2^-$	6.0×10^9 M⁻¹s⁻¹	35
122	$Br^- + ClOH^{.-} \rightarrow BrCl^{.-} + OH^-$	1.0×10^9 M⁻¹s⁻¹	27
123	$Br^- + Cl^. \rightarrow BrCl^{.-}$	1.2×10^{10} M⁻¹s⁻¹	27
124	$Br^- + Cl_2^{.-} \rightarrow BrCl^{.-} + Cl^-$	4.0×10^9 M⁻¹s⁻¹	35
125	$Br^- + CO_3^{.-} \rightarrow Br^. + CO_3^{2-}$	1.0×10^5 M⁻¹s⁻¹	38
126	$Br^- + O^{.-} \rightarrow product$	2.2×10^8 M⁻¹s⁻¹	47
127	$BrCl_2^- \rightarrow Cl_2 + Br^-$	9.0×10^3 s⁻¹	35
128	$BrCl_2^- + Br^- \rightarrow Br_2Cl^- + Cl^-$	3.0×10^8 M⁻¹s⁻¹	35
129	$HBr \rightarrow H^+ + Br^-$	5.0×10^{19} s⁻¹	4
130	$Br_2 + Br^- \rightarrow Br_3^-$	9.6×10^8 M⁻¹s⁻¹	27
131	$Br_2 + HO_2^. \rightarrow Br_2^{.-} + O_2 + H^+$	1.1×10^8 M⁻¹s⁻¹	27
132	$Br_2 + O_2^{.-} \rightarrow Br_2^{.-} + O_2$	5.6×10^9 M⁻¹s⁻¹	27
133	$Br_2 + H_2O \rightarrow HOBr + H^+ + Br^-$	9.7×10^1 s⁻¹	27
134	$Br_2 + H_2O_2 \rightarrow HBr + O_2$	1.3×10^3 M⁻¹s⁻¹	48
135	$Br_2 + Cl^- \rightarrow Br_2Cl^-$	5.0×10^4 M⁻¹s⁻¹	27
136	$Br_2Cl^- \rightarrow + Br_2 + Cl^-$	3.8×10^4 s⁻¹	27
137	$Br_2Cl^- + Cl^- \rightarrow BrCl_2^- + Br^-$	1.0×10^5 M⁻¹s⁻¹	27
138	$Br_3^- \rightarrow Br_2$	5.5×10^7 s⁻¹	27
140	$Br_3^- + HO_2^. \rightarrow Br_2^{.-} + HBr + O_2$	1.0×10^7 M⁻¹s⁻¹	27
141	$Br_3^- + O_2^{.-} \rightarrow Br_2^{.-} + Br^- + O_2$	3.8×10^9 M⁻¹s⁻¹	27
142	$OBr^- + H^+ \rightarrow HOBr$	5.0×10^{10} M⁻¹s⁻¹	4
143	$OBr^- + H_2O_2 \rightarrow Br^- + H_2O + O_2$	1.2×10^6 M⁻¹s⁻¹	49
144	$OBr^- + OH^. \rightarrow BrO^. + OH^-$	4.5×10^9 M⁻¹s⁻¹	27
145	$OBr^- + O_2^{.-} + H_2O \rightarrow Br^. + 2\,OH^- + O_2$	2.0×10^8 M⁻¹s⁻¹	27
146	$OBr^- + CO_3^{.-} \rightarrow CO_3^{2-} + BrO^.$	4.3×10^7 M⁻¹s⁻¹	50
147	$OBr^- + O^{.-} + H^+ \rightarrow OH^- + BrO^.$	2.9×10^9 M⁻¹s⁻¹	51

