

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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Introduction

Organic contaminants, such as pharmaceuticals and personal care products, are ubiquitous in drinking water sources, but are not completely removed by conventional drinking water treatment processes.¹ One approach to remove organic contaminants in drinking water is the use of advanced oxidation processes (AOPs). AOPs produce hydroxyl radical, an extremely powerful oxidant that is capable of degrading most organic compounds.¹ Implementing AOPs often requires costly retrofits, and is often not feasible within the physical confines of existing drinking water plants. Our research focuses on chlorine (i.e., hypochlorous acid) photolysis, which generates hydroxyl radical, chlorine radical, and ozone. Chlorine photolysis is less expensive to implement than many commonly used AOPs because it utilizes existing treatment plant infrastructure. This study seeks to identify the optimal conditions for chlorine photolysis as an AOP by combining laboratory experiments with kinetic modeling.

Background

Organic pollutants are pervasive in our environment. They come from many different sources, including agricultural and urban runoff, and residential and manufacturing effluent. These pollutants include compounds we use every day, such as pesticides and pharmaceuticals, that exhibit a range of environmental impacts. One example of a harmful pollutant is bisphenol A (BPA), which is an endocrine disrupter, that at very low concentrations can cause birth defects and altered sex ratios in fish.² Many of these compounds, such as carbamazepine, can also impact human health. Current drinking water treatment utilizes chlorine in the form of hypochlorous acid (HOCl) to disinfect the water. HOCl also reacts with dissolved organic matter (DOM) in the water, leading to the production of harmful

¹ Remucal, C.K., and D. Manley. "The efficacy of chlorine photolysis as an advanced oxidation process for drinking water treatment." *Environ. Sci.-Water Res. Tech.* (2016) 2: 565-579.

² Kang, Joon IK, et. Al. "Effects of bisphenol A on the reproduction of Japanese medaka (*Oryzias latipes*)." *Environ. Toxicol. Chem.* (2002) 21.11: 2394-2400.

disinfection byproducts (DBPs). Additionally, treatment with chlorine, or the other common alternatives, chloramine and ozone, does not remove organic contaminants from the drinking water. Combining traditional chlorination with ultraviolet (UV) photolysis has been shown to produce hydroxyl radical.³ This radical is very reactive, breaking down organic molecules through oxidation. Using this combined treatment process will likely alter the DBPs formed via treatment. By utilizing existing infrastructure with minimal changes, this method will allow us to remove organic pollutants from drinking water, thus making water cleaner and healthier for human consumption.

Progress to Date

The proposed research seeks to develop chlorine photolysis as an advanced oxidation process for contaminant removal, primarily in drinking water treatment systems. In order to determine the viability of this process we need to establish: (a) the kinetics of chlorine photolysis and oxidant production; (b) the efficacy of the oxidants in breaking down organic contaminants, and (c) the production of novel disinfection by-products in this system. The experimental set up and methods used to complete each part of the projects will be similar. Experiments will be conducted in a Rayonet photoreactor with irradiation at 254, 311, or 365 nm. Chlorine concentrations will be determined using the standard DPD colorimetric method, which relies on the reaction between N, N-diethyl-p-phenylenediamine and chlorine to produce a pink oxidation product which is then analyzed on a UV-visible spectrometer. Radical species will be measured using probe compounds, nitrobenzene and benzoic acid, analyzed using high-performance liquid chromatography. Contaminant concentrations will be measured by liquid chromatography-mass spectrometry, and degradation products and disinfection by-products will be identified by liquid chromatography-mass spectrometry and using the novel technique Fourier transform-ion cyclotron resonance mass spectrometry.

Literature review. We conducted a thorough review of the literature on chlorine photolysis for the Drinking Water Exposome issue of *Environmental Science: Water Research & Technology* (2016, 2, 565-579). The review, entitled “*The efficacy of chlorine photolysis as an advanced oxidation process for drinking water treatment,*” discusses the fundamental chemistry of chlorine photolysis. In addition, the review discusses the ability of chlorine photolysis to transform model probe compounds, target organic contaminants, and chlorine-resistant microorganisms. Finally, the review describes the limited available data on DBP formation in the AOP.

Chlorine photolysis kinetics. Photolysis of chlorine by UV wavelengths produces hydroxyl radical, and may produce chlorine radical. These radicals can react with other compounds in solution and form new oxidant species.³ The rate of chlorine photolysis is both pH- and wavelength-dependent. Due to the high molar absorptivity and low quantum yield of the hypochlorite anion and the low molar absorptivity and high quantum yield of hypochlorous acid, we hypothesized that chlorine loss will increase as pH increases (in the range 6-9, $pK_a = 7.5$), and hydroxyl radical production will decrease with decreasing pH. Both chlorine loss and hydroxyl radical production should increase at shorter wavelengths (in the range 254-

³ Nowell, Lisa H., and Jürg Hoigné. “Photolysis of chlorine at sunlight wavelengths – II. Hydroxyl radical production.” *Wat. Res.* (1992) 26.5: 599-605.

365 nm). Initial data support this hypothesis, with chlorine loss rate increasing with increasing pH, and probe loss (i.e. radical production) rate increasing with decreasing pH.

In addition to the production of hydroxyl radical, chlorine photolysis can also produce chlorine radical. The presence and concentration of chlorine radical can be determined by competition kinetics using two different radical probes. Nitrobenzene only reacts with hydroxyl radical, but benzoic acid reacts with both hydroxyl radical and chlorine radical. The loss rate of nitrobenzene alone allows for the determination of the steady-state concentration of hydroxyl radical. Competition between the two probe compounds and the known steady-state concentration of hydroxyl radical allows for the determination of the steady-state concentration of chlorine radical.

Determining the steady-state radical concentration alone is not enough to predict the contaminant loss rate, so we have begun to develop a kinetic-equilibrium model. This model will use the steady-state concentrations of hydroxyl and chlorine radical, determined experimentally for a given set of conditions, to predict the concentrations of other oxidants such as the chlorine radical anion that could also contribute to contaminant degradation. The overall contaminant loss rate is dependent on direct photodegradation, reaction with chlorine, and reaction with the oxidants present.

Conclusions

These preliminary results suggest that hydroxyl radical is produced during chlorine photolysis, making it a feasible advanced oxidation process. The wavelength of irradiation in these studies falls within the solar spectrum, so the presence of hydroxyl radical in this system suggests that chlorine photolysis could be used outdoors, in wastewater treatment or in chemical spill clean-up in addition to drinking water treatment. Developing a model of the kinetics of radical production will enable future users to predict the treatment parameters necessary for contaminant removal.

Next Steps

Contaminant Loss. Organic contaminants released by human activities encroach on drinking water sources, and have been found in measureable concentrations in drinking water sources. This proposal will focus on pharmaceutical compounds with large environmental and health implications such as estrogen, or those that are highly prevalent such as carbamazepine. The loss rate of the contaminants in the chlorine photolysis system is based on direct photolysis, oxidation by chlorine, and oxidation by the radical species. Using the model developed during phase one, the theoretical loss rate of the target contaminant will be determined. This loss rate will be validated by experimental results. The degradation products will be characterized using LC-MS.

Characterization of Disinfection By-Products. Disinfection by-products are the result of reactions between a disinfectant and organic molecules in the treatment system. Some of the disinfection by-products are regulated by the EPA, but most have not yet been identified. Chlorine photolysis changes the concentration and identity of the oxidants present in the treatment system, therefore I hypothesize that chlorine photolysis will lead to the formation of new disinfection by-products. These disinfection by-products will be identified by the novel technique FT-ICR MS.