540SR92080

United States
Environmental Protection
Agency

February 1993

EPA

SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Emerging Technology Summary

Laser Induced Photochemical Oxidative Destruction of Toxic Organics in Leachates and Groundwaters

Organic compounds, specifically chlorinated aromatic compounds and unsaturated organic compounds, are major contaminants in groundwater. These specific species also tend to rank high on the list of the U.S. Environmental Protection Agency (EPA) priority pollutants, even at the low (mg/L) concentrations that are normally found in groundwater. The technology described in this report has been developed under the Emerging Technology Program of the Superfund Innovative Technology Evaluation (SITE) Program. Organic compounds in wastewater are photochemically oxidized by applying ultraviolet (UV) radiation using an excimer laser. The photochemical reaction is capable of producing the complete mineralization of a variety of organic compounds at moderate to extremely low concentrations of the toxic compounds in water. The energy supplied by the laser is sufficient to stimulate photochemical reactions between the organics and the hydrogen peroxide employed as a chemical oxidant, causing photooxidation and/or phototransformation of the toxic organic species to carbon dioxide, water, and in the case of the chlorinated solvents, the halide ion. Additionally, the radiation is not absorbed to any significant extent by the water. The process has been developed as a final treatment step to reduce organic contamination in groundwater and industrial wastewaters to acceptable discharge limits.

Optimum conditions for the complete mineralization of several different classes of compounds were developed and demonstrated in the laboratory.

This summary was developed by the EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the Emerging Technology Program that is documented in a separate report (see Project Report ordering information at back).

Introduction

This report summarizes the results of a 2-yr bench-scale evaluation of the laser induced photochemical oxidative destruction (LIPOD) process sponsored by the SITE Emerging Technologies Program.

The LIPOD process is based on the photochemical destruction of toxic organic chemicals in dilute aqueous solutions. Energy is supplied by an excimer laser and is absorbed by the organic molecule and hydrogen peroxide, thus initiating the oxidation of the organic compound by the

Printed on Recycled Paper

SM-X2

hydrogen peroxide. The advantage of this process is that the narrow band UV radiation is preferentially absorbed by the organic molecules and hydrogen peroxide; little is absorbed by the surrounding water molecules; and the organic compounds are completely oxidized to carbon dioxide, water, and the inorganic ions present.

Unsaturated organic compounds, and particularly chlorinated organics, are major contaminants in groundwater at or near hazardous waste sites. These species also rank high on the EPA's list of priority pollutants, even at the parts per billion concentrations often found in wastewaters. Because of the very low concentrations, removal of these compounds from these waters is difficult and expensive. Carbon adsorption and UV-hydrogen peroxide or ozonation are currently used to detoxify these toxic wastes. The LIPOD process shows promise of excellent performance at a lower cost.

Process Description

LIPOD is a process developed to oxidize low levels of toxic organic compounds in contaminated waters to nontoxic species. The process has been under development for the past seven years, and its efficacy relies on the use of a coherent electromagnetic radiation source in the UV portion of the spectrum to activate an exothermic process in the presence of an oxidant so as to initiate a chain oxidation reaction. The UV source is an excimer laser that provides a high intensity coherent energy source. The oxidant is hydrogen peroxide, which is miscible with water in all proportions, hydroxyl radicals which are very powerful oxidants are produced when the laser beam impacts the hydrogen peroxide, and sufficient oxygen and/or hydroxyl radicals are formed to completely mineralize the organic compounds.

Unlike other UV irradiation processes in which the toxic molecules must be exposed continually to the UV radiation with both hydrogen peroxide or ozone present as the chemical oxidants, this process requires no ozone and the contaminant is exposed to the UV light source for only a very short time (< 50 sec) to initiate the oxidative chain reaction. The investigations have shown that only a portion of the fluid to be decontaminated needs to be exposed to the UV radiation source in the presence of hydrogen peroxide. This exposed fluid can be contacted with unexposed fluid and additional hydrogen peroxide and the entire fluid pool will undergo the chain oxidation reaction.

A typical process flow scheme is shown in Figure 1. The feed stream containing the toxic species and the hydrogen peroxide flows in a direction countercurrent to the laser beam in a photochemical reactor where the toxic compounds are irradiated. When oxidizing halogenated solvents, the reaction byproducts are carbon dioxide, water, and the corresponding halide ion.

