

HOMOGENEOUS AND HETEROGENEOUS PROCESSES IN ULTRASONIC AND HYDRODYNAMIC CAVITATION: APPLICATION TO TREATMENT OF AQUEOUS BIOCIDES, PESTICIDES AND HERBICIDES

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Introduction

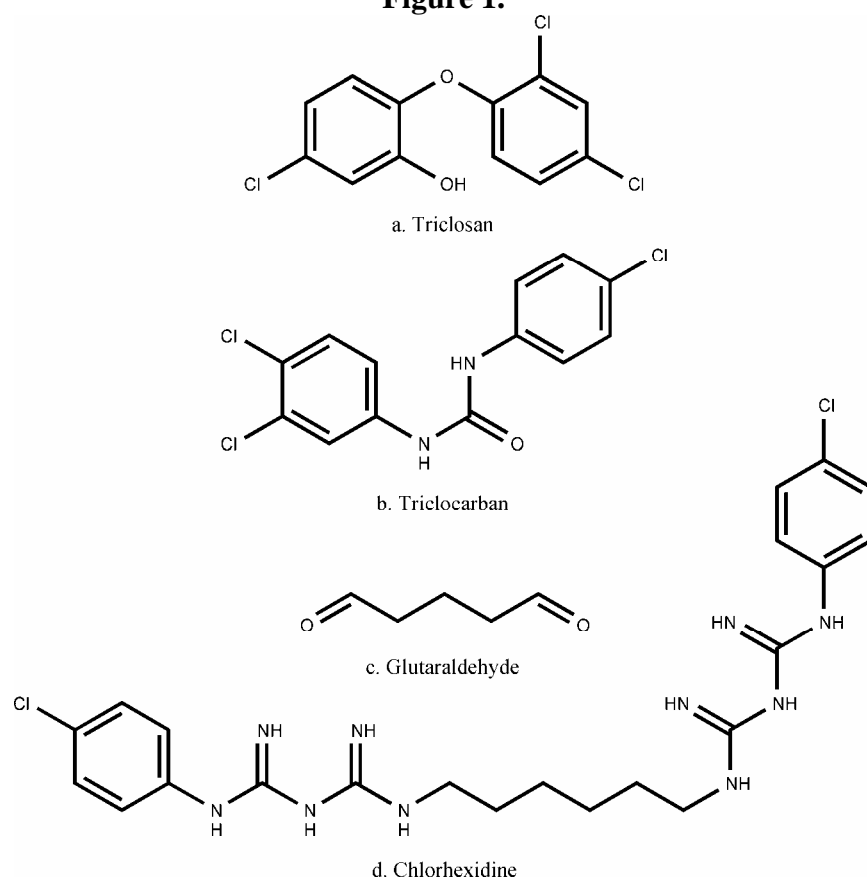
Biocidal compounds, in addition to various pesticides and herbicides, are found in many natural waters as a result of domestic, municipal and industrial wastewater discharge and non-point source pollution. Indeed recent surveys indicate that low levels of a broad range of bioactive compounds from household, agricultural, medical and industrial use are present at low levels in many natural waters (1, 2). For example Triclosan, the common antiseptic found in some soap products, was found in 57.6% of the United States water resources examined in a recent reconnaissance study (2). Concern has been raised about the potential environmental impact of these substances, including the development of antibiotic resistant microbes (3) and there is increasing interest to demonstrate efficient and economical approaches to removal from wastewater.

Advanced waste treatment processes using ultrasonic and hydrodynamic cavitation have shown their ability to induce reactive pathways in aqueous solution for the destruction of organic and inorganic compounds (4). Magnetostrictive and piezoelectric transducer horns used in ultrasonic irradiation of solutions can induce the growth and collapse of cavitation bubbles with extreme local temperature and pressures (5). Submerged cavitating liquid jets have been shown to offer an alternative, economic approach to stimulating widespread cavitation in solutions with a concomitant increase in process efficiency (6, 7). It has been shown that the cavitating solution production of highly reactive radicals, such as $\bullet\text{OH}$, can affect an *in situ* oxidation of many types of molecules. As well, heterogeneous reactions on surfaces such as TiO_2 and Fenton's type oxidations using iron salts appear to be favorably enhanced in the reactive environment produced by cavitation (8). Ultrasonic treatment has been coupled with wet oxidation, UV oxidation and biodegradation for wastewater treatment (9). In this work, we review the application of cavitation processes for the treatment of aqueous biocides, pesticides, and herbicides and demonstrate the use of these approaches in lab scale and process scale applications. Removal data and presumptive pathways of cavitation induced reaction are presented for a representative array of biocidal compounds found in commercial production and in wastewater treatment effluents.

Exposure to cavitation can greatly enhance various chemical reactions due to the extraordinary energies present the collapsing bubble microenvironment – exceeding the critical temperature (647 K) and pressure (22.4 MPa) of water (10). Ultrasonic cavitation research at 20 kHz is common due to the widespread availability of commercial sonicators at this frequency. Higher frequency research (i.e. 200–600 kHz) has demonstrated a higher efficiency of target compound degradation for some applications. Ultrasonic devices self-limit their performance by achieving cavitation in only a thin layer near the sonifier surface resulting in overall inefficiency. Previous work has demonstrated the ability of hydrodynamic cavitation generated by submerged cavitating jets to oxidize a number of compounds in aqueous solutions at very high energy efficiencies (11, 12).

