Abstract: Application of a UV/Chlorine Advanced Oxidation Process (AOP) for Destruction of Neonicotinoid Insecticides in Storm Water Runoff

Taylor Bradley
Stanford University

Introduction

To maintain and improve the integrity of water quality in urban areas, more specifically in agricultural areas with a high volume of storm water run off, it's imperative to study new and emerging contaminants. Recently, urban storm water runoff has become a breeding ground for Neonicotinoid (NNT) insecticides, which pose greater harm than expected. With a documented presence in nearly every sample collected from the Santa Barbara Creeks division in the months prior, researchers have found it necessary to discover new ways to degrade these compounds and learn more about their environmental effects. (City of Santa Barbara et. al 2015) The NNT's that were analyzed in these experiments were Acetamiprid (AMP), Clothianidin (CTN), Imidacloprid (ICP), Thiacloprid (TCP), and Thiamethoxam (TXM). While conventional wastewater treatment calls for an UV/Hydrogen Peroxide system that is effective in the degradation of most compounds found in surface and ground water, it is not as energy efficient as chlorine is expected to be. This paper will focus on the UV/Chlorine AOP in comparison to UV/Hydrogen Peroxide AOP in the degradation of NNT's.

Used as a disinfectant in swimming pools for decades, chlorine has proven to be effective in removing unwanted compounds from water by photolysis. This simple, yet complex idea is motored by the hydroxyl radical formed by the interaction of chlorine with UV photons. The UV/Chlorine system is favorable in the sense that it has the potential to save a great deal of money with regards to energy usage and ideally can degrade compounds more efficiently than hydrogen peroxide. There are a few advantages in using this system over hydrogen peroxide aside from reducing costs; Chlorine is proven effective against bacteria, viruses and waterborne pathogens, which are a major concern in terms of water quality (which is the focus of the research). This is all possible in evidence of Hypochlorous Acid having a higher quantum yield than that of Hydrogen peroxide.

Methods

The developed hypothesis stated that the UV/Chlorine AOP would be more efficient than UV/Hydrogen Peroxide for NNT removal. In order to validate that theory, the experimental design was created: a bench-scale testing which used a bench top collimated beam apparatus. In more detail, storm water samples were spiked with individual NNT's and exposed to UV light in a fixed fluence (500 mJ/cm^2) for a predetermined amount of time. At each predetermined time, a sample was taken and analyzed by the LC-MS/MS to portray the degradation kinetics of NNT's. Two Experiments were run for each NNT; one for chlorine and the other for hydrogen peroxide. Within each experiment there were three trials (A, B, and C) in which the concentration of chlorine or hydrogen peroxide increased (experimental concentrations were based on typical dosages found in industry). For the chlorine experiments, trials A, B and C required 1 mg/L, 2 mg/L and 4 mg/L of chlorine, respectively. The hydrogen peroxide trials A, B, and C only required 0.5 mg/L, 1 mg/L and 2 mg/L of hydrogen peroxide, respectively which was designed in that fashion so that it would be the same molar concentration, since hydrogen peroxide is half the molar mass of hypochlorous acid.

In order to make a fair comparison, there were four reactors included in the set-up. The first one was the dark control and the second was spiked with chlorine or hydrogen peroxide (depending on which experiment was being performed at the time) the first and second reactors were not exposed to UV light during the experimental time. The third reactor was another control as well whereas the fourth reactor was spiked with chlorine or hydrogen peroxide also. The difference between reactors three and four is that they were exposed to UV light during the experimental time.

Data Analysis/Results

In order to determine if NNT concentrations decreased over time, samples were analyzed with LC-MS/MS capabilities. Only four of the insecticides could be completely analyzed due to time restrictions and availability of the LC-MS/MS; CTN, AMP, TCP and ICP. For experiments A, B, and C, for each disinfectant, graphs of C/C0 vs. Time and Ln(C/C0) vs. Time were created to visually display the degradation and kinetics of the reactions. For each NNT, graphs of C/C0 vs. Time and Ln(C/C0) vs. Time, at every concentration of chlorine and hydrogen peroxide, in reactor 4, were plotted to compare the degradation and kinetics of the UV/Chlorine AOP vs. the UV/ Hydrogen Peroxide AOP.

Once the peaks were integrated of TCP and AMP, one could see that they didn't degrade within the sampling frame, which is normal behavior for those two compounds. Out of the two insecticides (CTN and ICP) that did degrade over time, CTN performed as expected; the reaction favored the highest dose of chlorine to effectively remove the particular NNT. ICP on the other hand didn't show significant differences in the degradation between the concentrations of chlorine or hydrogen peroxide themselves, or compared to each other. Even when looking at the graph of just reactor four's degradation and kinetics, it doesn't do a great job at displaying the removal of the compounds.

Conclusions

This research didn't provide any solid conclusions because only four out of the five NNT's could be completely analyzed. Two of the neonicotinoids (CTN and ICP) proved that the hypothesis was correct; chlorine is more efficient at degrading the NNT's over hydrogen peroxide. Although ICP did not degrade exactly as expected, the rate constants showed that chlorine was quicker and more efficient than that of hydrogen peroxide. In order to make fair conclusions, it is necessary to continue to run experiments for months to really capture the trends and the kinetics of the reactions between each NNT. It also may be necessary to change the experimental time and sampling time because some of the insecticides react differently than others. One of the main goals in conducting this research was to, overall, learn more about the behavior of the compounds, so see how they can be treated in industry. This was a good step in the right direction, yet it needs more time to provide results that are useable.