

# **Environmental Management Science Program**

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## **An Investigation of Homogeneous and Heterogeneous Sonochemistry for Destruction of Hazardous Waste**

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### Research Objective

The primary objective of this research project is to acquire a deeper fundamental knowledge of acoustic cavitation and cavitation chemistry, and in doing so, to ascertain how ultrasonic irradiation can be more effectively applied to environmental problems. The primary objective will be accomplished by examining numerous aspects of sonochemical systems and acoustic cavitation. During the course of the project, the research group will investigate the significance of physical variables during sonolysis, sonochemical kinetics and reactive intermediates, and the behavior of heterogeneous (solid/liquid) systems. An additional component of the project includes utilizing various techniques to image cavitation bubble cloud development.

### Research Progress and Implications

This report summarizes results after 2 years of a 3 year investigation. Four on-going projects will be described. The first project is the destruction of polychlorinated biphenyls at multiple ultrasonic frequencies. The second project is a comprehensive study of how ultrasonic frequency influences sonochemical reaction rates; in particular, hydrogen peroxide formation. Finally, the sonochemical destruction of the pesticides dichlorvos (at 500 kHz) and carbofuran (parallel-plate reactor) has been examined.

#### Polychlorinated Biphenyl Destruction

The sonolytic destruction of polychlorinated biphenyls (PCBs) has been performed. The ultrasonic frequency significantly impacted the reaction rate; a maximum pseudo – first order rate constant ( $0.5079 \text{ min}^{-1}$ ) was observed during sonication of 1.0 ppm 2-PCB in an Ar saturated solution at 358 kHz and a sound intensity of  $5.5 \text{ W cm}^{-2}$ . The three congeners exhibited variable rate constants: pseudo - first order rate constants for 0.87 ppm 2-PCB, 1 ppm 4-PCB, 20 ppb 2,4,5-PCB were  $0.128 \text{ min}^{-1} \pm 0.0007$ ,  $0.097 \text{ min}^{-1} \pm 0.001$ , and  $0.157 \text{ min}^{-1} \pm 0.003$  respectively, during irradiation at 20 kHz. The reaction rates were proportional to power intensity, and inversely correlated to initial concentration. Chlorine recovery as chloride ion was 78%, 76% and 69% for 2-PCB, 4-PCB, and 2,4,5-PCB respectively. Scavenging of hydroxyl radical by bicarbonate decreased the reaction rate by 53% at a bicarbonate concentration of 50 mM, indicating the important role of free-radical attack during sonochemical destruction of PCBs. Spin-trapping and electron spin resonance (ESR) indicated that phenyl radical is a reactive intermediate during the transformation of PCBs (2-PCB and 4-PCB) and biphenyl was detected with gas-chromatography/mass spectroscopy (GC/MS) analysis of sonicated solutions.

#### Sonolysis of Dichlorvos

The sonochemical destruction of dichlorvos was carried out at a sound frequency of 500 kHz with an acoustic output power ranging from 86 to 161 Watts. Power and sparge gas were important determinants of sonochemical destruction rates. The effect of acoustic power on the degradation rate was investigated for an Ar-saturated solution. The pseudo-first order rate constants for dichlorvos disappearance are  $0.0184 \pm 0.0014$ ,  $0.0258 \pm 0.002$ , and  $0.0374 \pm 0.0023 \text{ min}^{-1}$  for 86, 124, and 161 Watts respectively. The variation of the rate constants due to sparge gas (Argon, Oxygen, and Ar/O<sub>2</sub> mixture) was also examined. The pseudo-first order rate constants for dichlorvos disappearance, during sonication at 161 Watts, were  $0.0319 \pm 0.0035$ ,  $0.0374 \pm 0.0023$ , and  $0.0792 \pm 0.005 \text{ min}^{-1}$  for Oxygen, Argon, and

Argon/Oxygen mixture, respectively. Total Organic Carbon (TOC) analysis is used to determine the extent of complete mineralization (formation of carbon dioxide from organic carbon) during the destruction of dichlorvos. After 50 minutes of sonication at 161 Watts, the TOC concentration decreased by 20% for both Argon and Oxygen sparge and by 27% for the Argon/Oxygen mixture.

