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Aqueous Phase Disinfection with Power Ultrasound: Process Kinetics and Effect of Solid Catalysts

NILSUN H. INCE* AND RANA BELEN
Institute of Environmental Sciences, Boğaziçi University, 80815 Bebek-Istanbul, Turkey

The effectiveness of power ultrasound as a viable alternative for destroying pathogenic organisms in homogeneous and heterogeneous mixtures of aqueous solutions was investigated. The method involved monitoring of total coliform bacteria during sonication of *E. coli* suspensions in the absence and presence of equivalent mass concentrations of ceramic, metallic zinc, and activated carbon. It was found that disinfection by ultrasound is accelerated with solids in the order activated carbon > ceramic > metallic zinc. Process kinetics for each test system were assessed by nonlinear regression analysis of bacterial density vs time data, and the predicted model was found to resemble a well-known expression describing chlorination kinetics. The model denoted that in the presence of activated carbon the process rate was pseudo first order, and the required contact time to accomplish 50% kill was 2.8, 2.4, and 4 times shorter than it was in the zinc-catalyzed, ceramic-catalyzed, and noncatalyzed systems, respectively. It was further found that catalytic effects faded away with increased sonication time and/or reduced number of bacteria, denoting(i) decreased probability of bacterial contact with the solid−liquid interface; (ii) erosion of solid surfaces by vibrational effects; and (iii) reduced cavity formation due to degassing effects of ultrasound.

Introduction

Disinfection has become a challenging aspect of water treatment because of rapid elevation of health standards and the growing concern for pollution-free water resources. The most commonly practiced methods are those that involve chemical (e.g., chlorination and ozonation) and physical (e.g., treatment with heat and/or ultraviolet light at 254 nm) processes. Chlorination, as the most cost-effective of all, has been noted in recent years for its adverse health effects originated by residual chlorine, which reacts with natural organic matter to form carcinogenic byproducts. Ozonation has lately emerged as a viable alternative by virtue of its nonresidual effect, but more research is required to lower its operational costs and to protect the water from re-infection in the distribution system.

Decontamination of water bodies using ultrasonic techniques is a growing field, and the well-known effectiveness of power ultrasound (20−100 kHz) for its surface cleaning action has been successfully utilized in some patented systems applied in institutional and medical facilities for disinfecting nondisposable implements and accessories. Bacterial removal by these systems involves their dislocation from adhered surfaces and crevices, which are rather difficult to reach by conventional cleaning methods (*1*). Moreover, recent studies with aqueous systems have shown that power ultrasound is capable of inactivating bacteria, viruses, and fungi in water, but long contact or high intensities are required for accomplishing high rates of kill (*2, 3*). It was further shown that bacterial survival under ultrasonic effects exhibits an exponential behavior, and that although the shear forces set up by cavitation bubbles are insufficient to rupture the cells (unless by prolonged contact), they disengage the more delicate attachment sites of the DNA to the membrane (*4*). The results of a novel study on the effects of discrete frequencies and dissolved gases have shown that germicidal effectiveness of ultrasound depends strongly on the frequency (highest at 205 kHz), but moderately on the power intensity and gas properties, being highest in argon−oxygen mixtures (*5*).

Most of the above effects are mechanical in origin, arising from cavitation events, which consist successively of the formation, growth, and collapse of gas-filled microbubbles, during which temperatures of 5000 °C and pressures of 500−2000 atm are released (*6, 7*). At these extreme conditions, gases and vapors of the surrounding liquid (entrapped in the bubbles) undergo pyrolytic destruction to dissociate into a variety of radical species (*8, 9*). Depending on the vibrational frequency (which dictates cavity lifetime and collapse duration), some of these radicals may migrate to the solution bulk to attack the cellular membrane for biocidal effects, while some may recombine to form molecular oxidants to act as secondary biocides. The fragmentation of water molecules during the collapse of cavity bubbles results in hydroxyl radicals, which upon recombination are converted to hydrogen peroxide. Hence, this and the uncombined radicals are believed to act as chemical boicides in infected waters, and power ultrasound is capable of enhancing their effects by breaking up biological flocs and disrupting cell walls, leading to increased bacterial susceptibility and easier penetration of the biocide into the organism (*10*).

