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Soil Remediation Using High-Power Ultrasonics

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Abstract: The application of high power ultrasonics to concentrated slurries of soils and sediments is discussed and we show that very high destruction rates can be achieved for many of the more notorious chemical contaminants, including PCBs and organochloride pesticides. Results are presented which suggest that a convenient and cost-effective technology is generally applicable. Experiments have been conducted at laboratory and pilot plant scales showing that reduction of contaminant concentration by 90% or more can be achieved with low energy budgets and without the generation of dangerous breakdown products.

Keywords: Persistent organic pollutants (POPs), soil remediation, high-power ultrasound

INTRODUCTION

Soil Contamination: A Global Problem

Industrialization and technological development in modern times have produced and introduced various forms of organic and non-organic pollutants into the soil environment. Persistent organic pollutants (POPs) are a group of hazardous pollutants which are very difficult to clean from soils because of their tendency to bioaccumulate and persist in the environment. The fact that POPs can travel in air, water currents, and through the food chain, turned this problem into a worldwide threat, making it impossible for any nation to solve this problem by acting alone.

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The Stockholm Convention on Persistent Organic Pollutants has identified 12 of the most persistent and bioaccumulative chemicals, and has targeted them for priority action (1, 2). Over 151 countries have ratified the Stockholm Convention which came into force in May 2004 (3). The list of POP chemicals includes chlorinated and brominated aromatics such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans (PCDDs/PCDFs), polybrominated diphenyl ethers (PBDEs) and various organochlorine pesticides such as DDT, hexachlorobenzene (HCB), and α,β,γ-isomers of hexachlorohexane (HCH) (4, 5). Some POPs have been produced for different industrial applications such as pesticides, PCBs or polychlorinated naphthalenes (PCNs). Others, such as polycyclic aromatic hydrocarbons (PAHs) or PCDDs (6), are by-products of various industrial activities.

The need for an effective process to clean contaminated soils has promoted the development of new remediation technologies which could provide cost-effective treatments that meet the environmental guidelines of the relevant regulatory agencies. Sonochemistry, the chemical application of high power ultrasonics, is now an established discipline. The cavitational collapse of gas bubbles in a liquid medium can produce reactions not normally achievable under normal laboratory or industrial conditions. The aim of this research is to investigate whether high-power ultrasound can achieve a high level of destruction of persistent organic pollutants (POPs) present in soils and sediments.

High Power Ultrasound as a Soil Remediation Technology

Studies of the use of high power ultrasound for processing of minerals (7, 8) suggested that the phenomenon of cavitation, which takes place during the irradiation of liquids or slurries with high power ultrasound, could possibly provide the energy necessary to destroy organic contamination on the surface of soil particles.

Cavitation is a phenomenon which involves the formation, growth, and collapse of micro-bubbles created in a liquid during the rarefaction (or expansion) cycle of the sound wave, where the liquid molecules are pulled apart exceeding their critical molecular distance, producing voids. The "hot-spot" theory which explains the chemical effects of ultrasound due to cavitation, postulates that the bubbles collapse forming localized hot spots which reach temperatures and pressures in the order of 5000 K and 500 atm (9). The speed of the collapse is about 100 m/s and the heating and cooling rates are in the order of 10^{10} K/s (10, 11).

Solid particles in slurry have been shown to act as foci for the nucleation and collapse of bubbles. Theory (12) and experiment (13) have confirmed that the rupture of a bubble on a solid surface generates a high speed jet directed towards the surface (Figs. 1 and 2). As a result, the extreme conditions generated by the non-linear shock wave produced by bubble collapse are localised on the solid surface (10).

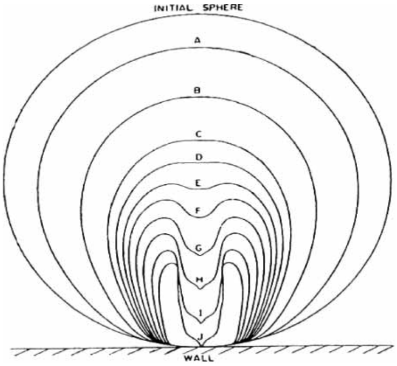


Figure 1. Predicted shapes of a bubble during collapse close to a solid boundary (12).

Since persistent organic pollutants (POPs) are hydrophobic and readily absorbed on the surface of soil particles, the energy released by cavitation in a soil or sediment slurry is selectively directed towards them. At the point of collapse, the temperature is high enough to decompose the organic pollutants. However, the bulk solution temperature remains unaffected as a result of the quick heating and cooling rates. Any decomposition products are immediately quenched, avoiding recombination reactions.