148	$HOBr \rightarrow H^+ + OBr^-$	7.9×10^1 s^{-1}	4
149	$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$	5.0×10^9 M^{-1}s^{-1}	52
150	$HOBr + HO_2^- \rightarrow Br^- + H_2O + O_2$	7.6×10^8 M^{-1}s^{-1}	49
151	$HOBr + H_2O_2 \rightarrow HBr + H_2O + O_2$	1.5×10^4 M^{-1}s^{-1}	1
152	$HOBr + OH^{\cdot -} \rightarrow BrO^\cdot + H_2O$	2.0×10^9 M^{-1}s^{-1}	27
153	$HOBr + O_2^{\cdot -} \rightarrow BrOH^{\cdot -} + O_2$	3.5×10^9 M^{-1}s^{-1}	49
154	$HOBr + HO_2^\cdot \rightarrow BrOH^{\cdot -} + H^+ + O_2$	3.5×10^9 M^{-1}s^{-1}	27
155	$HOBr + Cl^- \rightarrow BrCl + OH^-$	5.6×10^2 M^{-1}s^{-1}	46
156	$Br^\cdot + H_2O \rightarrow BrOH^{\cdot -} + H^+$	1.4×10^0 s^{-1}	28
157	$Br^\cdot + OH^- \rightarrow BrOH^{\cdot -}$	1.1×10^{10} M^{-1}s^{-1}	53
158	$Br^\cdot + Br^- \rightarrow Br_2^{\cdot -}$	1.2×10^{10} M^{-1}s^{-1}	27
159	$Br^\cdot + Br^\cdot \rightarrow Br_2$	1.0×10^9 M^{-1}s^{-1}	27
160	$Br^\cdot + OBr^- \rightarrow Br^- + BrO^\cdot$	4.1×10^9 M^{-1}s^{-1}	28
161	$Br^\cdot + H_2O_2 \rightarrow HO_2^\cdot + Br^- + H^+$	4.0×10^9 M^{-1}s^{-1}	27
162	$Br^\cdot + HO_2^\cdot \rightarrow H^+ + O_2 + Br^-$	1.6×10^8 M^{-1}s^{-1}	27
163	$Br^\cdot + CO_3^{2-} \rightarrow Br^- + CO_3^{\cdot -}$	2.0×10^6 M^{-1}s^{-1}	27
164	$Br^\cdot + HCO_3^- \rightarrow Br^- + CO_3^{\cdot -}$	1.0×10^6 M^{-1}s^{-1}	27
165	$Br^\cdot + Cl^- \rightarrow BrCl^{\cdot -}$	1.0×10^8 M^{-1}s^{-1}	27
166	$Br_2^{\cdot -} + H_2O_2 \rightarrow HO_2^\cdot + 2Br^- + H^+$	5.0×10^2 M^{-1}s^{-1}	27
167	$Br_2^{\cdot -} \rightarrow Br^\cdot + Br^-$	1.9×10^4 s^{-1}	27
168	$Br_2^{\cdot -} + Br_2^{\cdot -} \rightarrow Br_2 + 2Br^-$	1.9×10^9 M^{-1}s^{-1}	27
169	$Br_2^{\cdot -} + Br^\cdot \rightarrow Br_2 + Br^-$	2.0×10^9 M^{-1}s^{-1}	27
170	$Br_2^{\cdot -} + HO_2^\cdot \rightarrow O_2 + 2Br^- + H^+$	1.0×10^8 M^{-1}s^{-1}	48
171	$Br_2^{\cdot -} + HO_2^\cdot \rightarrow HO_2^\cdot$	4.4×10^9 M^{-1}s^{-1}	27
172	$Br_2^{\cdot -} + O_2^{\cdot -} \rightarrow O_2 + 2Br^-$	1.7×10^8 M^{-1}s^{-1}	48
173	$Br_2^{\cdot -} + OBr^- \rightarrow BrO^\cdot + 2Br^-$	6.2×10^7 M^{-1}s^{-1}	27
174	$Br_2^{\cdot -} + OH^\cdot \rightarrow HOBr + Br^-$	1.0×10^9 M^{-1}s^{-1}	48
175	$Br_2^{\cdot -} + OH^- \rightarrow BrOH^{\cdot -} + Br^-$	2.7×10^6 M^{-1}s^{-1}	48
176	$Br_2^{\cdot -} + CO_3^{2-} \rightarrow 2Br^- + CO_3^{\cdot -}$	1.1×10^5 M^{-1}s^{-1}	27
177	$Br_2^{\cdot -} + HCO_3^- \rightarrow 2Br^- + CO_3^{\cdot -} + H^+$	8.0×10^4 M^{-1}s^{-1}	27
178	$Br_2^{\cdot -} + Cl^- \rightarrow BrCl^{\cdot -} + Br^-$	4.3×10^6 M^{-1}s^{-1}	35
179	$Br_2^{\cdot -} + Cl_2^{\cdot -} \rightarrow Br_2 + 2\,Cl^-$	4.0×10^9 M^{-1}s^{-1}	27
180	$BrOH^{\cdot -} \rightarrow OH^\cdot + Br^-$	3.3×10^7 s^{-1}	53
181	$BrOH^{\cdot -} \rightarrow Br^\cdot + OH^-$	4.2×10^6 s^{-1}	53
182	$BrOH^{\cdot -} + H^+ \rightarrow Br^\cdot + H_2O$	4.4×10^{10} M^{-1}s^{-1}	53
183	$BrOH^{\cdot -} + Br^- \rightarrow Br_2^{\cdot -} + OH^-$	1.9×10^8 M^{-1}s^{-1}	53
184	$BrOH^{\cdot -} + Cl^- \rightarrow BrCl^{\cdot -} + OH^-$	1.9×10^8 M^{-1}s^{-1}	27
185	$Br_2OH^- + H^+ \rightarrow Br_2 + H_2O$	2.0×10^{10} M^{-1}s^{-1}	54
186	$Br_2OH^- \rightarrow HOBr + Br^-$	5.0×10^9 s^{-1}	54
187	$BrCl + H_2O \rightarrow HOBr + Cl^- + H^+$	1.0×10^5 s^{-1}	27
188	$BrCl + H_2O_2 \rightarrow HBr + HCl + O_2$	1.3×10^4 M^{-1}s^{-1}	27
189	$BrCl + O_2^{\cdot -} \rightarrow BrCl^{\cdot -} + O_2$	4.0×10^9 M^{-1}s^{-1}	27
190	$BrCl + HO_2^\cdot \rightarrow BrCl^{\cdot -} + O_2 + H^+$	5.0×10^8 M^{-1}s^{-1}	27
191	$BrCl + Cl^- \rightarrow BrCl_2^-$	1.0×10^6 M^{-1}s^{-1}	27
192	$BrCl + Br^- \rightarrow Br_2Cl^-$	3.0×10^8 M^{-1}s^{-1}	27
193	$BrCl^{\cdot -} + OH^\cdot \rightarrow BrCl + OH^-$	1.0×10^9 M^{-1}s^{-1}	27
194	$BrCl^{\cdot -} + HO_2^\cdot \rightarrow Br^- + Cl^- + O_2 + H^+$	1.0×10^9 M^{-1}s^{-1}	27
195	$BrCl^{\cdot -} + O_2^{\cdot -} \rightarrow Br^- + Cl^- + O_2$	6.0×10^8 M^{-1}s^{-1}	27
196	$BrCl^{\cdot -} + H_2O_2 \rightarrow Br^- + HCl + HO_2^\cdot$	5.0×10^3 M^{-1}s^{-1}	27
197	$BrCl^{\cdot -} + OH^- \rightarrow Br^- + ClOH^{\cdot -}$	3.0×10^6 M^{-1}s^{-1}	27
198	$BrCl^{\cdot -} + OH^- \rightarrow BrOH^{\cdot -} + Cl^-$	2.0×10^7 M^{-1}s^{-1}	27