Because long contact and large power are required to achieve high rates of disinfection by ultrasound, current research on ultrasonic means of bacterial inactivation is focused on combining the system with chemical processes to enhance the germicidal action of biocides and to reduce chemical requirements. It was shown that the ozone requirements for constant kill rates of *E. coli* were remarkably lowered by the use of power ultrasound in conjunction with ozonation, and the effect was attributed to increased ozone diffusion into the microbubbles to create a high gas−liquid surface area (*11, 12*). Recently, it was found that the degree of *E. coli* destruction is doubled when chlorine treatment is conjugated with ultrasonic irradiation at 20 kHz (*3*). Moreover, some researchers have reported that sonolysis of UV-irradiated TiO_2 suspensions in water with a 20 kHz unit enhanced the inactivation of *E. coli* by a synergy in hydroxyl radical formation (*13*).

The efficiency of ultrasonic systems in aqueous solutions can be improved by the addition of impurities such as soluble gases and/or solid particles to reduce the cavitational threshold (*14*). The resulting effect is the formation of excess cavitational nuclei for a larger number and variety of collapse events. In a biphasic solid−liquid medium irradiated by power ultrasound, major mechanical effects are reduction of particle size leading to powder dispersion and increased surface area; and the formation of liquid jets at solid surfaces

* Corresponding author fax: +90 212 257 5033; e-mail: ince@boun.edu.tr.

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by the unsymmetrical inrush of the fluid to the voids (*3, 10*). These jets not only provide surface cleaning, but also induce pitting and surface activation effects, and increase the rate of phase mixing and mass transfer (*14, 15*).

The study described herein was aimed to investigate and compare the effectiveness of power ultrasound in solute−liquid homogeneous and solid−solute−liquid heterogeneous systems for inactivating bacterial survival. The method involved monitoring of total coliform bacteria during sonication of aqueous solutions of *E. coli* in the absence and presence of ceramic, metallic zinc, and activated carbon (AC) granules, respectively. The process kinetics and catalytic effects of the test solids were established by nonlinear regression analysis of residual coliform density with time.

Experimental Section

Setup. The system consisted of a 20 kHz Bandelin Sonopuls HD2200 transducer, a 180 W horn-type sonicator, and an 80-mL glass cell equipped with a water cooling jacket to maintain a constant liquid temperature. The horn was submerged 1.5 cm into the test solution, where the power intensity was 0.674 Wml^{-1} as determined by calorimetry (*16*).

Preparation of the Stock Culture. A pure culture of *E. coli* was grown in Luria Bertani (LB) medium, prepared by mixing 1 g of Tryptone (DIFCO), 0.5 g of yeast extract (DIFCO), and 1 g of NaCl (Merck) in 100 mL of ultrapure deionized water; followed by sterilization in an autoclave for 1 h (*17*). A clean and healthy colony of *E. coli* was selected from the culture and placed in the growth medium in a closed container for 24 h to allow incubation at 37 °C in a shaking bath. The bacterial concentration in the medium at the end of the incubation period was approximately 10^{10} mL^{-1} in accordance with the membrane filter technique of coliform count, based on the formation of colonies in standardized Endo-Broth growth medium (*18*). The test solutions were prepared by serial dilutions of this stock using ultrapure deionized water and a phosphate buffer to prevent cell damage by osmotic pressure.

All reagents used during cultivation and analysis of bacterial count were of analytical grade, and materials such as Petri dishes, Petri pads, and filter papers were of Millipore quality.

Sonication and Control Experiments. Test solutions of *E. coli* after analysis of initial coliform density were irradiated for 20 min at constant temperature in the absence and presence of ceramic granules of irregular size (prepared in the laboratory), metallic zinc particles (0.6 × 0.25 mm) (Hach), and granular activated carbon (0.84 × 0.25 mm) (Aquatech), respectively. In heterogeneous samples, the mass concentration of the solids was 0.12 g L^{-1} in each run, irrespective of the solid type. Samples were withdrawn within short intervals in each set to monitor the change in coliform density with time. Each set was run three times to check repeatability and to report the results as arithmetic means of three independent measurements. Control experiments with each solid were run for 20 min in the absence of ultrasonic irradiation to detect if any reduction in bacterial density occurred by adsorption and/or other physicochemical processes.

