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Ultrasonic Process for Remediation of Organics-Contaminated Groundwater/Wastewater

by

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Ultrasonic Process for Remediation of Organics-Contaminated Groundwater/Wastewater

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ABSTRACT

A technology is being developed that employs ultrasonic-wave energy for remediation of groundwater/wastewater contaminated with volatile organic compounds such as carbon tetrachloride (CCl_4) and trichloroethylene (TCE). This paper presents the updated results of a laboratory investigation of ultrasonic groundwater remediation using synthetic groundwaters prepared with laboratory deionized water. Key process parameters investigated included steady-state temperature, contaminant concentration, solution pH, sonication time, and intensity of the applied ultrasonics-wave energy. High destruction efficiencies of the target contaminants were achieved, and the sonication time required for a given degree of destruction decreased with increasing intensity of the applied ultrasonic energy. The sonication time can be further reduced by adding a chemical oxidant such as hydrogen peroxide.

INTRODUCTION

Contamination of groundwater and soil with chlorinated organic compounds is a critical problem at many U.S. Department of Energy (DOE) and other government and industrial sites. The most common organic contaminants at DOE sites are carbon tetrachloride (CCl_4), trichloroethylene (TCE), and perchloroethylene (PCE), all of which are Resource Conservation and Recovery Act (RCRA) components. Some DOE sites are also contaminated with nonvolatile and soluble/insoluble organic compounds, polychlorinated biphenyls (PCBs) and pesticides, transuranic and low-level radioactive wastes, and mixed (chemical/radioactive) wastes. The estimated cost to remediate contaminated DOE sites over the next 30 years is as high as $100-200 billion.

To address this issue, Argonne National Laboratory is developing an innovative ultrasonic detoxification process that could ultimately be used to clean up contaminated soil and groundwater/wastewater at affected sites. Unlike other commercial techniques — such as pumping/stripping and pumping/activated carbon adsorption, which produce residual streams that require additional treatment to destroy the organic compounds — this process involves using intense ultrasonic-wave energy to transform the chlorinated organic compounds directly into nonhazardous end products. The results of initial experiments conducted at Argonne confirmed that the ultrasonic detoxification can be used to reduce the concentrations of CCl_4 in water (to less than 2 ppb) and soil (to less than 1 ppm). A conceptual process design of an ultrasonic soil detoxification system has been completed. The final goals of this project are to establish a successful large-scale demonstration unit, and to transfer the technology to private companies to make it commercially available for broader applications.

In addition to the destruction of organic compounds, potential applications of this process include removal of radioactive compounds from the soil matrix; these metals can be subsequently recovered from the treated soil. Preliminary cost estimates also indicate that the technology would be less costly than incineration for treating soils and sludges contaminated with PCBs. When fully developed, this technology will provide a cost-effective alternative for detoxifying soils and groundwater and reduce the amount of waste produced during remediation of contaminated sites.

In this paper, we present the results of an investigation of the ultrasonic irradiation of CCl_4 in laboratory-simulated groundwater at various pH values, temperatures, and power intensities. Kinetic data and selected chemical mechanisms are also proposed and discussed.

EXPERIMENTAL CONSIDERATIONS

Irradiations were carried out with an ultrasonic power supply (Sonics & Materials, VC 600) with a continuously variable output from 0 to 600 W, operating at 20 kHz. Figure 1 shows the schematic diagram of the experimental apparatus. The sonication vessel was a borosilicate glass cell with a stainless steel collar, which could be screwed onto the horn of the ultrasonic probe so that the probe could be immersed into the sample solution as sonication proceeded. The temperature inside the reaction vessel was kept relatively constant by circulating cooling water in a constant-temperature bath, which was continuously monitored by a thermocouple probe and temperature readout.

All of the chemicals used, such as CCl_4, were certified, ACS-grade chemicals purchased from Mallinckrodt, Inc. The standard CCl_4 solution, prepared by stirring the neat liquid with laboratory deionized water overnight, was used to prepare all of the sample solutions for the subsequent experiments. The analysis of CCl_4 was carried out by using a gas chromatograph equipped with an electron capture detector. The pH value of the sample solution in the pH-effect study was determined by using a Cole-Parmer Chemcadet pH/ion/mv meter (model 5986-50), which was calibrated before use with standard solutions of pH 4, 7, and 10.

