"USE OF SONICATION FOR IN-WELL SOFTENING OF SEMIVOLATILE ORGANIC COMPOUNDS"

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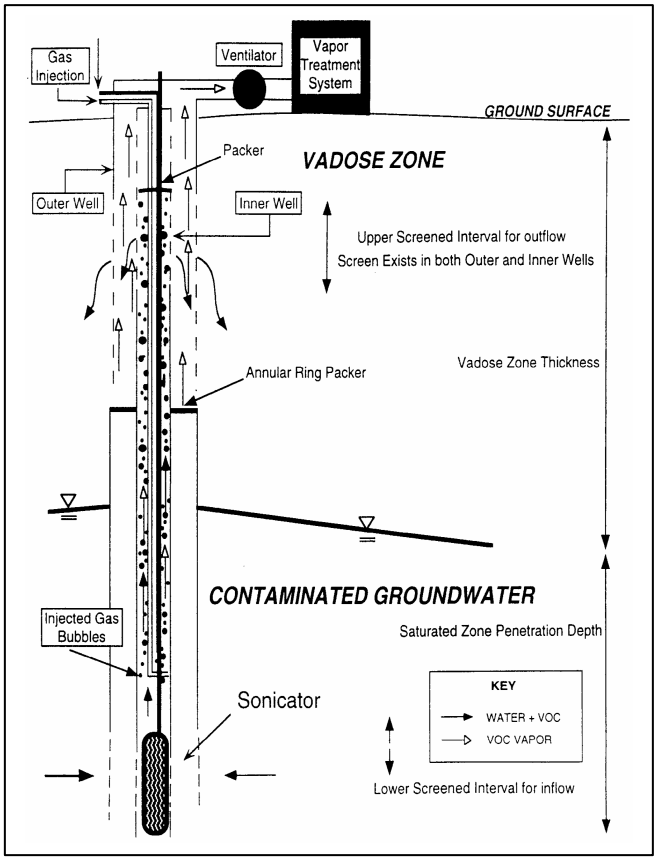
Introduction

Acoustic cavitation (commonly termed sonication) involves the application of sound waves being transmitted through a liquid as a wave of alternating cavitation cycles. Compression cycles exert a positive pressure on the liquid, pushing molecules together, while expansion cycles exert a negative pressure, pulling molecules away from each other. The chemical effects of sonication are a result of acoustic cavitation. During rarefaction, molecules are torn apart forming tiny microbubbles, that grow to a critical size during the alternating cavitation cycles, and then implode releasing a large amount of energy. Temperatures on the order of 5,000°K and pressures up to 500 to 1,000 atmospheres have been observed in microbubble implosions, while the bulk solution stays near ambient. The collapsing bubble interface results in the formation of hydroxyl and hydrogen radicals. These radicals destroy chlorinated organics and petroleum hydrocarbons very effectively.



The performance can be further enhanced through the addition of advanced oxidants (e.g., ozone (O_3), hydrogen peroxide (H_2O_2), etc.), and incorporation of recent advancements in the acoustic cavitation field. The destruction of organic pollutants can occur via several mechanisms. The organic pollutant inside the cavity and in the interfacial region can undergo pyrolysis reactions (or combustion reactions if oxygen is present) during the implosion. Free radicals (e.g., •OH, •H) formed due to thermolysis of water molecules may react with the organic in the interfacial region or in the solution near the interface. Three primary pathways have been identified for compound degradation, including: (1) hydroxyl radical oxidation, (2) direct pyrolytic degradation, and (3) supercritical water reactions. In aqueous solution, water vapor present in the microbubble is homolytically split during bubble collapse to yield •H and •OH radicals, while chemical substrates present either within or near the gas-liquid interface of the collapsing microbubble are

subject to direct attack by •OH. Volatile compounds such as carbon tetrachloride, trichloroethylene, benzene, toluene, ethylbenzene, xylene, and MTBE readily partition into the vapor of the growing cavitation microbubbles and then undergo direct pyrolysis during transient collapse.