199	$BrCl^{\cdot-} + HCO_3^- \rightarrow Br^- + HCl + CO_3^-$	3.0×10^6 M^{-1}s^{-1}	27
200	$BrCl^{\cdot-} + CO_3^{2-} \rightarrow Br^- + Cl^- + CO_3^-$	6.0×10^6 M^{-1}s^{-1}	27
201	$BrCl^{\cdot-} + BrCl^{\cdot-} \rightarrow Br^- + Cl^- + BrCl$	4.7×10^9 M^{-1}s^{-1}	27
202	$BrCl^{\cdot-} + Cl_2^{\cdot-} \rightarrow 2Cl^- + BrCl$	2.0×10^9 M^{-1}s^{-1}	27
203	$BrCl^{\cdot-} + Br_2^{\cdot-} \rightarrow Br_2 + Cl^- + Br^-$	4.0×10^9 M^{-1}s^{-1}	27
204	$BrCl^{\cdot-} \rightarrow Cl^{\cdot} + Br^-$	2.0×10^3 s^{-1}	55
205	$BrCl^{\cdot-} \rightarrow Cl^- + Br^{\cdot}$	6.1×10^4 s^{-1}	55
206	$BrCl^{\cdot-} + Br^- \rightarrow Br_2^{\cdot-} + Cl^-$	8.0×10^9 M^{-1}s^{-1}	35
207	$BrCl^{\cdot-} + Cl^- \rightarrow Cl_2^{\cdot-} + Br^-$	1.1×10^2 M^{-1}s^{-1}	35
208	$Br_2Cl^- \rightarrow BrCl + Br^-$	1.7×10^4 s^{-1}	27
209	$Br_2Cl^- \rightarrow BrCl + Cl^-$	1.7×10^5 s^{-1}	35
210	$NOM + OH^{\cdot} \rightarrow product$	7.2×10^4 (mg/L)$^{-1}$s^{-1}	56
211	$NOM + SO_4^- \rightarrow product$	2.5×10^4 (mg/L)$^{-1}$s^{-1}	57
212	$NOM + Cl^{\cdot} \rightarrow product$	1.3×10^4 (mg/L)$^{-1}$s^{-1}	58
213	$NOM + Cl_2^{\cdot-} \rightarrow product$	1.0×10^2 (mg/L)$^{-1}$s^{-1}	Assumed
214	$NOM + CO_3^- \rightarrow product$	3.7×10^2 (mg/L)$^{-1}$s^{-1}	56
215	$NOM + Br^{\cdot} \rightarrow product$	1.0×10^4 (mg/L)$^{-1}$s^{-1}	*
216	$NOM + Br_2^{\cdot-} \rightarrow product$	1.0×10^2 (mg/L)$^{-1}$s^{-1}	*
217	$NOM + BrCl^{\cdot-} \rightarrow product$	1.0×10^2 (mg/L)$^{-1}$s^{-1}	*
218	$HOCl + Aniline \rightarrow product$	9.0×10^3 M^{-1}s^{-1}	*
219	$HOCl + 17\beta - estrodiol \rightarrow product$	2.5×10^2 M^{-1}s^{-1}	*
220	$HOCl + sulfamethoxazoel \rightarrow product$	1.0×10^2 M^{-1}s^{-1}	*
221	$HOCl + carbamezepine \rightarrow product$	1.0×10^2 M^{-1}s^{-1}	*