METHODS

This study seeks to evaluate the effectiveness of high power ultrasound as a remediation technique by measuring the reduction in concentration of several organic pollutants such as hexachlorobenzene (HCB), PCB 1254, 1,2,3,4-tetrachloronaphthalene (TCN), total petroleum hydrocarbon (TPH),

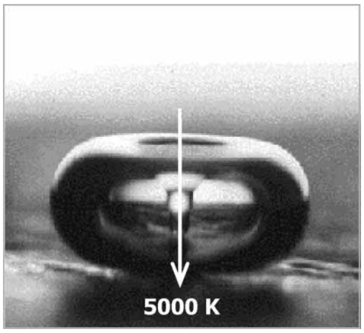


Figure 2. Experimental confirmation of jet formation in bubbles (13).

atrazine, and simazine, from various solid matrices. Three solid matrices were used in the experiments: glass beads which were used as an ideal soil model, washed river sand, and soil from a contaminated site.

Glass beads of mean diameter 90 μm were spiked with PCB 1254 at initial concentrations of 39 and 45 ppm (39 and 45 μg/g) and with HCB at an initial concentration of 96 ppm. River sand, predominantly in the size range of 120 to 150 μm, was spiked with TCN at an initial level of 200 ppm. Soil, predominantly clay, from a contaminated industrial site contained atrazine, simazine and TPH at 14, 37, and 490 ppm respectively. The samples to be treated were prepared in a 30% slurry (by weight) with deionized water. Since all of these pollutants are virtually insoluble in water, the contaminant concentration in the liquid phase at the start of runs was negligible.

Two systems, each of different scale but otherwise similar, were used to treat the contaminated slurry ultrasonically. The first system consisted of a small scale (110 ml), bench-top setup (Fig. 3) which used a Misonix XL-2020 Sonicator (cell disruptor) equipped with a 12.5 mm tip diameter high intensity horn, which delivered approximately 160 W of power, at a frequency of 20 kHz. The second was a larger scale (1500 ml) system (Fig. 4) consisting of a Dr. Hielscher Sonicator equipped with a 38 mm tip diameter high intensity horn, which delivered up to 1700 W of power, at a frequency of 20 kHz. In both cases, the contaminated slurries were pumped through the closed system using a peristaltic pump. The reaction cell was further enclosed by a cooling jacket to prevent excessive temperature increase during sonication.

The zone located below the ultrasonic tip (5 in Fig. 3) is called the reaction zone which is the area where the highest cavitation activity takes place. The flow cell was designed to ensure a uniform slurry flow throughout the whole cell and the passage of all solids through the reaction zone, with the slurry flowing up through the reaction zone towards the horn tip.

The solids were irradiated by power ultrasound for various residence times. At the end of each selected residence time, a sample was collected for chemical analysis. At the end of the ultrasonic treatment, the water present in the slurry was filtered from the solids and also collected for chemical analysis.

Samples were collected in glass tubes lined with a Teflon or polytetrafluoroethene (PTFE) septum and stored at 4°C. The low temperature minimizes the effect of evaporation and chemical decomposition, and the risk of contamination or absorption by contact with plastics are avoided, thus preserving the samples until chemical analysis can be performed.

The chemical analysis of the TCN samples was carried out using an Agilent 6890 Series II Gas Chromatograph coupled to a Series 5970 Mass Selective Detector and a model 7683 Autosampler. The GC/MS is supported by its own system software, the MSD ChemStation, and the NIST (National Institute of Standards and Technology) mass spectral

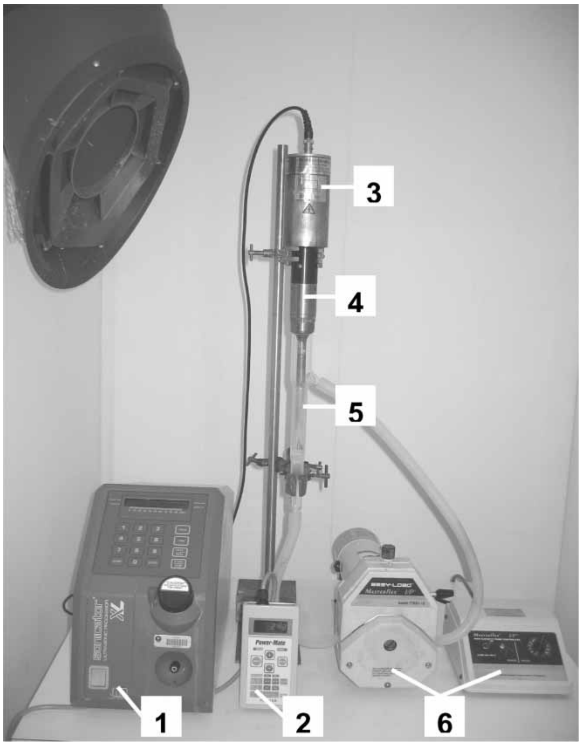


Figure 3. Bench-top experimental setup showing: (1) power generator, (2) power meter, (3) piezoelectric transducer, (4) Ultrasonic horn, (5) flow cell, (6) peristaltic pump and controller.