### **Sonolysis of Carbofuran**

The purpose of this particular study was to examine a larger volume, higher power flow-through reactor. Carbofuran, a carbamate pesticide, has been found in the groundwater of at least seven states, and the United States Environmental Protection Agency (U.S. E.P.A) has established a maximum contaminant level (MCL) of 0.04 mg/L. The sonochemical degradation of carbofuran in a parallel plate near-field acoustical processor (NAP) was carried out with simultaneous irradiation at 16 and 20 kHz, and a total power of 1800 W. The degradation rate constants increase with increasing power density and decreasing initial (bulk) concentration. The nature of the cavitating gas (Ar or Ar/O<sub>2</sub>) also determined how quickly carbofuran was destroyed during sonication. Experiments were conducted with varying power-to-volume ratios (1.65, 4.22 and 5.55 W mL<sup>-1</sup>), initial concentrations of either 25 μM or 130 μM, and a dissolved gas of either 100% Ar or 80:20 (v/v) Ar/O<sub>2</sub>. The maximum rate constant,  $k = 0.0749 \pm 0.0008 \text{ min}^{-1}$  is observed during sonication at 5.55 W mL<sup>-1</sup>, at an initial concentration of 25 μM, and with Ar/O<sub>2</sub> as the saturating gas. Nitrate and nitrite were quantified and 86% of the organic nitrogen in carbofuran is recovered as NO<sub>x</sub>. Tracer studies using the conservative tracer sodium chloride (NaCl) were performed to characterize the hydrodynamic behavior of the NAP reactor.

### **Hydrogen Peroxide Production**

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) production rates during acoustic cavitation in Ar-saturated water have been investigated over a range of frequencies and power intensities. Results from tests conducted at four ultrasonic frequencies (205, 358, 618, and 1071 kHz) and seven power intensities at each of the four frequencies (1.0, 2.0, 3.1, 4.1, 5.1, 7.7 and 8.2 W cm<sup>-2</sup>) show a direct correlation between zero-order H<sub>2</sub>O<sub>2</sub> production and power intensity. Moreover, the H<sub>2</sub>O<sub>2</sub> production rate at 358 kHz tended to be greater than those at 205, 618 and 1071 kHz, for a given intensity. At 205 kHz, a maximum production rate is observed at 5.1 W cm<sup>-2</sup>; however, the production rates increase with intensity (up until 8.0 W cm<sup>-2</sup>) at each of the other three frequencies. The H<sub>2</sub>O<sub>2</sub> formation rate for each frequency-intensity combination was determined over the course of 45 minutes of sonication; and each combination was tested in triplicate. The results of this study show that of the four frequencies tested, 358 kHz is the most efficient in terms of H<sub>2</sub>O<sub>2</sub> production; an optimal efficiency of 0.3 nmoleJ<sup>-1</sup> occurs at 358 kHz and 4.1 W cm<sup>-2</sup>.

### **Planned Activities**

Further investigations of chemical kinetics and transformation products will be carried out during the final phase of the project. In order to truly understand sonochemical effects, the behavior of the individual bubbles and the bubble clouds must be more finely resolved. Physical characterization of cavitation bubble clouds will also be performed. Thus, a more fundamental link will be established between bulk, observable parameters and sonochemistry, via the physics and hydrodynamics of the cavitating cloud.

### **Other Access To Information**

Professor Hua's Web URL is: [http://CE.www.ecn.purdue.edu/CE/Fac\\_Staff/FACULTY/hua](http://CE.www.ecn.purdue.edu/CE/Fac_Staff/FACULTY/hua)