Vapor stripping operations have as their goal to transfer the volatile contaminants from the liquid phase (i.e., groundwater) to the vapor phase (i.e., air). The combination of sonication and aeration/ozonation/hydrogen peroxide (shown schematically in the figure above) results in enhanced organic destruction and better liquid/vapor contact (i.e., better mixing) to facilitate the transfer of the degraded or partially degraded products into the gas phase. The addition of ozone (made through electric discharge of oxygen) into the liquid phase coupled with application of sonication considerably enhances the formation of hydroxyl radicals resulting in enhanced destruction of chlorinated organic compounds in solution. Hydroxyl radicals (•OH) are highly reactive non-specific reactants capable of oxidizing a wide variety of contaminants to carbon dioxide, hydrochloric acid (if chlorinated organics are present), and water. After mass transfer from the liquid phase into the gas phase, the water is pumped to a packer in the dual extraction well, resulting in the water (stripped of the volatile organic compounds (VOCs)) being returned into the subsurface, while the VOC-enriched vapor phase is passed through the second well and is sent to an above-ground vapor treatment system (that could involve capture on activated carbon/regeneration using ultrasonics, or thermal oxidation).

Materials and Methods

Sonication/vapor stripping experiments were performed in a reactor used to treat the chlorinated organic contaminants in groundwater employing sonication alone, vapor stripping alone, or combined sonication/vapor stripping. The reactor is a glass vessel with an ultimate capacity of 1.0-L; normally the reactor is operated using a sample volume of ~500-mL. Batch experiments were performed separately on each of the chlorinated organic contaminants (CCl_4, TCE, TCA, and PCE). Initial contaminant concentrations ranged anywhere from ~1 to ~100 mg/L. The sonicator had an ultrasonic frequency of 20 kHz; the applied power intensity was 12.3-, 25.3-, and 35.8 W/cm^2. The batch reactions were operated normally for up to 10 minutes treatment time, with samples withdrawn for GC analysis every 2 minutes. The batch experiments were operated using either sonication alone, vapor stripping alone, or using the combined sonication/vapor stripping technique. Air injection rates used in these experiments were nominally 0- (sonication alone), 500-, 1000-, and 1500-mL/min.

Experiments were also performed in a continuous flow mode. For these experiments, the ultrasonic frequency was 20 kHz, with an applied power intensity of 35.8 W/cm^2. Air injection rates used in these experiments were nominally 0- (sonication alone) and 500-mL/min. The initial concentration of the chlorinated organic contaminant was nominally 50 mg/L. The residence time within the reactor was set at 5, 8, and 10 minutes. The reactor volume was 500-mL.

Chemical analyses were performed using a Hewlett Packard 7694 Automatic Headspace Sampler for use with the Hewlett Packard 5890 Gas Chromatograph. Headspace analysis is well-suited for analysis of volatile and semivolatile organic compounds in water, and avoids the column degradation caused by liquid injection of water. The headspace sampling method includes ten minutes equilibration of samples at 70°C with shaking, programmed vial pressurization, venting, sample loop fill (1 mL loop volume), and 0.30 minute injection time. Equilibration time was selected by measuring area response for times ranging from 1 to 60 minutes. A 30 meter megabore fused capillary DB-624 column was selected based on its sensitivity and selectivity in analysis of chlorinated organic compounds. The HP 5890 chromatograph is equipped with both flame ionization and electron capture detectors. In the analytical range for this project (0.1 to 100 ppm), flame ionization provided adequate resolution and reproducible detection. The electron capture detector was found to be too sensitive for detection of major components, but is useful in examining sonicated samples for minor breakdown products. The GC temperature program was set for 1 minute at 90°C, ramping 10°/minute to 140°, then 25°/minute to 200°, and held for 2 minutes at 200°C. Standards

