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Destruction of Pesticides and their Formulations in Water Using Short Wavelength UV Light

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The presence of toxic materials in surface and ground water is a problem of growing significance. Increasingly, toxic anthropogenic chemicals are being detected in water supplies resulting in public concern and regulatory restrictions. Pesticides may enter the aquatic environment by a variety of routes. The major source of pesticides in surface water is reported to be from agricultural runoff (Edwards 1973). Clearly, there is a need to develop methods to decontaminate not only drinking water supplies, but also the sources of contamination. Decontamination of water poses economic and logistical challenges since the pollutants are usually present in low concentrations and distributed over a wide area. A number of strategies have been proposed and tested to destroy toxic materials in water. These processes include the treatment of the water by wet air oxidation (Heimbuch and Wilhelmi 1985), oxidation of the pollutants using supercritical water (Thomason and Modell 1984), and a number of photochemically based treatments (Crosby et al 1986; Glaze et al 1980; Hager and Smith 1985; Hager and Smith 1986; Mauk et al 1976; Sundstom and Klei 1986).

The photochemical processes have received much attention in the past few years from researchers and regulators. Ultraviolet light combined with ozone as the oxidant is one method that has been explored as a means to destroy toxic organics in water (Glaze et al 1980; Sundstrom and Klei 1986) and has been shown to be effective in destroying a number of pesticides in water (Mauk et al 1976). Hydrogen peroxide (H_2O_2) is the other major oxidant used in combination with UV light to effect the destruction of hazardous materials in water. UV light and hydrogen peroxide have been used successfully to destroy a number of organics in water (Hager and Smith 1985; Hager and Smith 1986; Sundstrom and Klei 1986; Weir et al 1987).

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In this study, we examined the effectiveness of a photoreactor equipped with a high pressure mercury vapor lamp for the destruction of three pesticides and the inert ingredient m-xylene in water. Captan, chlordane, PCNB, and m-xylene in aqueous solutions were selected as model compounds for this study based on their use, resistance to UV degradation, and potential presence in formulated pesticide materials. The factors that influence the performance of the system were investigated.

MATERIALS AND METHODS

A Perox Pure Model SQ-5 photoreactor (Peroxidation Systems, Inc. (Tuscon, AZ)) was used for all experiments. The ultraviolet light is supplied by a high-pressure mercury vapor lamp of proprietary design mounted axially within the oxidation chamber inside a quartz tube. H_2O_2 was pumped into the system's flow stream by a peristaltic pump calibrated to replenish the H_2O_2 destroyed by the UV lamp during use of the instrument.

Hydrogen peroxide, 30% unstabilized. Deionized water was used for all experiments. m-Xylene, 94.3% m-xylene with the balance ortho and para isomers, Matheson, Coleman and Bell, Norwood, OH. Captan (CAS 133-06-2) (N-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide), analytical grade, 99% purity supplied by Stauffer Chemical Company, Richmond, CA. Captan technical grade, 87.3% purity, Matheson, Coleman and Bell, Norwood, OH. Pentachloronitrobenzene (CAS 82-68-8), analytical standard, recrystallized, 99% purity by GC/ECD. Pentachloronitrobenzene, technical grade, 95% purity, Sigma, St Louis, MO. ACS reagent grade solvents. Methanol, HPLC grade, Fisher, Fair Lawn, NJ. Xylenes, certified ACS, Fisher. All other solvents were pesticide residue grade. Sodium metabisulfite, granular, Mallinckrodt, St. Louis, MO. Atlox Emulsifiers 3403F and 3404F, Imperial Chemical International, Wilmington, DE. Bond Elute C-8 extraction columns, 500 mg, 2.8 ml capacity, Analytichem International, Harbor City, CA.

Recovery of chemicals from aqueous solution was accomplished by collecting triplicate 50 mL samples from a sampling valve located between the reservoir and the oxidation chamber at intervals before and after the UV lamp was turned on. The pH and H_2O_2 concentration were measured using indicator strips. H_2O_2 was neutralized by adding aqueous 0.2 N sodium meta-bisulfite. Each sample was extracted from water using a C-8 solid phase extraction column and the chemicals removed from the column using an organic solvent(s) specific for each chemical. The solvents used to extract the chemicals from the columns are as follows: captan, PCNB, and chlordane - 2 ml ethyl acetate followed by 2 ml hexane, m-xylene - 2 x 4 ml benzene. Quantitation was performed by capillary gas chromatography using a digital reporting integrator and external standards to establish a standard curve.

RESULTS AND DISCUSSION

H_2O_2 was depleted in the system at a rate of 20 ppm/min from an initial concentration of 115 ppm. Concentrations of up to 500 ppm H_2O_2 were easily maintained by using the peristaltic pump. The normal operating temperature of the reaction solution in the Perox Pure Model SQ was 52-57°C with a cooling water flow of 12 l/min. Deionized water was used for all experiments and the initial pH of the aqueous solutions were pH 5.3-5.5.