For a typical experiment, a 15-mL sample solution, diluted from the standard solution, was prepared and irradiated for a desired length of time. After sonication ceased, the irradiated solution was extracted, dehydrated, and stored in a Teflon-sealed sampling bottle for future treatment or analysis.

RESULTS AND DISCUSSION

Sonochemical destruction of organic compounds results from the formation of microbubbles when ultrasonic-wave energy is transmitted in the liquid media. The microbubbles gradually grow with the ultrasonic frequency cycles until they attain a critical size, then finally collapse. As a result, a large amount of energy and pressure is released. Local temperatures of up to 5000 K have been measured (1), and pressures of up to 1,000 atmospheres have been calculated (2). Water molecules under these conditions are decomposed to extremely reactive radicals, such as the hydroxyl radical ($OH^{\cdot}$) and atomic hydrogen ($H^{\cdot}$). If organic compounds are present, they are directly destroyed (because of the high temperatures and pressures) or oxidized by the radicals. The final products of this process may be hydrogen, carbon dioxide, and/or some inorganic compounds, if the reaction is complete.

Exposure of CCl_4 solutions to ultrasound in the presence of dissolved air results in a decrease of the CCl_4 in the solutions. Greater than 99% removal efficiency was obtained during our experiment. Figure 2 shows the plot of CCl_4 versus sonication time at various initial concentrations. Initial concentrations as high as 8 ppm dropped to about 0.5 ppm after 5 minutes of irradiation, while initial concentrations of 1.6 ppm dropped to about 0.05 ppm after 5 minutes of irradiation. The concentration of residual CCl_4 decreased exponentially with sonication time. In addition, the decreasing rate apparently followed first-order kinetics within the current experimental concentration range. An average first-order rate constant of $k=0.7\ \text{min}^{-1}$ was determined.

Temperature control in the reaction vessel is an important factor in maintaining a high destruction rate of CCl_4 in the solution. In sonochemistry, one should not attempt reactions in a solvent (here, water) that is near its boiling point (100°C), because the rarefaction cycle causes the water to boil as a result of the reduced pressure generated; consequently, any cavitation bubbles formed will fill with water vapor almost instantly. This water vapor could reduce the extremes of temperature and pressure generated and thus decrease the direct destruction efficiency of the organics. On the other hand, the secondary reactions occurring in the liquid phase may be enhanced by operating the system at higher temperatures.

Figure 3 shows the effect of a steady-state temperature on the destruction efficiency of CCl_4. About 80% removal efficiency was observed for 4 minutes of irradiation; removal efficiency remained unchanged within a temperature range of 20-60°C. These results illustrate that, within this temperature range, increasing the steady-state temperature of the irradiation solutions seems to have little effect on the CCl_4 destruction efficiency. In other words, manipulating the system at the optimum temperature range allows high removal efficiencies within reasonable operation times.

Ultrasonic power intensity is also an important factor affecting the CCl_4 destruction rate. In general, any increase in intensity will increase the sonochemical effect (3). However, intensity cannot be increased indefinitely (4, 5). With an increase in power intensity, the bubbles may grow so large during rarefaction that the time available for their collapse is insufficient; consequently, the effective coupling of the ultrasonic energy to the system is reduced.

Figure 4 shows the effect of power intensity on the destruction of CCl_4. After 1 minute of irradiation, the residual CCl_4 decreases with increasing power intensity. More CCl_4 molecules are destroyed at higher power intensities. Within the current experimental range, the destruction rate seems to have a linear relationship to the power intensity. Although threshold intensity was not determined, it is estimated to be lower than the 0.95 W/cm^2 shown in this figure. The destruction rate is negligible if the power delivered into the solution is lower than the threshold intensity.