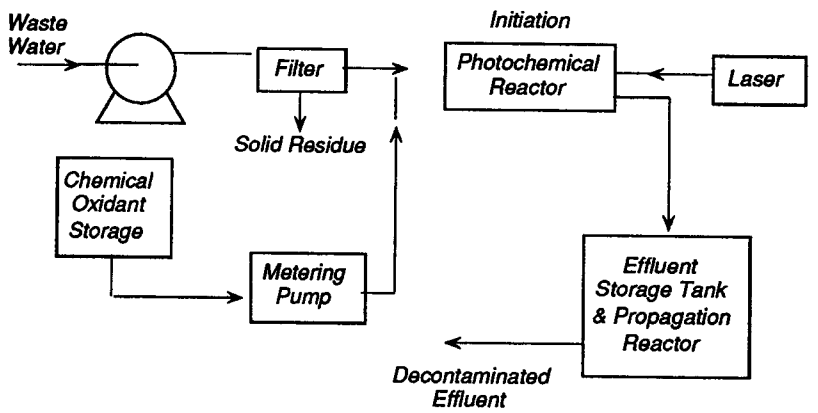

Figure 1. *Process flow scheme for the laser induced photochemical oxidative destruction process.*

Process Performance

The test compounds selected for this project are frequently found in wastewaters and have the ability to absorb the energy from the wave length chosen for this excimer laser; other wave lengths can be produced by other excimer laser beams to react with other compounds. The ability of the process to destroy a given toxic compound is defined in terms of the percent destruction achieved.

$$\text{Percent destruction achieved} = \frac{C_{in} - C_{out}}{C_{in}} X100$$

where C_{in} = feed toxic organic concentration

C_{out} = effluent toxic organic concentration

The UV light initiates a chain reaction. Part of the destruction occurs during the initiation phase of the reaction when the reactants are exposed to the light source (time 0 on the following figures is after this initiation); and the remaining destruction occurs as the reaction propagates in the absence of light. Table 1 and Figure 2 show the destruction of six compounds during initiation and propagation periods. The system was found to be dependent on an initiation and a propagation phase. Limited destruction was achieved during the photochemical initiation phase for all compounds irradiated. Greater destruction can be achieved during this phase only at the expense of applying greater irradiation dosage. Analysis and observation of the propagation process showed that significant changes in the percent destruction after a number of days depended on the concentration of the toxic organic compound and of the chemical oxidant, hydrogen peroxide, and the irradiation dose applied during the initiation phase.

Process performance results with chlorobenzene as the test toxic compound are presented in the next several figures. The impact of chemical oxidant concentration on reaction kinetics is shown in Figure 3. The stoichiometric quantities of chemical oxidant used in typical applications are minuscule, and in all cases over the range studied, greater than 95% destruction was achieved. The effect of irradiation dose and toxic organic concentration on the rate of destruction in the propagation phase are shown in Figures 4 and 5 respectively. The system is cost efficient, non-labor intensive; reaction byproducts in the effluent are nontoxic. Percent destruction achieved has in some instances been greater than 99%.

Conclusions

Laboratory scale testing of the LIPOD process has shown that the process is capable of destroying 90% or more of a variety of toxic organic compounds in dilute water solutions. The effects of organic concentration of the toxic compound, oxidant concentration, and irradiation dosage have been determined for a series of representative organic compounds. On the basis of these results, the cost of a commercial-scale process has been estimated and found to be very competitive with existing technologies that are now in use for wastewater detoxification. Costs range from $30 to $70/1000 gal treated for the complete conversion of toxic organic compounds, present initially at the 50 ppm

Table 1. Destruction of Toxic Organic Compounds by Laser with H_2O_2 at the Stoichiometric Concentration

Compound	Irradiation dose, photons per molecule	Percent destruction at end of initiation period	Propagation time (hr)	Percent destruction at end of propagation period
Benzene	10	29	96.0	91
Chlorobenzene	10	31	113.5	98
Chlorophenol	10	34	72.0	>99
Dichloroethene	10	18	624.0	88
Benzidine	10	48	288.0	88
Phenol	10	35	72.0	>99

level in the solution, to carbon dioxide and water.

