

NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title: Study of the viability of chlorine photolysis as an advanced oxidation process in water treatment systems

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Background and Introduction

Overview. Organic contaminants such as industrial solvents, pesticides, pharmaceuticals, and personal care products are released into the environment through runoff and waste water. Many of them are persistent in surface and groundwater. The organic contaminants are not removed from drinking water during standard drinking water treatment. While the health effect of organic contaminants has not yet been determined by epidemiological studies, many of these contaminants are known to be toxic in high doses. Multiple processes have been proposed to remove organic contaminants from drinking water but they all require expensive additions to treatment plant infrastructure. Chlorine photolysis is one solution to both organic contamination, because it produces a suite of reactive oxidants, and the high cost of implementation, because it has viable solar applications. **The purpose of the following study is to quantify the production of reactive oxidants, capable of degrading contaminants in drinking water, during chlorine photolysis.**

Chlorine photolysis degrades organic contaminants by producing reactive oxidant species, making it an advanced oxidation process. Advanced oxidation processes (AOPs) use reactive oxidants, primarily hydroxyl radical ($\bullet\text{OH}$) to degrade organic contaminants. In the case of chlorine photolysis, $\bullet\text{OH}$ and other reactive oxidants are produced by the reaction of ultraviolet wavelengths of light ($h\nu$) with “free-available chlorine” or hypochlorous acid, commonly known as bleach. Hypochlorous acid has an acid dissociation constant of 7.5 which means that in natural water systems (i.e. drinking water) both hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) are present in solution. Both HOCl and OCl^- react with light to form reactive oxidant species (Figure 1). The rate of chlorine degradation with light is dependent on how well it absorbs light, determined by the molar

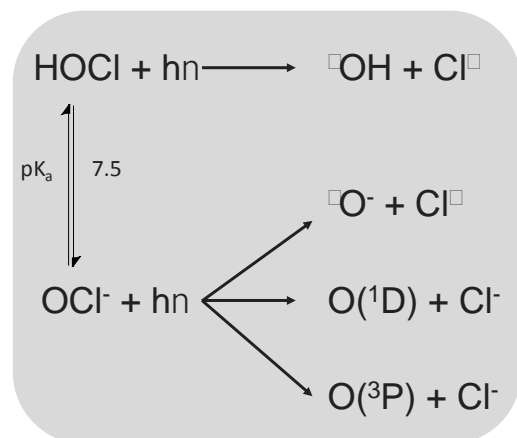


Figure 1. Production of reactive oxidants by reaction of chlorine with ultraviolet light.

absorptivity, which is much higher for OCl^- than for HOCl . The production of reactive oxidants by the photolysis reaction is determined by the quantum yield (or efficiency) of the reaction, which is much higher for HOCl than for OCl^- .

Hypothesis. The degradation of chlorine and the production of reactive oxidants will be determined by fundamental parameters such as molar absorptivity and quantum yield.

Study Goals and Research Objectives. The goal of this research is to be able to quantify the production of reactive oxidants during chlorine photolysis. In order to achieve this the study has two objectives:

- 1. Experimentally determination the direct chlorine photolysis rate constant and the production of measurable reactive oxidants.**
- 2. Develop a kinetic model to quantify the production of other reactive oxidants produced during chlorine photolysis.**

Needs Served. This research fills a current gap in the understanding of how chlorine photolysis degrades organic contaminants. Previous studies have determined the rate constants for many reactions that happen in this system, and other studies have looked at the degradation of contaminants of interest by reactive oxidants or by chlorine photolysis. Current scientific understanding of what types of reactive oxidants are produced and in what quantities is still lacking. This study seeks to fill that gap by determining reactive oxidant production under different conditions during chlorine photolysis.

Progress to Date

Chlorine photolysis is known to produce $\bullet\text{OH}$ and other reactive oxidants capable of degrading organic contaminants. Understanding how the production of reactive species changes with pH and photolysis wavelength is crucial to predict the ability of chlorine photolysis to degrade organic contaminants. Past research on the production of reactive species has focused on UV-C wavelengths for irradiation, primarily 254 nm. More recent research does include UV-A and UV-B light, often in the form of solar simulators, but is focused on contaminant degradation or pathogen inactivation, not the mechanisms of reactive oxidant formation. Identifying the reactive oxidants present under different conditions during chlorine photolysis is essential to developing an accurate model of the system, which can then be used to predict contaminant degradation under water treatment conditions.

Objective 1: Experimental determination of the direct chlorine photolysis rate constant and the production of measurable reactive oxidants.