library. All other GCMS analyses were performed at the Australian Government Analytical Laboratories (now part of the National Measurement Institute) using standard extraction procedures (14).

RESULTS AND DISCUSSION

The GC/MS results for glass beads spiked with PCB 1254 at levels of 45 ppm and 39 ppm (Fig. 5) showed that one minute of sonication achieved 90% destruction of the contaminant, and 99% was reached after 7 minutes. In the case of glass beads spiked with 96 ppm of hexachlorobenzene (Fig. 6), 91% and 97% were destroyed after 1 and 10 minutes respectively. The destruction rates, for both PCB 1254 and HCB, follow a first-order exponential decay which has been represented by the solid lines in Figures 5 and 6. The results for the treatment of sand spiked with TCN at an initial concentration of 200 ppm (Fig. 7) showed that 81% of the TCN concentration was

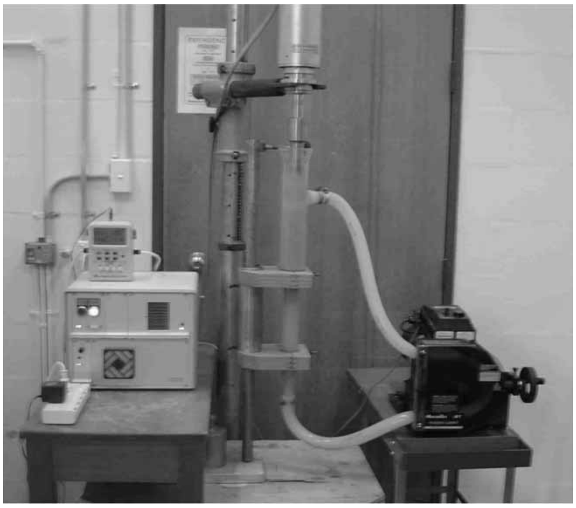


Figure 4. Larger scale experimental setup.

reduced after 1 minute of sonication and that an ultrasonic exposure of 10 minutes destroyed 91% of the pollutant. The treatment of PCB 1254, HCB, and TCN were performed using the bench-top system. The contaminated clay soil was tested in the larger system and TCN tests have been repeated many times in both systems and in a small 4 kW pilot plant achieving similar or better destruction rates. The chemical analysis of the water at the

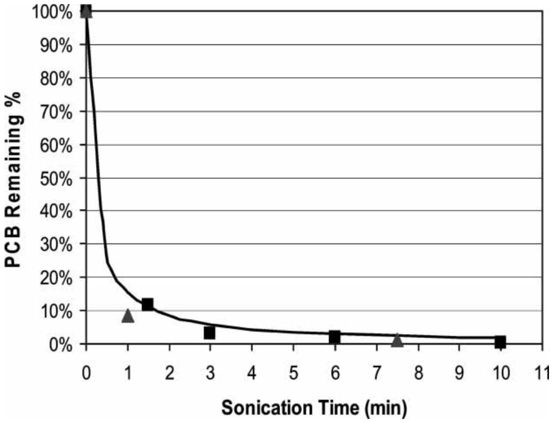


Figure 5. PCB 1254 remaining on glass beads at different sonication times. Initial concentration: 39 ppm ▲ and 45 ppm ■. The solid line is a non-linear first-order fit of the experimental data.

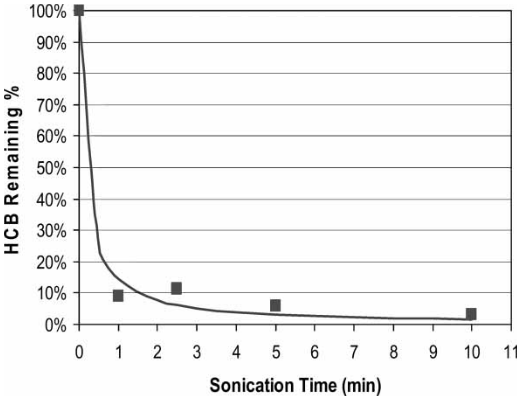


Figure 6. HCB remaining on glass beads at different sonication times. Initial concentration: 96 ppm. The solid line is a non-linear first-order fit of the experimental data.

end of the process showed that contaminant content in the liquid phase was only 5 μg/L. Additionally, there was no evidence of breakdown products in either the liquid or solid phase.