Recommendations

Results to date suggest that the LIPOD process has excellent potential for effective removal of organic compounds from wastewater and that further development of this process is warranted. Treatability studies in the laboratory using actual wastewater samples from hazardous waste sites are needed to establish how the process performs on waste containing a variety of organic compounds and inorganic salts. Successful completion of these treatability studies would lay the groundwork for commercialization of the process.

The full report was submitted in fulfillment of Cooperative Agreement No. CR 815330020 by Energy and Environmental Engineering, Inc., under the sponsorship of the U.S. Environmental Protection Agency.

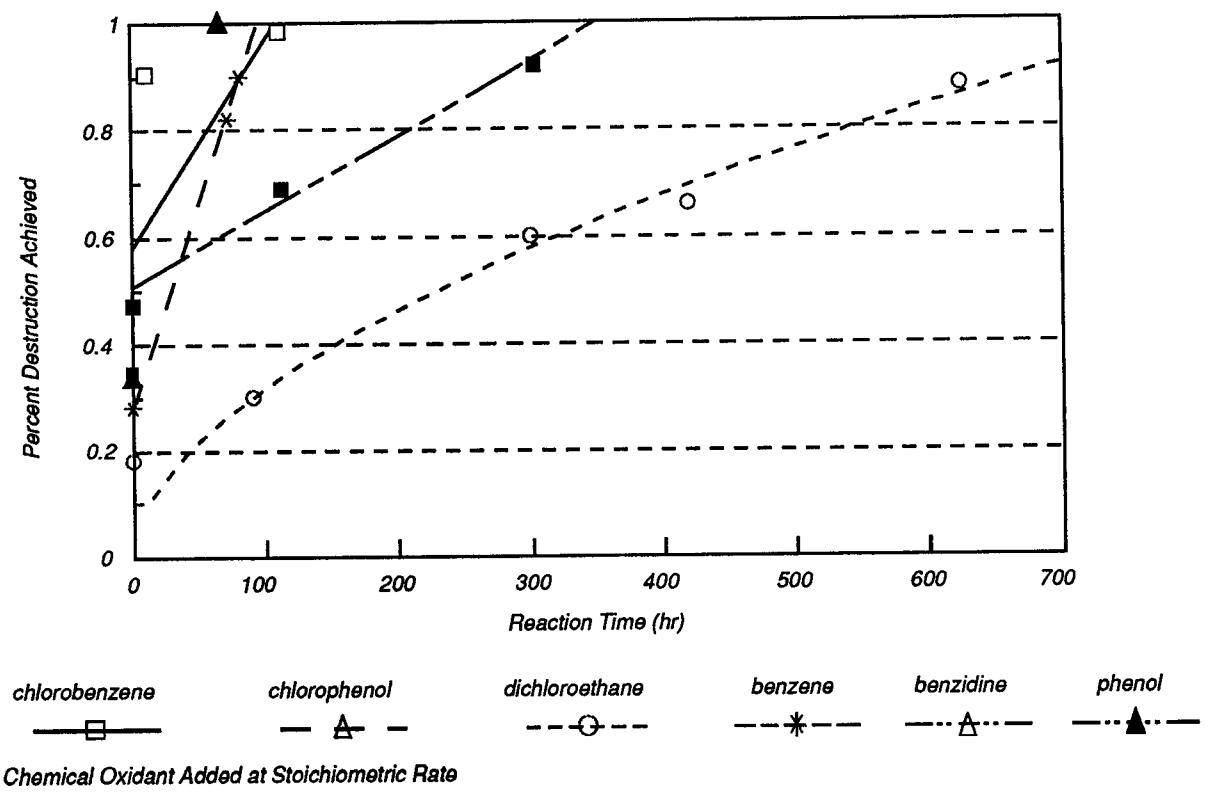

Figure 2. Destruction of contaminants by laser.

