

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

Graduate Fellow: Devon Manley Bulman

Advisor: Christina K. Remucal

Institution: University of Wisconsin-Madison

Background and Introduction

Agricultural, industrial, and urban processes release organic contaminants into our environment every day. These organic compounds, such as pesticides, industrial solvents, and pharmaceuticals, threaten human and ecosystem health and are not removed by typical drinking water treatment processes such as sedimentation, filtration, or disinfection. However, many of these chemicals can be destroyed in drinking water by using advanced oxidation processes (AOPs), which generate hydroxyl radical to oxidize organic contaminants.¹ Oxidizing organic compounds removes them from the water by taking away electrons from the contaminant and breaking the chemical bonds. Radicals are good oxidants because they have an unpaired electron, which is unstable, so they steal electrons from other molecules.

There is a cost benefit analysis to AOPs however. Although AOPs can be effective in removing organic contaminants, most traditional AOPs are costly to implement. In addition to changing treatment plant infrastructure to accommodate additional tanks, most AOPs require costly chemicals such as hydrogen peroxide, and have high energy costs associated with the generated of powerful ultraviolet light. Our research focuses on determining the efficacy of chlorine (i.e. hypochlorous acid) photolysis, a relatively new AOP. If chlorine photolysis generates similar oxidizing power when compared with traditional AOPs it would be more cost effective due to lower chemical costs and fewer infrastructure changes needed as most municipalities used chlorine or chloramine for disinfection currently. The energy cost of generating ultraviolet light would be the same as other AOPs during municipal treatment, but we are also investigating the use of chlorine photolysis at wavelengths in the solar spectrum for an energy cost free alternative.

In addition to the potential cost benefits of chlorine photolysis, this AOP has the potential to generate more powerful treatment with a suite of reactive oxidants. Most commonly used AOPs utilize the generation of hydroxyl radical to react with contaminants, or in the case of UV/hydrogen peroxide, the ultraviolet light, hydrogen peroxide and the generated hydroxyl radical can react with contaminants. In the case of chlorine photolysis contaminants can be reacted with ultraviolet light, hypochlorous acid, and hydroxyl radical along with a suite of other reactive oxidants including chlorine radical, dichloride radical anion, hypochlorite radical, and ozone.

The focus of this research was selected after an extensive literature review on AOPs in general and chlorine photolysis in particular. To date, there have been many studies on the mechanisms of other AOPs, and many studies on the efficiency of chlorine photolysis in removing organic contaminants, but no studies on the kinetics of radical production during chlorine photolysis.¹ While the studies of

contaminant degradation may seem more useful from a water treatment perspective, these studies only provide the degradation rate and pathway for a single molecule, or class of molecules. This is a very important part of the story, but it does not allow us to predict the loss rate of other compounds. Focusing on contaminant loss rates does not provide any information on what oxidants are produced in the system that may not react with a given molecule, but could be crucial in degrading other contaminants. This is the gap we seek to fill by combining laboratory experiments on the production of various radicals with a kinetic model to determine how effective chlorine photolysis is at generating multiple different reactive oxidants.

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. 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. Research progress to date has focused on the first objective, and this objective will combine laboratory experiments with a kinetic model. 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. Probe compounds are used to measure compounds that are otherwise impossible to measure. For example, hydroxyl radical cannot be directly measured in water because it reacts away quickly, but by adding a compound that reacts with hydroxyl radical in a known way (i.e. nitrobenzene) we can measure the loss of the probe and calculate how much hydroxyl radical must have been present to remove that much probe. The kinetic model will be developed using the Kintecus modelling software, with rates determined experimentally and from the literature.

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.

Presentation of Results. Preliminary results from the first project objective (chlorine photolysis kinetics) were presented at two conferences in the past year:

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

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

Chlorine photolysis kinetics. Photolysis of chlorine by UV wavelengths produces hydroxyl radical and chlorine radical. These radicals can react with other compounds in solution and form new oxidant

species. The rate of chlorine photolysis is both pH- and wavelength-dependent. Due to the high molar absorptivity (ability to absorb light) and low quantum yield (amount of product produced per unit of light absorbed) 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. 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, due to the highly complex nature of the system, so we have begun to develop a kinetic-equilibrium model. This model will use the observed chlorine loss rate under different conditions to predict the concentrations of hydroxyl radical, chlorine radical, and ozone, as well as other oxidants such as the chlorine radical anion that could also contribute to contaminant degradation. The overall contaminant loss rate is dependent on direct photo-degradation, reaction with chlorine, and reaction with the oxidants present. Preliminary model results show good agreement between the experimentally determined steady state concentrations of hydroxyl radical and chlorine radical, and the modeled data.

Conclusions

These preliminary results suggest that hydroxyl radical and chlorine radical are produced during chlorine photolysis, making it an effective advanced oxidation process. 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. Therefore, chlorine photolysis could be used in places that do not have the resources and infrastructure for typical 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

Determination of Ozone Production. As mentioned above, ozone is an important oxidant in this system because it is a strong oxidant. Much like the use of nitrobenzene and benzoic acid to measure hydroxyl and chlorine radicals, cinnamic acid is a reliable probe for ozone. We will determine the presence of ozone experimentally as another way to validate the kinetic model.

Characterization of Disinfection By-Products. Disinfection by-products are the result of reactions between a disinfectant and an organic molecule 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 we hypothesize that chlorine photolysis will lead to the formation of new disinfection by-products. Regulated disinfection by-products can be measured using Gas Chromatography with Electron Capture Detection. Novel disinfection by-products will be identified using Fourier Transform-Ion Cyclotron Resonance Mass Spectrometry, only recently adapted to the analysis of water samples containing a complex mixture of organics, or Orbitrap Mass Spectrometry.

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