The breakdown of m-xylene, a common component of emulsifiable concentrate pesticide formulations, was examined in anticipation of using the unit for destroying formulated pesticide products. The degradation of m-xylene followed first-order kinetics. In experiments with UV light and 115 ppm hydrogen peroxide, an average half life of 4.0 minutes was observed from initial concentrations of 36.1 ppm and 56.7 ppm m-xylene. Without H_2O_2 present, the half life of m-xylene was 5.7 minutes starting with an initial concentration of 22.6 ppm. M-xylene was degraded by the high intensity, short wavelength UV light that the system generates and the rate was enhanced only slightly by the presence of hydrogen peroxide. M-xylene was stable in 100 ppm H_2O_2 for 48 hours in the dark. All reported values of m-xylene were corrected for an average recovery of 84.5% ± 4% with a method detection limit of 0.1 ppm.

The water solubility of captan is 3.3 ppm at 20°C. Methanol was used as a carrier solvent when higher concentrations of captan were investigated. The breakdown of captan followed first order kinetics under all conditions. At 1 ppm concentrations, captan was found to be degraded with a half life of 1.4 minutes. This half life was seen with or without the presence of hydrogen peroxide or carrier solvent indicating that the high intensity, short wavelength UV light is responsible for captan's destruction. The finding that methanol, an efficient radical scavenger, has no impact on captan's breakdown rate is consistent with a breakdown mechanism not involving hydroxyl radicals.

The half-life of captan increased substantially to 2.9 minutes when the initial captan concentration was elevated to 72 ppm in a 10% methanol solution. The half life was further increased to 6.4 minutes when an intial captan concentration of 133 ppm was prepared using a commercially available wetable powder formulation. The reasons for this are not unequivocally demonstrated, but the slower breakdown rate was likely due to the higher initial concentration of captan and/or the presence of the wetable powder formulation. Since the wetable powder formulation makes a cloudy aqueous solution when mixed with water, it is likely that the slower breakdown rate may be attributed to the cloudiness of the wetable powder solution by preventing UV light from contacting the pesticide or the H_2O_2. Yet another explanation for the slower breakdown is that WP suspensions are biphasic and the rate of photolysis may be limited by the rate of captan solvation into the aqueous phase from the non-aqueous phase. Captan exhibited a half life of 100 hours in a solution of 100 ppm H_2O_2 in the dark and this rate does not significantly contribute to the rate produced by the photoreactor.

Tetrahydrophthalamide (THPI) was the major breakdown product from captan identified by gas chromatography using a nitrogen-phosphorous specific detector and combined gas chromatography/mass spectrometry. Besides THPI, chloroform, hydrogen sulfide, and a large amount of carbon dioxide were detected in the head space above the reservoir. Since the unit is a closed system, off gases are unlikely to escape into the atmosphere. There was a steady drop in the pH of the waste water during the course of each experiment consistent with the formation of CO_2 and acidic breakdown products. All reported captan values were corrected for an average recovery of 95% ± 9% with a method detection limit of 0.03 ppm.

Since the water solubility of PCNB is only 0.44 ppm at 20°C and approximately 1.2 ppm at 35°C, experiments with PCNB at concentrations of 1 ppm were done in deionized water at 35°C. Experiments at 2 ppm were done in 5% isopropanol/water at 20°C. PCNB concentrations at 10 ppm and 1000 ppm were run using a lab generated emulsifiable concentrate formulation containing xylenes and a mixture of anionic and nonionic emulsifiers.

PCNB was rapidly degraded in optically clear water by the high intensity, short wavelength UV light from the lamp with or without the presence of hydrogen peroxide. The breakdown of PCNB without isopropanol, H_2O_2, or formulating materials followed second order kinetics with an average half-life of 2.6 minutes at initial concentrations ranging from 0.09 to 2.4 ppm. PCNB breakdown in the presence of a carrier solvent or formulation materials displayed biphasic first order kinetics. That is, there was a constant rate of PCNB destruction from an initial concentration of 2 ppm until a concentration of about 0.2 ppm was reached, whereupon a remarkably slower rate of breakdown was established. The half-life values calculated for these two phases demonstrates the marked difference between phases with a half life of 2.6 minutes calculated for the initial phase and 23.8 minutes for the second phase of the reaction. PCNB is not measurably degraded by hydrogen peroxide alone in the dark over a 48 hour period.

UV light with a 100:1 ratio of H_2O_2 to PCNB proved to be optimum for degrading of PCNB in aqueous solutions. Under these conditions, the half life of PCNB was 1.3 minutes. When isopropanol was used as a carrier solvent (to increase PCNB concentration and as a radical scavenger), the half life was 2.9 minutes. This value is very close to the rate using UV light only and is evidence that radical formation is an important contribution to PCNB breakdown when H_2O_2 is present.

When PCNB concentration was increased to 8.6 ppm using a 0.1% (w/w) emulsifiable concentrate formulation, the half life extended to 6.8 minutes. This is consistent with the results from the m-xylene and captan data, since increasing the concentration of the contaminant in question slows down the rate of degradation. However, as with formulated captan, the results are likely more attributable to the cloudy aqueous solution resulting from the formulation.

