NWRI GRADUATE FELLOW FINAL 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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Clean drinking water is essential to human life. It is one of the most important issues in developing regions, and as water scarcity increases even developed nations are looking for adaptive strategies to treat their drinking water. One major areas of concern in drinking water treatment is the removal of organic contaminants such as pharmaceuticals, personal care products, pesticides, industrial solvents, and other chemicals. These compounds are difficult to remove from drinking water without costly infrastructure development to install and maintain an advanced oxidation process or activated carbon filter. My research focuses on the mechanism behind an emerging advanced oxidation process, chlorine photolysis, that has the potential to improve drinking water treatment utilizing existing infrastructure in developed regions. The process could be used in regions that currently do not have the resources to build and maintain a drinking water treatment and distribution system.

Background and Introduction

Advanced oxidation processes are used to remove organic contaminants from drinking water by generating hydroxyl radical. Hydroxyl radical oxidizes organic contaminants, breaking them down into smaller, ideally less-toxic molecules. Previous research shows that reacting hypochlorous acid (i.e. free-available chlorine, or bleach) with UV light creates multiple reactive species including hydroxyl radical, and that this system is capable of degrading some organic contaminants (Remucal and Manley 2016). Very few studies have investigated the formation of degradation products, which means that researchers are unsure if the organic contaminants are reacting with hydroxyl radical or with other reactive oxidant species, including reactive chlorine species. Past research has shown that these reactive chlorine species, such as chlorine radical, can react with organic contaminants and form chlorinated products. Additionally, most past studies have utilized light at 254 nm and neutral pH. While neutral pH is relevant for natural waters and the environment, the 254 nm UV light is the most commonly used wavelength for drinking water treatment. Variation in both pH and wavelength could have an effect of the formation of reactive oxidants. This study seeks to understand how varying pH and wavelength can change the production of reactive oxidants during chlorine photolysis.

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 occur in this system, and other studies have evaluated 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 Since the Beginning of Your NWRI Fellowship

Objective 1. The first objective of this work is to determine the chlorine photolysis rate constant and reactive oxidant productions under a variety of conditions. The chlorine loss rate constant varies with pH and wavelength due to the change in light absorption by chlorine. Understanding how chlorine degradation changes is important due to regulation of both disinfectant use and efficacy. Quantifying reactive oxidants allows us to determine the most effective treatment conditions.

To measure the chlorine loss rate constant, samples at pH 5-10 and were photolyzed in a Rayonet merry-go-round photoreactor with single-wavelength bulbs at 254, 311, or 365 nm. The chlorine concentration was measured at various times after the reaction began to determine how quickly chlorine was degraded. The concentration of various oxidants was measured using probe compounds, as most oxidants degrade too quickly to be measured directly. The probe compounds react with one or more of the oxidants in a well-understood mechanism, and the degradation of a probe compound or the formation of a known product can be used to determine the concentration of an oxidant such at hydroxyl radical. Nitrobenzene, benzoate, and cinnamic acid were selected as probe compounds due to their selectivity to hydroxyl or chlorine radical, and ozone. Each of these probe compounds also resists direct degradation by UV light. The concentration of the probe compounds was measured using high-performance-liquid-chromatography.

The results from this objective are still preliminary and have not yet been published. **These preliminary results demonstrate that radical production varies by irradiation wavelength, but the concentration remains within an order of magnitude.** We observed trends in both chlorine loss and radical production that can largely be explained by changes in molar absorptivity and quantum yield.

Objective 2. The second objective is to develop a kinetic model to help quantify the formation of reactive oxidants. Previous studies have published kinetic models using literature rate constants and used them to describe qualitative trends in their experimental data. All of the published models were developed to describe the formation of reactive oxidants at 254 nm, ignoring the other wavelengths where oxidant production is different. Additionally, they do not look at the formation of oxidants we determined to be present in objective 1. To correct for this, we added numerous radical reactions to ensure that all reactive oxidant species found to be present in experimental reactions were determined in the model.

The kinetic model is run using the Kintecus modelling software and uses a tableau approach to calculate the variation in concentration of chlorine and reactive oxidants with time. This approach is commonly

used in advanced oxidation processes, and similar models have been developed for the hydrogen peroxide photolysis system, which is a simpler system to model. Current model results using the model developed in this study have improved on the prediction of both chlorine loss and radical production over literature models, though the model does not yet accurately predict experimental results. This is the main focus of current research in this study.

Discussion of Results.

The preliminary results suggest that hydroxyl radical, chlorine radical, and other oxidant species are produced during chlorine photolysis, making chlorine photolysis an effective advanced oxidation process. At all wavelengths 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 include both the traditional treatment wavelength (254 nm) and light within the solar spectrum (311 and 365 nm). This means that hydroxyl radical is produced by chlorine photolysis under conditions found on the Earth's surface, and chlorine photolysis could be utilized in solar treatment applications. The production of hydroxyl radical is produced at similar concentrations across a pH range, requiring less chemical input to ensure adequate reactive oxidant production. Both the kinetic model and the experimental results predict the formation of previously overlooked oxidants.

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, looking at the formation of potentially harmful disinfection by-products (a result of reaction between oxidants and naturally occurring organic matter) during chlorine photolysis.

Presentations

Devon Manley Bulman and Christina K. Remucal (2018) "Effect of solution conditions on reactive oxidant production during chlorine photolysis" (*Poster Presentation)* AEESP special symposium for the AEESP Distinguished Lecture Series.

Devon Manley Bulman and Christina K. Remucal (2018) "Effect of solution conditions on reactive oxidant production during chlorine photolysis" (*Poster Presentation)* Water @ UW Symposium.

Christina Remucal and Devon Manley Bulman (2017) "Effect of solution conditions on reactive oxidant production during chlorine photolysis" (*Poster Presentation)* Association of Environmental Engineering and Science Professors Conference, Ann Arbor, MI

Devon Manley and Christina K. Remucal (2017) "Effect of solution conditions on reactive oxidant production during chlorine photolysis" 253rd National Meeting of the American Chemical Society, San Francisco, CA

Citations

Remucal, Christina K., Devon Manley. "The efficacy of chlorine photolysis as an advanced oxidation process for drinking water treatment." Environmental Science: Water Research and Technology (2016):2(4) pp. 565-579.