were initially prepared in volumetric flasks. Due to analyte volatility, this was changed to injection by syringe through the vial septum of the chlorinated compounds into measured water mass. Planned sample size was 5 mL in 10 mL vials, however this was reduced to 1 mL in 10 mL vials to avoid overloading the column with analyte. Response of carbon tetrachloride standards held in sealed vials over a 0.25 to 48 hour time range was evaluated to determine how long samples could be stored prior to GC analysis. It was found that vials analyzed within three hours after sampling gave the most reproducible response. Vials showed a drop in response to approximately 80% at 15 hours, and to 20-40% at 25 hours. Since the hydrolysis rate for CCl_4 in water is very low, there appears to be loss through the vial seal or septum. Therefore all subsequent samples and standards were analyzed as closely as possible to the actual sampling time, and all within three hours. Five analyte standards were prepared each day for the initial calibration curve, and check standards were performed late in the day, or when any questionable sample result was obtained.

Results and Discussion

Experiments were performed involving the use of sonication alone, vapor stripping alone, and the combined in-well sonication/in-well vapor stripping system to treat chlorinated organic contaminants in groundwater [e.g., carbon tetrachloride (CCl_4), trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), and 1,1,2,2-tetrachloroethylene (PCE)]. These contaminants were all spiked to desired initial concentrations in artificial groundwater using saturated contaminant solutions; initial contaminant concentrations in the groundwater typically ranged from ~1 to ~100 mg/L. Pretreating groundwaters by use of sonication techniques forms volatile organic compounds (VOCs) that can be more efficiently removed by in-well vapor stripping and *in-situ* biodegradation. Figure 1 shows the results from batch treatment of groundwater containing ~50 mg/L of the chlorinated organic compounds, using both sonication alone and sonication+vapor stripping. These results show that while sonication is capable of removing ~30% of the TCA after 10 minutes reaction time, the combined sonication/vapor stripping system can remove nearly 97% after 4 minutes treatment time, and nearly 100% removal after 10 minutes. This figure indicates that the rate constants for the combined system are nearly an order of magnitude higher than those for sonication alone (and for vapor stripping alone).

Based on these promising results, continuous-flow tests were conducted using a continuous flow, stirred tank reactor in which sonication and vapor stripping were performed simultaneously to treat the contaminated artificial groundwater. The residence time in the continuous flow system ranged from 5 to 10 minutes. Figure 2 shows the results from bench-scale sonication experiments (20 kHz, with an applied power intensity of 35.8-W/cm^2) performed without and with air stripping. Using sonication alone, removal of TCA ranged from 14% to 36%, while the combined system (using 500 mL/min air flow rate in combination with sonication) resulted in removals of TCA ranging from 72% to 97%, depending on the residence time used, once again showing a considerable enhancement in the removal of TCA from solution as a consequence of combining the sonication and vapor stripping technologies. These pilot tests showed that the system was very stable, resulting in steady-state operating conditions.

Figure 2 shows the residual TCA concentration following application of sonication alone and sonication+vapor stripping for continuous flow conditions; for reactor residence times ranging from 5 to 10 minutes, removals of CCl_4 and TCA were 74% to 88% and 72% to 97%, respectively, for a one-pass system. Sonication alone or vapor stripping alone results in removals ranging from ~20% to ~50%; however, combining sonication with vapor stripping enhances removal of CCl_4, TCE, TCA, and PCE as compared to removal by either system alone (sonication or vapor stripping) by nearly an order of magnitude, and results in synergistic behavior enhancing removal efficiency. The combination of sonication with vapor stripping results in much better mixing, creation of much finer bubbles, thereby enhancing mass transfer from the liquid phase to gaseous phase, and enhancing the destruction of the chlorinated organic compounds during the microbubble implosions.