We will quantify the degradation of chlorine and the production of reactive oxidant species across a pH range (5-10) and variety of irradiation wavelengths (254, 311, 365 nm). It is important to understand the kinetics of chlorine loss under different conditions because the final chlorine concentration is important for water treatment. When chlorine is used as a disinfectant in drinking water treatment in the U.S., there must be a minimum residual concentration through the distribution system. Additionally, knowing the rate of chlorine photolysis under different conditions will be the crucial input

variable for the kinetic model developed in objective 2. Finally, the direct photolysis rate will determine treatment parameters such as dose and residence time, should this treatment strategy be applied in a water treatment plant.

The experiment phase of the research will focus on determining the reactive oxidants $\bullet\text{OH}$, $\text{Cl}\bullet$, and O_3 . Both $\bullet\text{OH}$ and $\text{Cl}\bullet$ were selected because they are the primary direct products of chlorine photolysis and are likely to be important oxidants in this system. Ozone (O_3) was selected because it is a common alternative to chlorine for primary disinfection, is a strong oxidant, and validates the photolysis mechanism for $\text{O}(^3\text{P})$ production (Figure 1). Nitrobenzene, benzoate, and cinnamic acid have been selected as probe compounds. Probe compounds will be added and probe loss (for nitrobenzene and benzoate) or product formation (for cinnamic acid) will be quantified by high-performance liquid-chromatography. Nitrobenzene alone measures the production of $\bullet\text{OH}$, and has been selected due to low reactivity with light and other constituents. The $\text{Cl}\bullet$ can be determined by competition kinetics using both nitrobenzene and benzoate. Nitrobenzene reacts with only $\bullet\text{OH}$, while benzoate reacts with both and $\text{Cl}\bullet$. Competition between the loss of these probes can show the production of $\text{Cl}\bullet$. Cinnamic acid reacts with O_3 to produce benzaldehyde, and the production of O_3 can be determined by the production of benzaldehyde. Production of a specific product from the reaction of O_3 with cinnamic acid minimizes interference.

Objective 2. Development of a kinetic model to quantify the production of other reactive oxidants produced during chlorine photolysis.

A kinetic model will be developed in the software program Kintecus utilizing literature reactions and rate constants. This model will contain reactions between various chlorine, oxygen, and hydrogen-containing species and allow us to determine the formation of other reactive species during chlorine photolysis. The model will be informed by experimental results, and will match the loss rate of both HOCl and OCl^- to experimental data. Previous models of chlorine photolysis have been developed to approximate contaminant loss data, but most of the previous models neglected results where the pH is higher than the pK_a of chlorine. Evaluating the kinetic model at $\text{pH} > \text{pK}_a$ is important because when OCl^- is the dominant species, the mechanisms of radical production change, and $\bullet\text{OH}$ and $\text{Cl}\bullet$ are no longer the primary photoproducts. $\text{O}(^1\text{D})$ and $\text{O}(^3\text{P})$ begin to dominate, and quickly react to become $\bullet\text{OH}$ and O_3 respectively (Figure 1). While previous models may match lower pH data, being able to determine oxidant production at higher pH is important when plant influent ranges from pH 6-9.

Discussion of Results.

The preliminary results suggest that hydroxyl radical and chlorine radical are produced during chlorine photolysis, making chlorine photolysis an effective advanced oxidation process. At longer wavelengths (311 and 365 nm) the chlorine loss rate constant and probe loss are predicted by fundamental parameters (molar absorptivity and quantum yield). The wavelength of irradiation in these studies is within the solar spectrum. This means that hydroxyl radical is produced by chlorine photolysis under conditions found on the Earth's surface. The production of hydroxyl radical is produced at similar concentrations across a pH range, requiring less chemical input to ensure adequate reactive oxidant

production. Therefore, chlorine photolysis could be used in places that do not have the resources and infrastructure for typical drinking water treatment. The model is not accurately predicting chlorine loss at $\text{pH} > \text{pK}_a$ due to the over-prediction of some species at high pH.

Conclusions

Chlorine photolysis is a good candidate for removing organic contaminants from drinking water. The photolysis of free available chlorine produces reactive oxidants at all pH and wavelength conditions in this study. The model is still in development, but preliminary results suggest that it will be able to quantify the reactive oxidants produced. Quantifying reactive oxidant production during chlorine photolysis is important because reactive oxidant concentrations determine the efficacy of contaminant removal, which is the ultimate goal of any advanced oxidation process.

Next Steps

Understanding the rates and mechanisms of reactive oxidant production is the first step in validating chlorine photolysis as an advanced oxidation process. In order to complete this work, we need to complete the kinetic model by determining the cause of over-produced species at high pH. Additionally, we need to complete the probe experiments using cinnamic acid to complete the picture drawn by the nitrobenzene and benzoate experiments. Once these steps are complete, the research will move on to the next phase, which includes looking at the formation of potentially harmful disinfection by-products (a result of reaction between oxidants and naturally occurring organic matter) during chlorine photolysis.