*Rate constants are estimated (detail in Text S3)

Appendix C-3 Probe method to determine steady state concentration of radicals

Nitrobenzene, benzoic acid and N,N-dimethylaniline were utilized to probe the steady state concentration of $HO^{\bullet}$, $SO_4^{\bullet-}$, $Cl^{\bullet}$, $Cl_2^{\bullet-}$ and $CO_3^{\bullet-}$. The control experiments showed a negligible direct photo-degradation for all probe compounds. Nitrobenzene exclusively reacts with $HO^{\bullet}$, therefore is the best probe for $HO^{\bullet}$. First, the experimentally observed pseudo first order decay rate of nitrobenzene (k_{obs}) was obtained and $[HO^{\bullet}]_{ss}$ was calculated based on Equation 1.

$$-\ln\left(\frac{[NB]_t}{[NB]_0}\right) = k_{HO-NB}[HO^{\bullet}]_{ss}t \qquad (Eq.\ 1)$$

$[NB]_t$ is the concentration of nitrobenzene at time t; $[NB]_0$ is the initial concentration of nitrobenzene; k_{HO-NB} is the first-order rate constant between $HO^{\bullet}$ and nitrobenzene, *i.e.*, 3.2×10^9 $M^{-1}s^{-1}$).[59]

$[CO_3^{\bullet-}]_{ss}$ is calculated based on equation 2 analogously.

$$-\ln\left(\frac{[N,NDMA]_t}{[N,NDMA]_0}\right) = k_{CO3-N,NDMA}[CO_3^{\bullet-}]_{ss}t \quad (Eq.\ 2)$$

k_{CO3-NB} is the first order rate constant between $CO_3^{\bullet-}$ and N,N-dimethylaniline (1.4×10^9 $M^{-1}s^{-1}$).[60]

$[Cl^{\bullet}]_{ss}$ and $[SO_4^{\bullet-}]_{ss}$ were simultaneously calculated using Equation 3 and 4

$$-\ln\left(\frac{[BA]_t}{[BA]_0}\right) = (k_{HO-BA}[HO^{\bullet}]_{ss} + k_{SO4-BA}[SO_4^{\bullet-}]_{ss} + k_{Cl-BA}[Cl^{\bullet}]_{ss})t \qquad (Eq.\ 3)$$

$$-\ln\left(\frac{[1,4D]_t}{[1,4D]_0}\right) = (k_{HO-1,4D}[HO^{\bullet}]_{ss} + k_{SO4-1,4D}[SO_4^{\bullet-}]_{ss} + k_{Cl-1,4D}[Cl^{\bullet}]_{ss})t \quad (Eq.\ 4)$$

$k_{HO-BA}=4.3\times10^9$ $M^{-1}s^{-1}$); $k_{SO4-BA}=1.2\times10^9$ $M^{-1}s^{-1}$); 1.4×10^9 $M^{-1}s^{-1}$, $k_{Cl-BA}=1.8\times10^{10}$ $M^{-1}s^{-1}$).[61-63]