The power requirements for a sonolytic system and the combined sonication/vapor stripping system were determined for an ultrasonic power intensity of 35.8 W/cm^2 treating water containing 50 mg/L of CCl_4 or TCE. For batch treatment, the electrical energy per unit mass is calculated using the equation listed below:

$$EE/M = (10^6 xPxt)/[60xVx (C_i-C_f)]$$

where: EE/M = electrical energy per unit mass of contaminant removed (kWh/kg)
Sonication Power Capacity = 600 W
Power Intensity = 35.8 W/cm^2 (or 17%)
P = 600 W x 0.17 = 102 W = 0.103 kW
t = Treatment time (min) = 10 min.
V = Total volume of the solution (L) = 0.5 L
C_i = Initial contaminant concentration (ppm) = 50 mg/L
C_f = Final contaminant concentration (ppm)

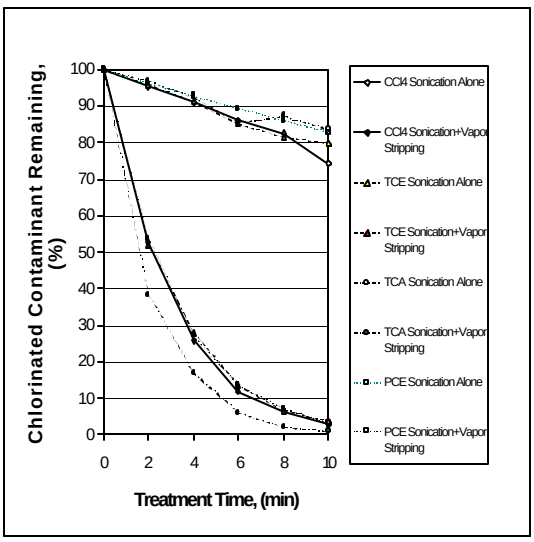


Fig. 1. Residual chlorinated organic compound remaining after batch sonication and sonication+vapor stripping treatment.

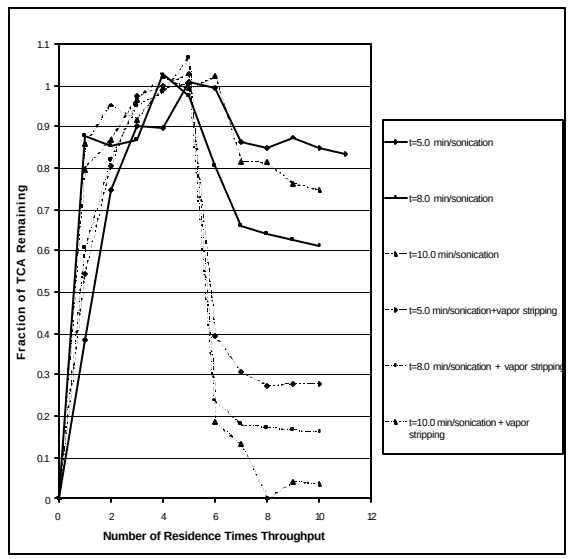


Fig. 2. Residual chlorinated organic compound remaining after continuous sonication and sonication+vapor stripping treatment.

C_f can be calculated using the first-order equations from the batch sonication, vapor stripping, and the combined sonication/vapor stripping experiments. Results from these power requirement calculations for the above set of conditions are shown in Figure 3. These results show that the combined in-well sonication/in-well vapor stripping system is considerably less energy intensive than using sonication alone; the power requirement for a given removal efficiency of CCl_4 or TCE is nearly an order of magnitude lower for the combined in-well sonication/in-well vapor stripping system than by sonication alone. Similar power requirement calculations and data have been collected for the petroleum hydrocarbon system.

In summary, the innovative technology couples in-well sonication, in-well vapor stripping, and *in-situ* biodegradation into an integrated process. By partially destroying the SVOCs (e.g., opening up the benzene-ring structures), the ability to remove the resultant VOCs and biotreatment of the resultant organics is enhanced (over the case of biotreatment alone). Advantages of this technique include:

- Remediation is performed *in-situ* (i.e., does not require handling or disposing of water at the ground surface);
- Treatment systems complement each other and their combination has the potential to drastically reduce or remove SVOCs and VOCs;
- System has the potential to add other innovative components (such as *in-situ* chemical treatments or surfactants);
- Ability to convert hard-to-degrade organics such as chlorinated organics and heavy organics (e.g., polyaromatic hydrocarbons) into more volatile organic compounds;
- Ability to destroy chlorinated organic compounds;
- Ability to remove residual VOCs and softened SVOCs through the combined action of in-well vapor stripping and biodegradation;
- Improved *in-situ* biotreatment of contaminated soils and groundwater; and
- Cost-effective and improved efficiency thereby shortening the time required to clean-up a contaminated site.