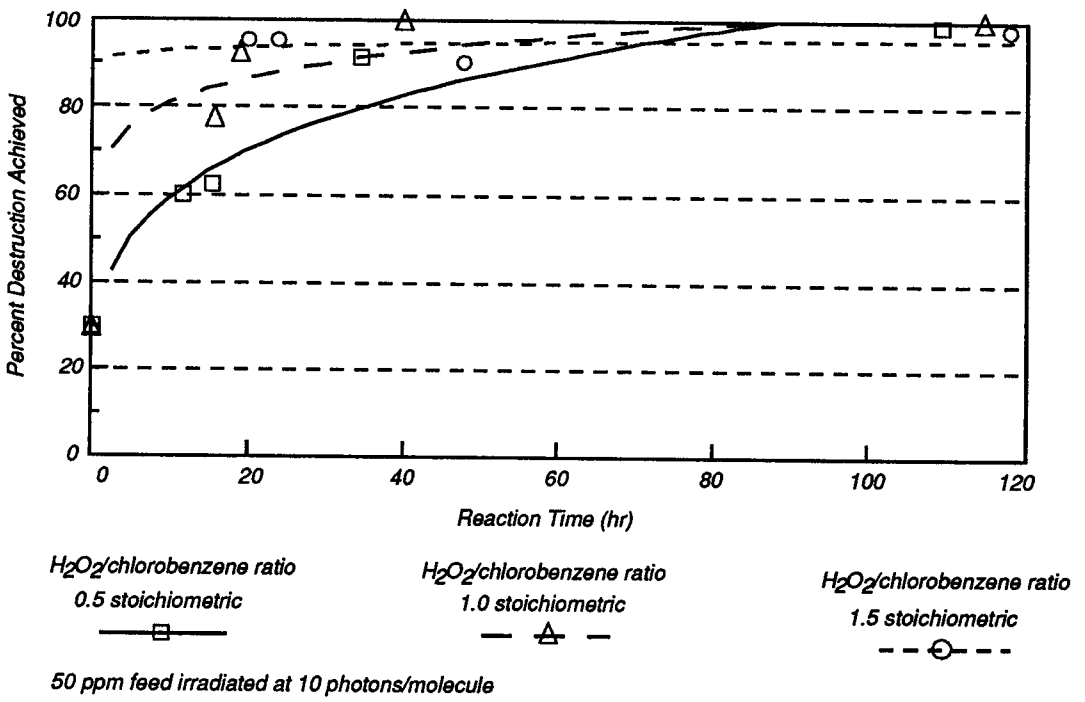

Figure 3. *Destruction of chlorobenzene by laser. Effect of chemical oxidant (H_2O_2) by concentration.*