In the UV/S$_2$O$_8{}^{2-}$, the contribution of Cl$_2{}^{\bullet-}$ to benzoic acid and 1,4-dioxane degradation was minimal because the steady state concentration of Cl$_2{}^{\bullet-}$ was low and its reactivity with the contaminants was lower than Cl$^{\bullet}$.[61] In UV/HOCl system, the steady-state concentration of Cl$_2{}^{\bullet-}$ could be high enough to make significant contribution to contaminant degradation because the reverse reaction of ClOH$^{\bullet-}$ with Cl$^-$ (Reaction 54 in **Appendix C-2**) produced a significant amount of Cl$_2{}^{\bullet-}$. Therefore, [Cl$^{\bullet}$]$_{ss}$ and [Cl$_2{}^{\bullet-}$]$_{ss}$ were simultaneously calculated using the following equations:

$$-\ln\left(\frac{[BA]_t}{[BA]_0}\right) = (k_{HO-BA}[HO^{\bullet}]_{ss} + k_{Cl2-BA}[Cl_2^{\bullet-}]_{ss} + k_{Cl-BA}[Cl^{\bullet}]_{ss})t \qquad \text{(eq 5)}$$

$$-\ln\left(\frac{[1,4D]_t}{[1,4D]_0}\right) = (k_{HO-1,4D}[HO^{\bullet}]_{ss} + k_{Cl2-1,4D}[Cl_2^{\bullet-}]_{ss} + k_{Cl-1,4D}[Cl^{\bullet}]_{ss})t \quad \text{(eq 6)}$$

$k_{Cl2\text{-}BA}$= 1.0×10^6 - 1.0×10^8 M^{-1}s^{-1}, $k_{Cl2\text{-}1,4D}$=1.0×10^6 - 1.0×10^8 M^{-1}s^{-1} (**Appendix C-4**).

Appendix C-4 Rate constants of reactions involving radicals

Nitrobenzene, benzoic acid and N,N-dimethylaniline were utilized to probe the steady state concentration of $HO^\bullet$, $SO_4^{\bullet-}$, $Cl^\bullet$, $Cl_2^{\bullet-}$ and $CO_3^{\bullet-}$. The control experiments showed a negligible direct photo-degradation for all probe compounds. Nitrobenzene exclusively reacts with $HO^\bullet$, therefore is the best probe for $HO^\bullet$. First, the experimentally observed pseudo first order decay rate of nitrobenzene (k_{obs}) was obtained and $[HO^\bullet]_{ss}$ was calculated based on Equation 1.

$$-\ln\left(\frac{[NB]_t}{[NB]_0}\right) = k_{HO-NB}[HO^\bullet]_{ss}t \qquad \text{(Eq. 1)}$$

$[NB]_t$ is the concentration of nitrobenzene at time t; $[NB]_0$ is the initial concentration of nitrobenzene; k_{HO-NB} is the first-order rate constant between $HO^\bullet$ and nitrobenzene, *i.e.*, 3.2×10^9 $M^{-1}s^{-1}$).[59]

$[CO_3^{\bullet-}]_{ss}$ is calculated based on equation 2 analogously.

$$-\ln\left(\frac{[N,NDMA]_t}{[N,NDMA]_0}\right) = k_{CO3-N,NDMA}[CO_3^{\bullet-}]_{ss}t \quad \text{(Eq. 2)}$$

k_{CO3-NB} is the first order rate constant between $CO_3^{\bullet-}$ and N,N-dimethylaniline (1.4×10^9 $M^{-1}s^{-1}$).[60]

$[Cl^\bullet]_{ss}$ and $[SO_4^{\bullet-}]_{ss}$ were simultaneously calculated using Equation 3 and 4

$$-\ln\left(\frac{[BA]_t}{[BA]_0}\right) = (k_{HO-BA}[HO^\bullet]_{ss} + k_{SO4-BA}[SO_4^{\bullet-}]_{ss} + k_{Cl-BA}[Cl^\bullet]_{ss})t \qquad \text{(Eq. 3)}$$

$$-\ln \left(\frac{[1,4D]_t}{[1,4D]_0}\right) = (k_{HO-1,4D}[HO^\cdot]_{ss} + k_{SO4-1,4D}[SO_4^{\cdot-}]_{ss} + k_{Cl-1,4D}[Cl^\cdot]_{ss})t \quad \text{(Eq. 4)}$$

k_{HO-BA}=4.3×10^9 M^{-1}s^{-1}); k_{SO4-BA}=1.2×10^9 M^{-1}s^{-1}, Neta et al, 1977); 1.4×10^9 M^{-1}s^{-1}, k_{Cl-BA}=1.8×10^{10} M^{-1}s^{-1}). [6163]