The relationship between initial pH value and CCl_4 destruction is shown in Figure 5. Residual CCl_4 decreases with increasing pH value — between pH 3 to pH 9 within the same sonication period. Better sonication efficiency was observed at higher initial pH values; however, such improvement increasingly diminishes as the pH is raised above 6. Because most of the irradiations were conducted at near-neutral conditions for groundwater treatment, the initial pH value seems to have a minimal effect on CCl_4 removal.

CONCLUSIONS

This study demonstrates that the ultrasonic process is a promising and effective method for destruction of low concentrations of chlorinated organic compounds such as CCl_4 in water. Removal efficiencies of greater than 99% were achieved through this process. For the treatment of water containing CCl_4, the major reactions may be the bond-cleavage of water and of CCl_4 in the collapsing cavitation hole. Under the current experimental conditions, physical operating conditions, such as steady-state temperature and pH value of the irradiated solution, were found to have little effect upon the CCl_4 destruction rate. However, the CCl_4 destruction rate was significantly affected by the intensity of the ultrasonic energy, with the destruction rate increasing proportionally to the intensity.

ACKNOWLEDGMENT

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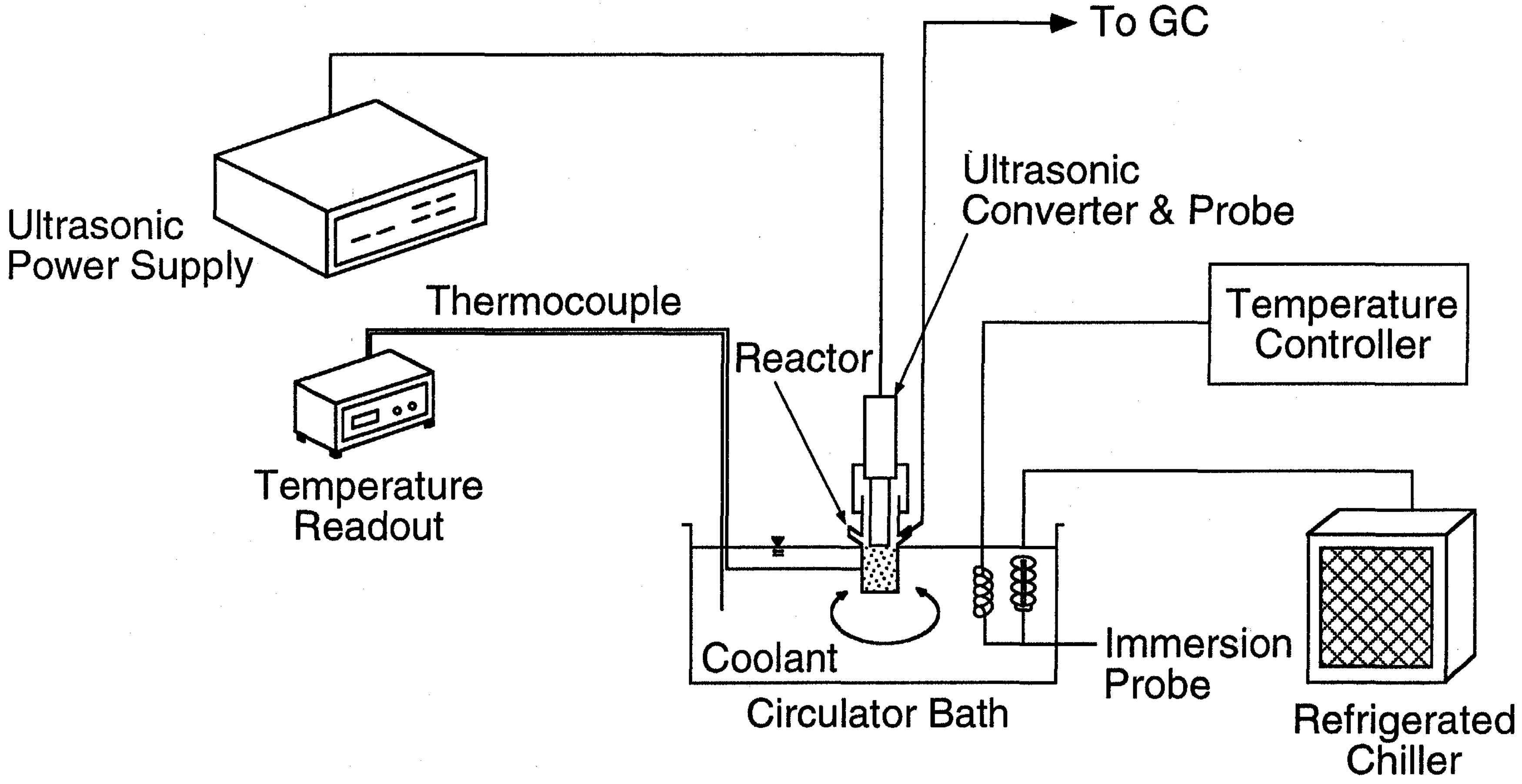
Table & Figure Captions:

Figure 1.	Experimental Apparatus
Figure 2.	CCl_4 Decrease Versus Sonication Time; $[CCl_4]$=8 ppm, 1.6 ppm, 0.53 ppm
Figure 3.	Effect of Steady-State Temperature on CCl_4 Sonication
Figure 4.	Effect of Power Intensity on CCl_4 Sonication
Figure 5.	Effect of Initial pH Value on CCl_4 Sonication

EXPERIMENTAL APPARATUS



To GC

Ultrasonic
Converter & Probe

Ultrasonic
Power Supply

Thermocouple

Reactor

Temperature
Controller

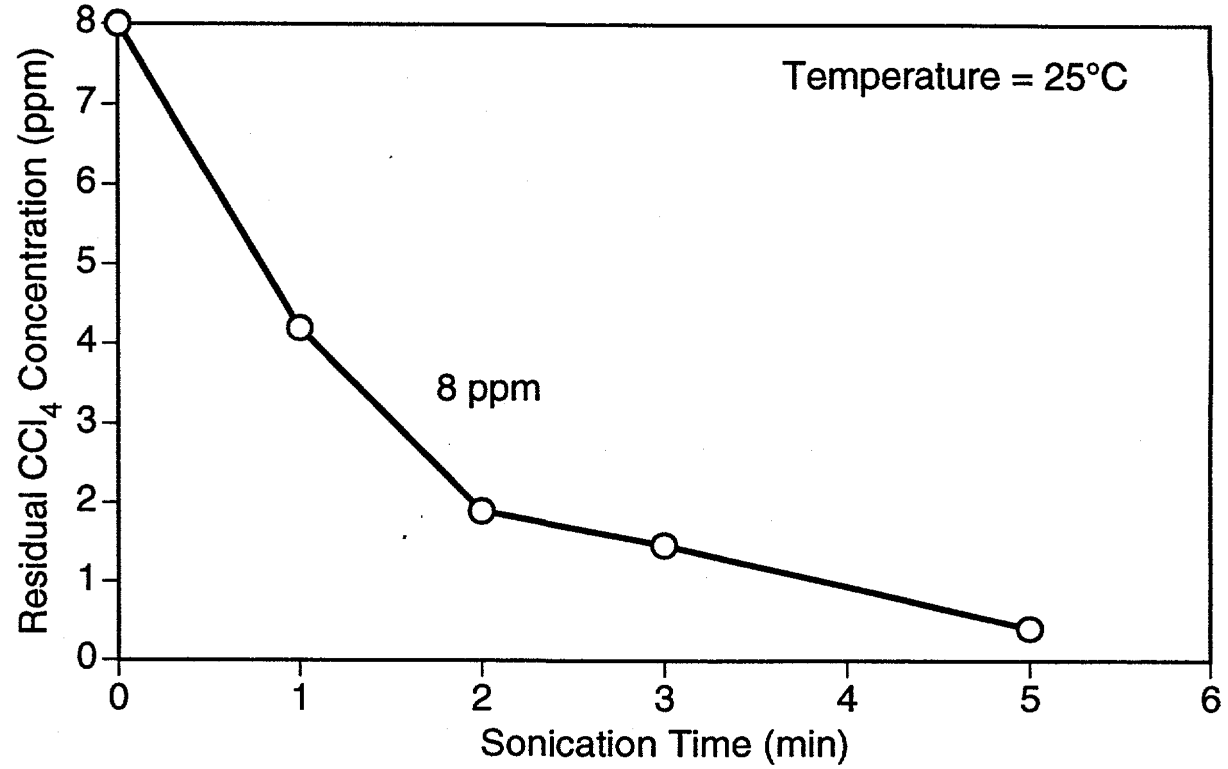
Temperature
Readout

Coolant

Circulator Bath

Immersion
Probe

Refrigerated