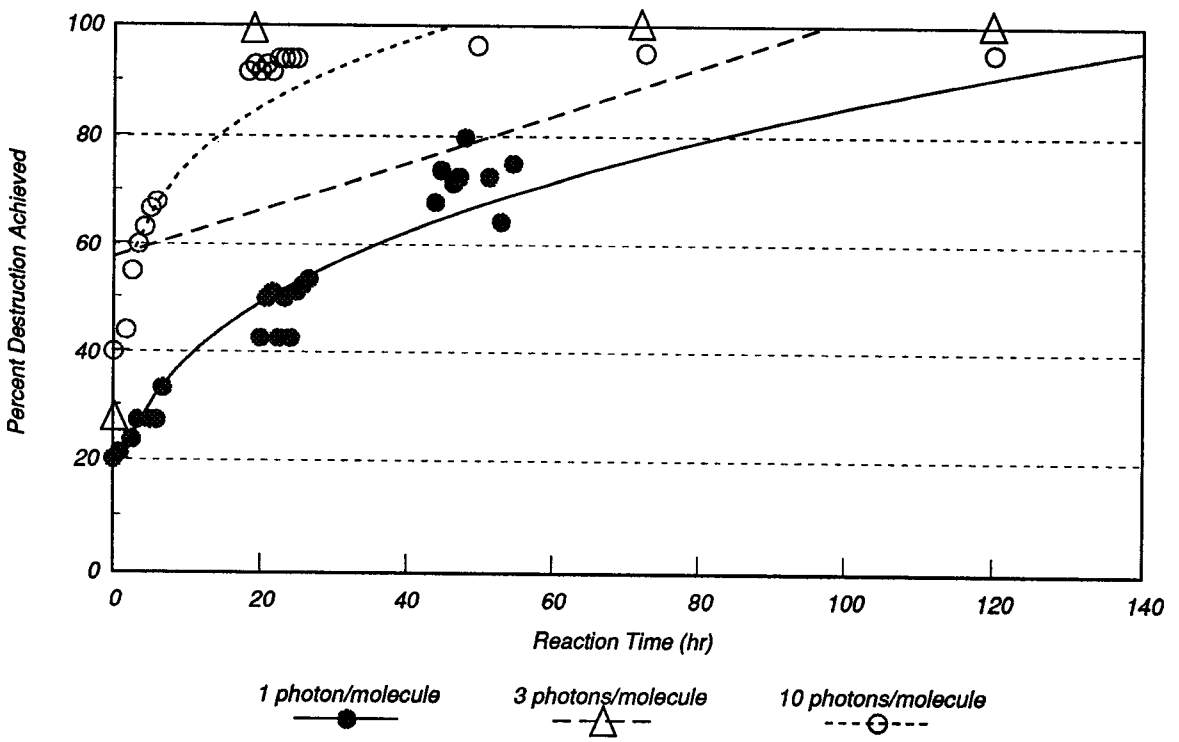

Figure 4. *Destruction of chlorobenzene by laser. Effect of number of photons/molecule of chlorobenzene.*

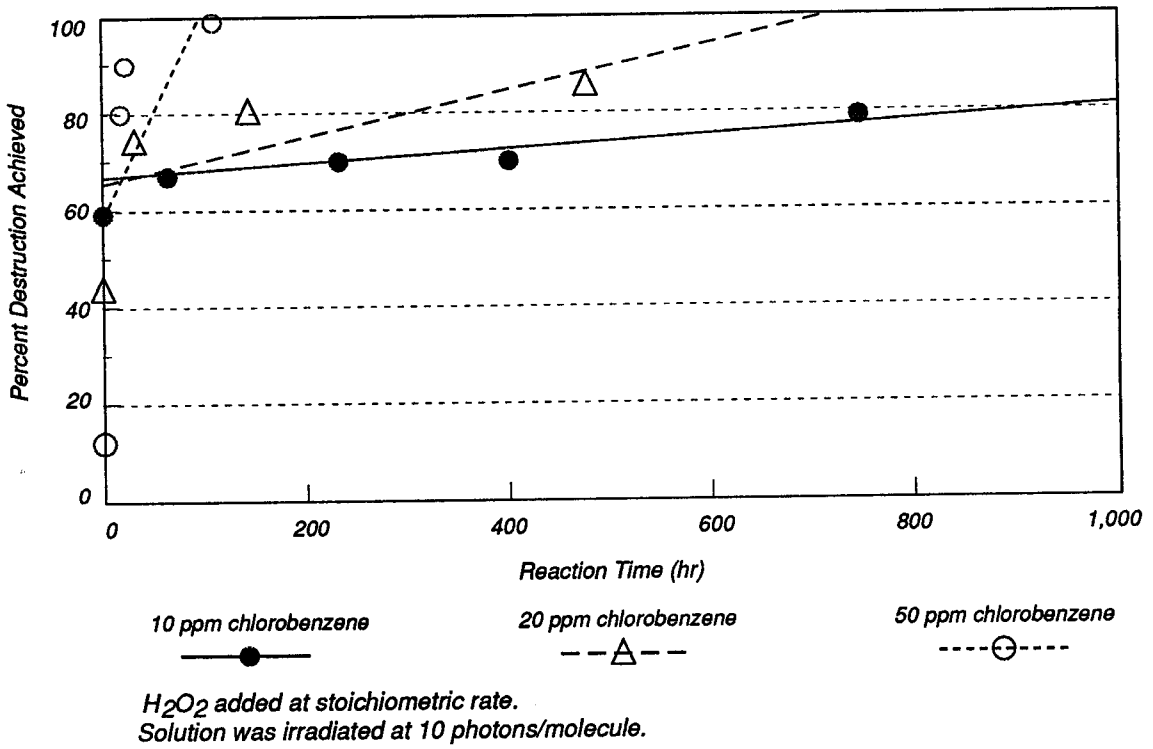

Figure 5. *Destruction of chlorobenzene by laser. Effect of chlorobenzene concentration.*

*U.S. Government Printing Office: 1993 — 750-071/60194

This Project Summary was prepared by the staff of Energy and Environmental Engineering, Inc., Somerville, MA 02143
***Ronald Lewis** is the EPA Project Officer (see below).*
The complete report, entitled "SITE-Emerging Technologies; Laser Induced Photochemical Oxidative Destruction of Toxic Organics in Leachates and Groundwaters," (Order No. PB93-131431/AS; Cost: $19.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

United States
Environmental Protection Agency
Center for Environmental Research Information
Cincinnati, OH 45268

Official Business
Penalty for Private Use
$300

EPA/540/SR-92/080

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35