Formulated PCNB was used to generate a 1000 ppm solution (using a 0.2% emulsifiable concentrate composed of xylenes and emulsifiers) and reacted in the system. The results showed no detectable destruction of the pesticide. A visual inspection of the oxidation chamber and quartz tube after two hours of operation lead to the descovery that large amounts of material from the waste water solution had adhered to the quartz tube creating an opaque coating. When the sludge was scraped off and analyzed by GC-ECD, it was found to contain 70,000 ppm PCNB.

Degradation products of PCNB included pentachlorophenol (PCP), which was first observed at the 2 minute interval. PCP was rapidly destroyed, however, and was not detected in samples taken after 8 minutes. Other products also detected by gas chromatography/mass spectrometry include minute quantities of 2,3,4,5-tetrachloronitrobenzene and 2,3,5,6-tetrachloronitrobenzene. None of these products were quantified due to their low concentrations. The tetrachloronitrobenzene products are consistent with photolytic reductive dechlorination of PCNB. All reported PCNB values were corrected for an average recovery of 88.8% ± 8% with a limit of detection of 0.005 ppm.

Chlordane, a persistent insecticide and termiticide, is no longer manufactured in the United States, but due to it's persistence, extensive use in the past, and it being a member of the chlorinated polycyclic hydrocarbon compounds, it was included in this study. Two experiments were conducted with chlordane: UV light only, and UV light with 115 mg/L of $H2O2$ using 1.0 ppm solutions of Chlordane prepared in aqueous solution. As in the case with captan and m-xylene, hydrogen peroxide had no effect on the rate of chlordane breakdown. Chlordane was destroyed following first order kinetics with a half life of 3.9 minutes with or without hydrogen peroxide present. As the breakdown of chlordane progressed, the gas chromatogram of the sample extract showed a marked shift in the population of peaks towards early eluting and apparently more volatile compounds. At a reaction time of 32 minutes, the mass spectra of the major GC peaks show the presence of a number of low molecular weight chlorinated compounds. Tentative identification of these peaks was difficult due to the multitude of isomers present in the starting material.

Oxidation of chemicals by the UV-H_2O_2 process using low and medium pressure mercury vapor lamps hinges on the generation of hydroxyl radicals. The hydroxyl radicals are formed when an H_2O_2 molecule absorbs a photon of sufficiently energetic UV light, and cleaves homolytically (Baxendale and Wilson 1957). The hydroxyl radical is a short lived, extremely potent oxidizing agent capable of oxidizing organics to carbon dioxide, water and inorganic salts. The quantum yield of hydroxyl radicals from hydrogen peroxide is low at long wavelengths and increases to a value of 1 as the wavelength of UV light decreases to 254 nanometers (Baxendale and Wilson 1957).

Like other UV emitting systems, the UV light source in the system used in this study emits at 254 nm , and is effective at generating hydroxyl radicals from hydrogen peroxide. However, the 5000 watt high-pressure mercury vapor lamp also emits strongly over the entire region between 190 and 400 nm, and is effective not only at generating hydroxyl radicals from H_2O_2 but also causing electronic transitions in many organic molecules. These electronic transitions can lead to the reaction of the organic molecule with itself (internal rearrangements), solvent molecules, hydroxyl radicals, and hydrogen peroxide by reductive, oxidative, and free radical processes. Thus, the high pressure mercury vapor lamp is potentially capable of degrading organics without the presence of a hydroxyl radical source.

Summarizing the results of this study, it can not be over emphasized that though the system used in this study rapidly degrades m-xylene and the pesticides captan, PCNB and chlordane in optically clear water, the optical clarity of the waste water is critical to the success of the pesticide breakdown. When waste solutions become cloudy, as might be expected in some field use situations, the pesticide breakdown rates with the Model SQ are greatly diminished. This was seen most clearly when the Model SQ was used to breakdown PCNB with the pesticide formulated as an emulsifiable concentrate. Emulsifiable concentrates are common pesticide formulations. The half life of the breakdown of a 8.6 ppm solution of PCNB created as a 0.1% emulsifiable concentrate formulation was 6.8 minutes. In the case of a 1000 ppm solution of PCNB created as a 0.2% emulsifiable concentrate formulation, there was no detectable destruction. This is cause for concern in field use situations where the Model SQ may be employed in the treatment of formulated pesticide products. The Model SQ is most suited for the treatment of dilute pesticides in ground water or surface runoff water and in it's present configuration is not recommended for the destruction of high concentrations of formulated pesticides that may be encountered in hazardous waste sites, the disposal of banned formulated pesticides, or the destruction of pesticides applied to seeds. The rate of breakdown of m-xylene, captan, and chlordane in waste water by the system used was not significantly dependent on the presence of H_2O_2, although the rate of PCNB breakdown did improve when H_2O_2 was added.

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