Several agricultural chemicals, including insecticides and herbicides, have been studied in sonochemical treatment research. The organophosphorous insecticide parathion was degraded by 20 kHz sonolysis (13). The herbicides atrazine and alachlor followed first order decomposition kinetics under ultrasonic treatment (14). Aqueous solutions of pentachlorophenol and atrazine were degraded more efficiently at 500 kHz than 20 kHz (15). Pentachlorophenol sonochemical oxidation was also successfully demonstrated as a pretreatment prior to biological wastewater treatment (16). Refractory 2-chlorophenol was mineralized using 20 kHz irradiation at 160 W with Fenton's reagent (Fe^{2+} and H_2O_2) (8) in addition to an observation of a free radical mechanism of sonochemical reaction in aqueous solution (17). The herbicide chlorpropham and its primary metabolite, 3-chloroaniline, were more efficiently degraded at 482 kHz than 20 kHz (18). Carbofuran decomposition was studied in a parallel plate, near-field acoustical processor at 16 and 20 kHz at 1800 W (19). The study reports an enhanced degradation of this carbamate with increasing power and decreasing initial concentrations. In the sonochemical irradiation of dichlorvos at 500 kHz, a doubling of the degradation rate constant was observed with an acoustic power increase from 86 to 161 watts (20). The mineralization pathway includes the formation of metastable intermediates dimethyl phosphate and formate. For treatment of this insecticide, a sparge gas of 6:4 argon and oxygen yielded the highest decomposition rate constant.

Figure 1.



Biocides are used to control microbes that may cause disease and odor, spoil food or water, or damage textiles and equipment. There are thousands of biocidal formulations in the marketplace and many of these fall into the major categories of aldehydes (i.e. glutaraldehyde), quaternary ammonium compounds, alcohols (i.e. isopropanol), heavy metals (i.e. silver), the bisbiguanides (i.e. chlorhexidine), the phenolics (i.e. Triclosan), the oxidizers (i.e. H_2O_2), and the halogens (i.e. iodine). In this work we explore the comparative application of ultrasonic and hydrodynamic cavitation on the degradation of aqueous Triclosan, Triclocarban, glutaraldehyde and chlorhexidine (Figure 1).

Material and Methods

Test Materials

Triclosan, 2,4,4'-Trichloro-2'-hydroxydiphenyl ether; Triclocarban, 1-(4-chlorophenyl)-3-(3,4-dichlorophenyl)urea; Glutaraldehyde, 1,3-diformylpropane; and chlorhexidine, 1,1'-Hexamethylenebis[5-(4-chlorophenyl)biguanide] solutions at 1 mg/L concentration were examined. Ferrous iron (as FeCl₂) was added to selected solutions. Titanium dioxide powder (TiO₂) was added to selected solutions. Solution pH was modified with the addition of dilute solutions of mineral and organic acids.

Sonication Apparatus

Ultrasonic irradiation experiments used a Branson Sonifier Model 450 20 kHz sonication unit with a ¾ in. horn attachment. Batch and flow reactors were used with a thermostatted water jacket at 25 °C

Jet Cavitation Apparatus

The submerged hydrodynamic cavitation unit (DYNAJET®, Dynaflo, Inc.) has been described in detail elsewhere (6, 7, 11, 12).

Analysis:

Test materials were analyzed by an Agilent 5973 GC-MSD and micro ECD using a DB-17 capillary column.

Results and Discussion

We report on the application of hydrodynamic cavitation to biocide contaminated water by the use of submerged cavitating liquid jets and ultrasound to trigger cavitation and induce oxidation in the bulk solution. In the jet application, controlled oxidation experiments were conducted in recirculating flow loops using a variety of configurations and operating conditions including temperature, ambient and pump pressures, pH, and flow rates. Visualization utilizing high speed video (8,000 f/s) and numerical models of cavity bubble dynamics were employed to interpret results and improve performance.

Cavitation bubbles rarely behave spherically. Typically, due to initial or boundary condition asymmetries and to bubble interaction, the bubbles, upon collapse, form high speed reentering jets. Computations show the potential for extremely high pressures generated during the collapse both in the bubbles and in focused areas of the liquid behind the jets. In practice, bubbles often occur in “clouds” in which bubble/bubble interaction and bubble deformation effects occur. In the submerged cavitating jets, elongated, rotating, and ring shaped bubble cavities form, which have been found to also form reentering jets during collapse.

Findings on the desirability of operating at atmospheric ambient pressures and low driving pressures, and of maximizing cavity surface area are discussed. A system can operate using a conventional pump operated at modest pressures. For practical applications, such a process is simpler, more flexible, and easily scaled over a broad range of capacities. The cavitation can be made to be much more intense, aggressive, and to have large cavity surface area and volume within a given liquid volume. In addition, the jet flow induces a large degree of mixing. These results suggest a great potential for the use of cavitation in practical scale waste treatment and remediation systems.

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