Chiller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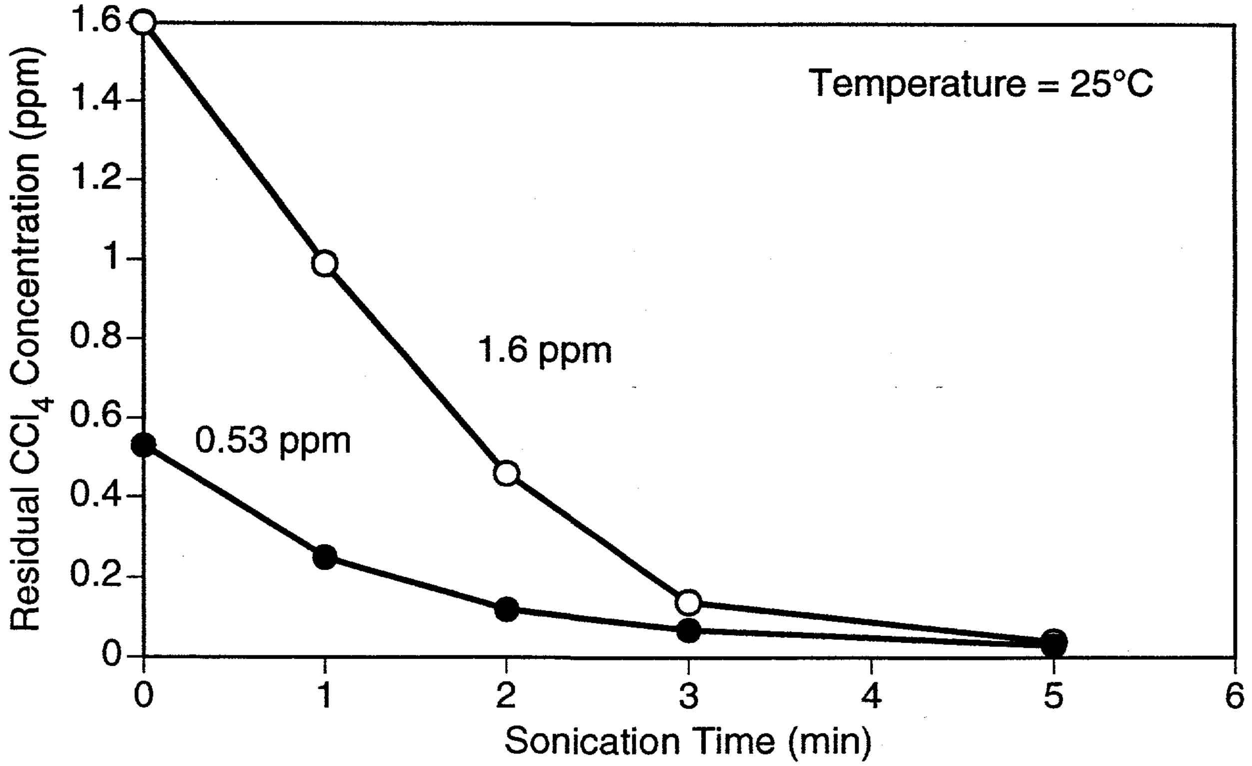
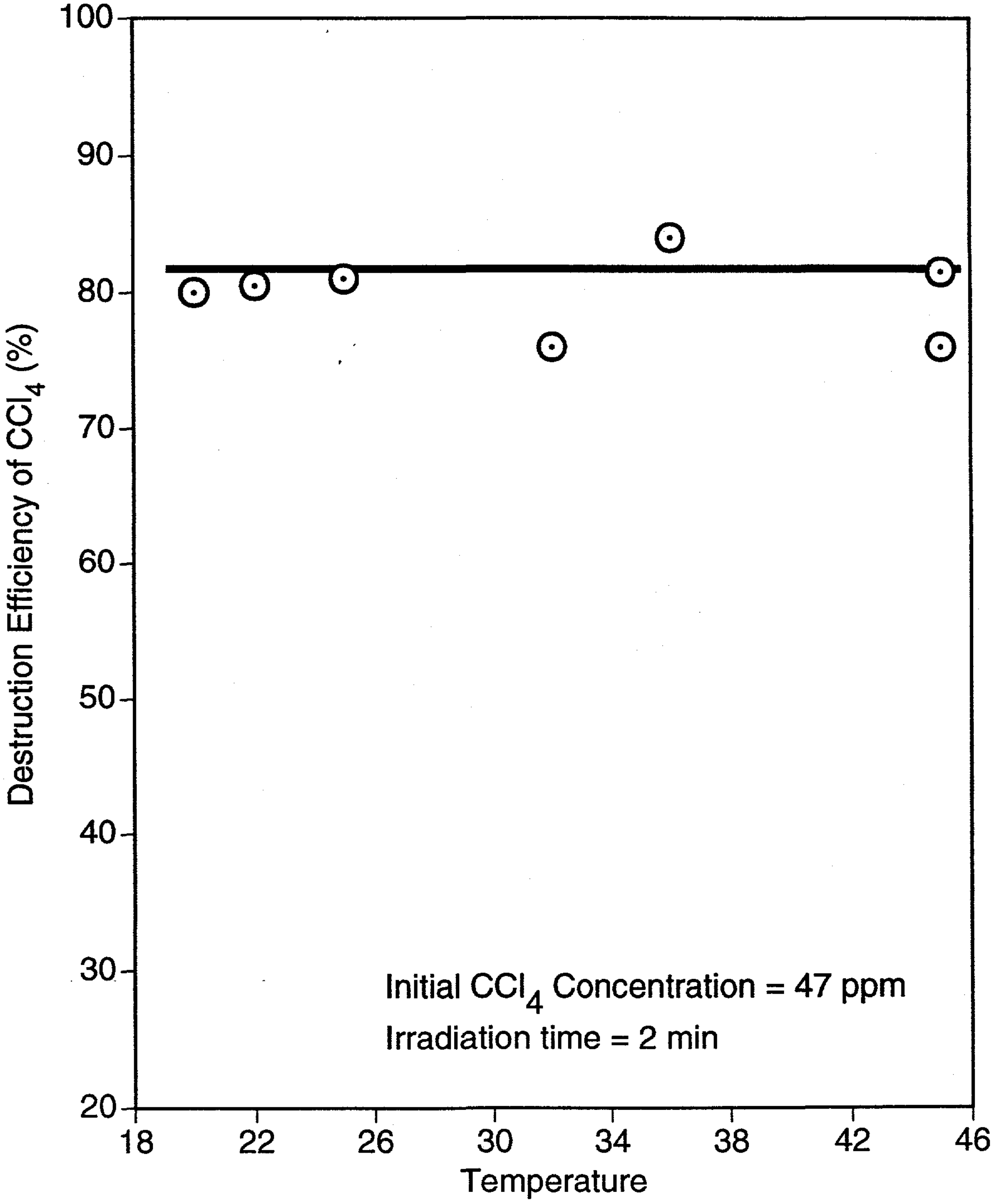
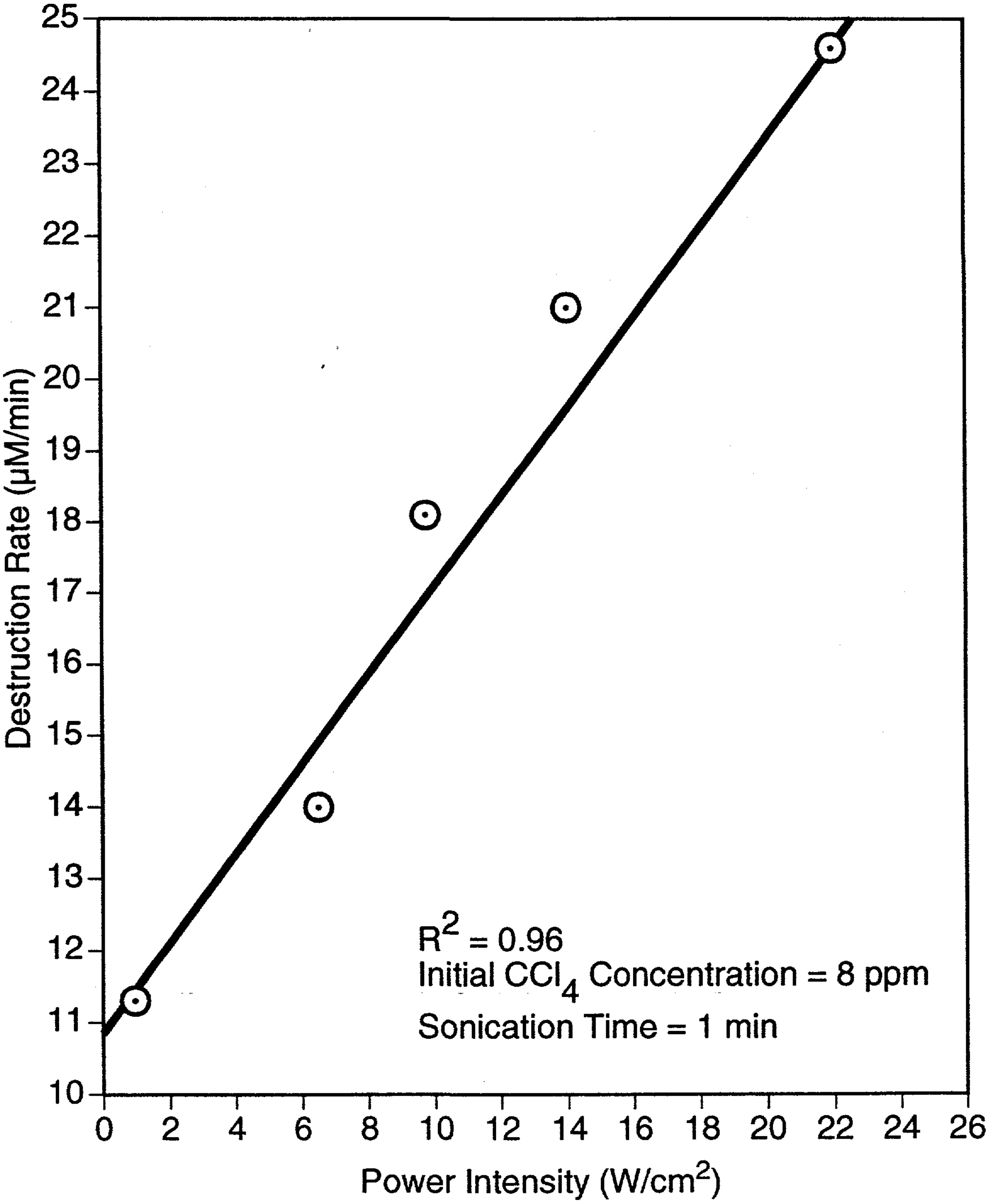
8 ppm
Residual CCl4 Concentration (ppm)
0
1
2
3
4
5
6
7
8
Sonication Time (min)
0
1
2
3
4
5
6


Temperature = 25°C
1.6 ppm
0.53 ppm
Residual CCl4 Concentration (ppm)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Sonication Time (min)
0
1
2
3
4
5
6

EFFECT OF STEADY-STATE TEMPERATURE ON CCl_4 SONICATION



EFFECT OF POWER INTENSITY ON CCl_4 SONICATION



EFFECT OF INITIAL PH VALUE ON CCl_4 SONICATION