Figure 8 shows the results for a contaminated soil from an industrial site polluted with atrazine, simazine and TPH. This experiment was conducted on the larger scale (1.7 kW) laboratory unit. Destruction rates higher than 94% were achieved after 2 minutes of ultrasonic treatment. In fact, the TPH concentration fell from 490 ppm to less than the detectable limit of 25 ppm after 25 seconds of sonication.

The destruction rates achieved for all the contaminants used in this study are similar, even though these contaminants differ in structure and

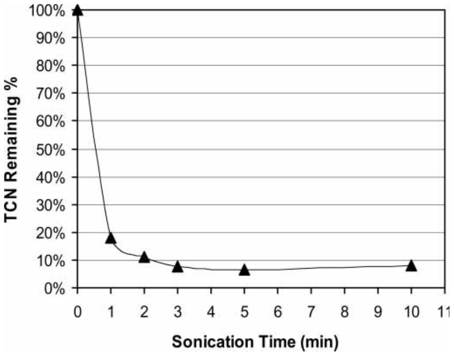


Figure 7. Tetrarchloronaphthalene (TCN) remaining in sand at different sonication times. Initial concentration: 200 ppm.

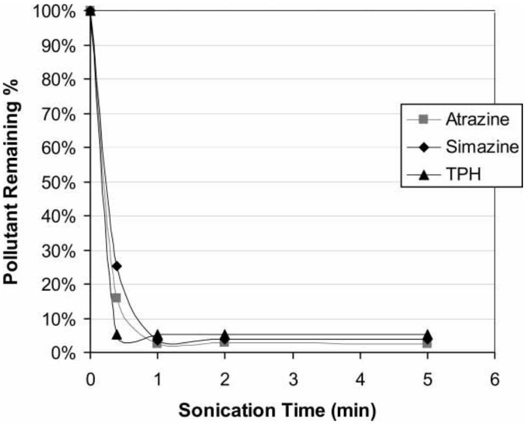


Figure 8. Atrazine, simazine and TPH remaining in sand at different sonication times. Initial concentration: 14 ppm ■, 37 ppm ◆, and 490 ppm ▲.

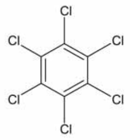
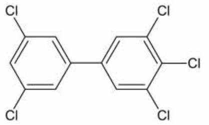
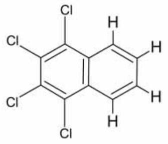
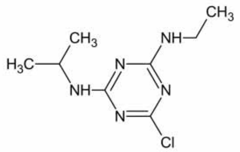
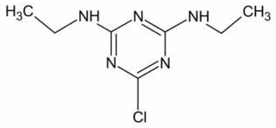
Chemical Name	Chemical Structure
Hexachlorobenzene	
PCB 1254	
1,2,3,4-Tetrachloronaphthalene	
Atrazine	
Simazine	

Figure 9. Chemical structures of the pollutants.

vary in Cl content from 21% for simazine to 75% for hexachlorobenzene (See Fig. 9). This suggests that the destructive effect of cavitation is not selective for the type of pollutant, and that cavitation will decompose any organic pollutant which is absorbed on a solid matrix where a bubble is collapsing.

The encouraging features of these results are (1) the absence of dangerous breakdown products, and (2) the low operating costs. Our findings on the energy efficiency of ultrasonic treatment are in direct opposition to current opinion which is that it is neither economically attractive nor feasible unless used in conjunction with other processes (15, 16). No breakdown products were observed in the liquid or solid phases, even at trace levels. If these rates of reduction of contaminants in these experiments could be maintained on a larger scale, the required energy is approximately 100 kW/hr per tonne of contaminated soil. This is of course a gross extrapolation and we are currently working with TCN-spiked sand in a 1/4 tonne per day pilot plant to better assess the energy demands.

CONCLUSIONS

The study described in this paper demonstrates the potential of high power ultrasound as a method for remediation of POP-contaminated soils and sediments. The achievement of a high level of pollutant reduction in short treatment times, and the absence of dangerous breakdown products are factors that make the use of high power ultrasound a promising alternative for soil remediation. Further studies on a larger scale are under way to optimise the operational conditions and produce the most cost-effective results.

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