In the UV/S$_2$O$_8$$^{2-}$, the contribution of Cl$_2$$^{\cdot-}$ to benzoic acid and 1,4-dioxane degradation was minimal because the steady state concentration of Cl$_2$$^{\cdot-}$ was low and its reactivity with the contaminants was lower than Cl$^\cdot$.[61] In UV/HOCl system, the steady-state concentration of Cl$_2$$^{\cdot-}$ could be high enough to make significant contribution to contaminant degradation because the reverse reaction of ClOH$^{\cdot-}$ with Cl$^-$ (Reaction 54 in **Appendix C-2**) produced a significant amount of Cl$_2$$^{\cdot-}$. Therefore, [Cl$^\cdot$]$_{ss}$ and [Cl$_2$$^{\cdot-}$]$_{ss}$ were simultaneously calculated using the following equations:

$$-\ln \left(\frac{[BA]_t}{[BA]_0}\right) = (k_{HO-BA}[HO^\cdot]_{ss} + k_{Cl2-BA}[Cl_2^{\cdot-}]_{ss} + k_{Cl-BA}[Cl^\cdot]_{ss})t \quad \text{(eq 5)}$$

$$-\ln \left(\frac{[1,4D]_t}{[1,4D]_0}\right) = (k_{HO-1,4D}[HO^\cdot]_{ss} + k_{Cl2-1,4D}[Cl_2^{\cdot-}]_{ss} + k_{Cl-1,4D}[Cl^\cdot]_{ss})t \quad \text{(eq 6)}$$

k_{Cl2-BA}= 1.0×10^6 - 1.0×10^8 M^{-1}s^{-1}, $k_{Cl2-1,4D}$=1.0×10^6 - 1.0×10^8 M^{-1}s^{-1} (**Appendix C-4**).

Appendix C-5 Rate constants of reactions involving radicals

The rate constants for all six compounds were mostly obtained from NIST database.[64] When the value was not available, a range of the rate constant was estimated base on existing known values for similar compounds. For example, the reaction mechanism of $Cl^•$ and $Br^•$ are very similar to $HO^•$, and the rates are comparable to the rates of $HO^•$,[37,64] thus a $\pm10\%$ of $HO^•$ rate was assigned to $Cl^•$ or $Br^•$. The estimation also based on the reaction mechanism of the specific radical with different type of molecules. For example, $Cl^•$ reacts fast with aromatic compounds and amine containing compounds (10^9–10^{10} $M^{-1}s^{-1}$),[64] moderately fast with unsaturated aliphatic compounds (10^8–10^9 $M^{-1}s^{-1}$) and slow with saturated aliphatic compounds including chlorinated or brominated compounds (10^4–10^6 $M^{-1}s^{-1}$). $Br^•$ has high reaction rates with aromatic compounds (10^9–10^{10} $M^{-1}s^{-1}$) and low reactivity with aliphatic alcohols (10^4-10^6 $M^{-1}s^{-1}$).[64]

A relatively high reactivity also applies to $Cl_2^{•-}$, $ClBr^{•-}$, $Br_2^{•-}$ and $CO_3^{•-}$.[4,58] Therefore, a $\pm10\%$ rate was assigned based on known rates for any of the above radicals. With a comparison of available rate constants from the NIST database, $Cl_2^{•-}$ has high reaction rates (10^8 $M^{-1}s^{-1}$) with unsaturated aliphatic compounds than with aromatic (10^6–10^8 $M^{-1}s^{-1}$). Low reactivity with unsaturated carboxylic (10^6 M^{-1} s^{-1}). $CO_3^{•-}$ reacts fast with compounds containing amines (10^8–10^9 $M^{-1}s^{-1}$),[64] but low reactivity with aromatic compounds (10^4–10^6 $M^{-1}s^{-1}$). The rates of direct oxidation by HOCl were estimated when the literature values were not available. For example, the oxidation rates for aniline, 17β-estradiol, sulfamethoxazole and carbamazepine by HOCl was estimated based on their known

reaction rates with O_3.[65] The direct oxidation of 1,4-dioxane by HOCl is negligible based on experimental verification.

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