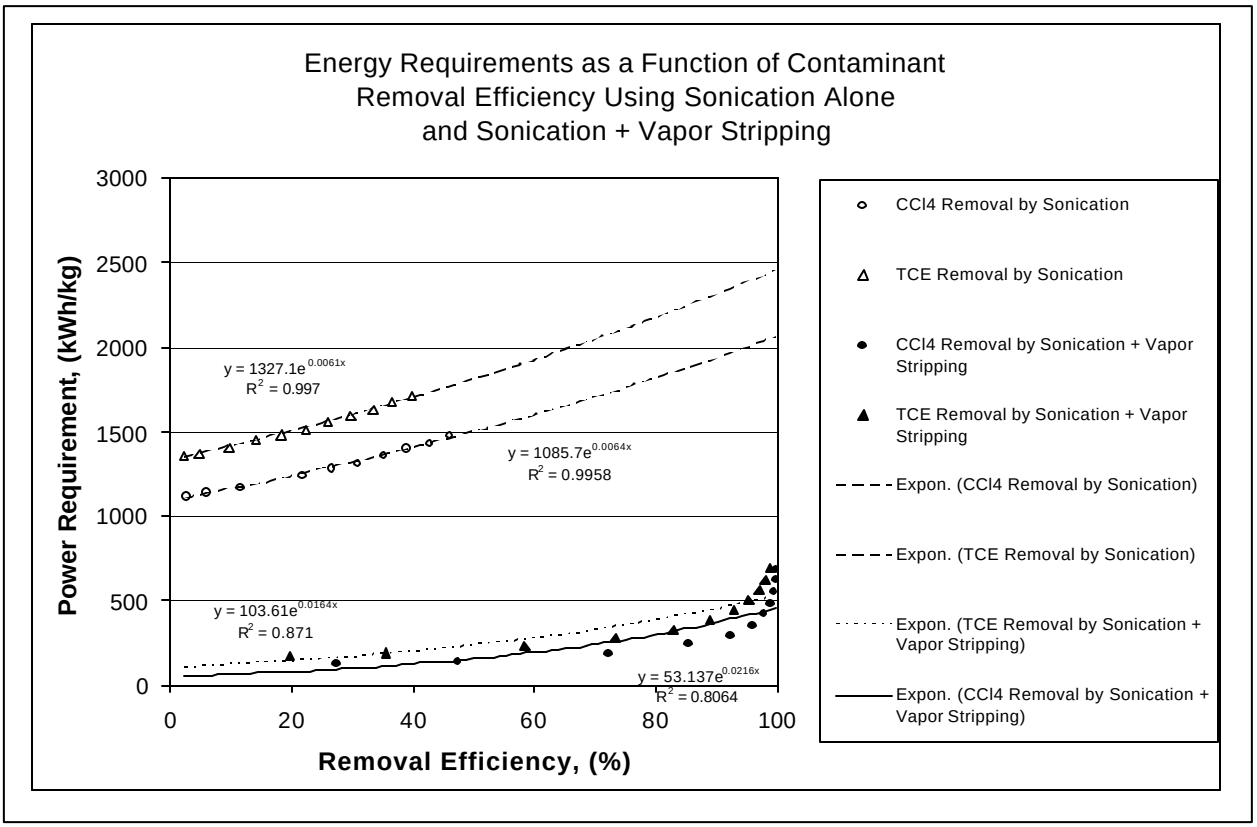


Figure 3. Energy requirements as a function of contaminant removal efficiency using sonication alone and sonication+vapor stripping.

Acknowledgments

This research project was funded by DOE's Environmental Management Science Program (EMSP). This project is a collaborative effort involving Argonne National Laboratory's Energy Systems Division and Environmental Research Division, and the California Institute of Technology and Stanford University.