Results and Discussion

Individual Effects of Ultrasound and the Test Solids. Comparative patterns of *E. coli* survival during 20 min contact with power ultrasound and the test solids (controls) separately are presented in Figure 1. (The data points represent arithmetic means of three measurements from three independent runs of the same test with equal sampling intervals.) It was found that the concentration of coliform bacteria in all systems decreased with time, but ultimate reduction was

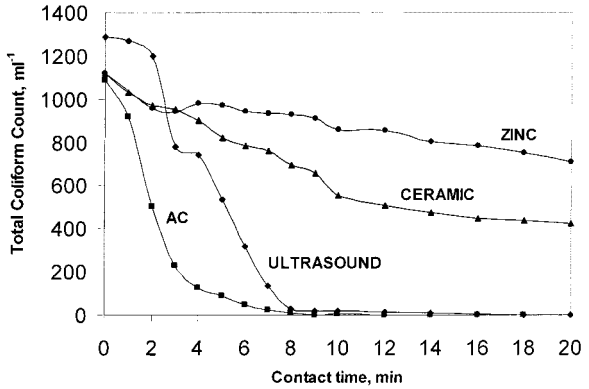

FIGURE 1. Individual effects of power ultrasound and the control solids on the survival pattern of *E. coli* during 20-min contact with each.

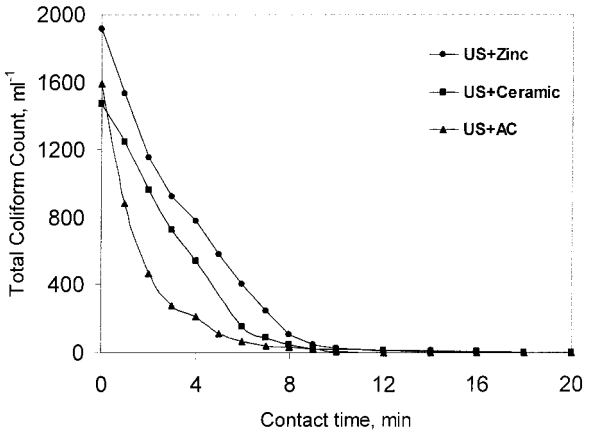

FIGURE 2. The relative profiles of *E. coli* survival upon the joint effects of power ultrasound and the test solids during 20-min contact.

achieved only with activated carbon and ultrasonic irradiation. The mechanism of removal in the control schemes (without ultrasound) involves the diffusion of bacterial colonies in the solid−liquid interface for sorption and/or adsorption on the solid surfaces. The strikingly larger efficiency of removal with AC than with the other two solids is due to the "activated" surface of the former to favor adsorption processes, while the similar efficiency achieved with power ultrasound is a consequence of the mechanical effects brought about by cavitation phenomena.

Combined Effects. Comparative rates of inactivation in the three heterogeneous systems upon combined effects of ultrasound and solid impurities are presented in Figure 2. It was found that all three solids induced catalytic effects in the ultrasonic inactivation of bacteria, the effects increasing in the order AC > ceramic > zinc. The acceleration or catalysis is due to the chain of events between increased cavitational nuclei and enhanced mechanical effects of ultrasound for attritioning, milling, and dispensing solid particles, and activating their surfaces. The observed order on the other hand, is a consequence of the differences in surface and crystalline properties of the solids. Each solid exhibited a different degree of brittleness in the order AC > ceramic > zinc, reproducing the catalytic order shown in Figure 2. As brittleness is an indicator of the attritional capacity, diminution of AC particles by mechanical effects of ultrasound was largest, leading to the largest number of cavity nuclei, and largest effects of cavitational collapse. In fact, within the first minute of irradiation, activated carbon granules were completely converted into powders, by which surface/volume ratios are effectively enlarged. The disintegration of ceramic granules took a longer time, and powders appeared with

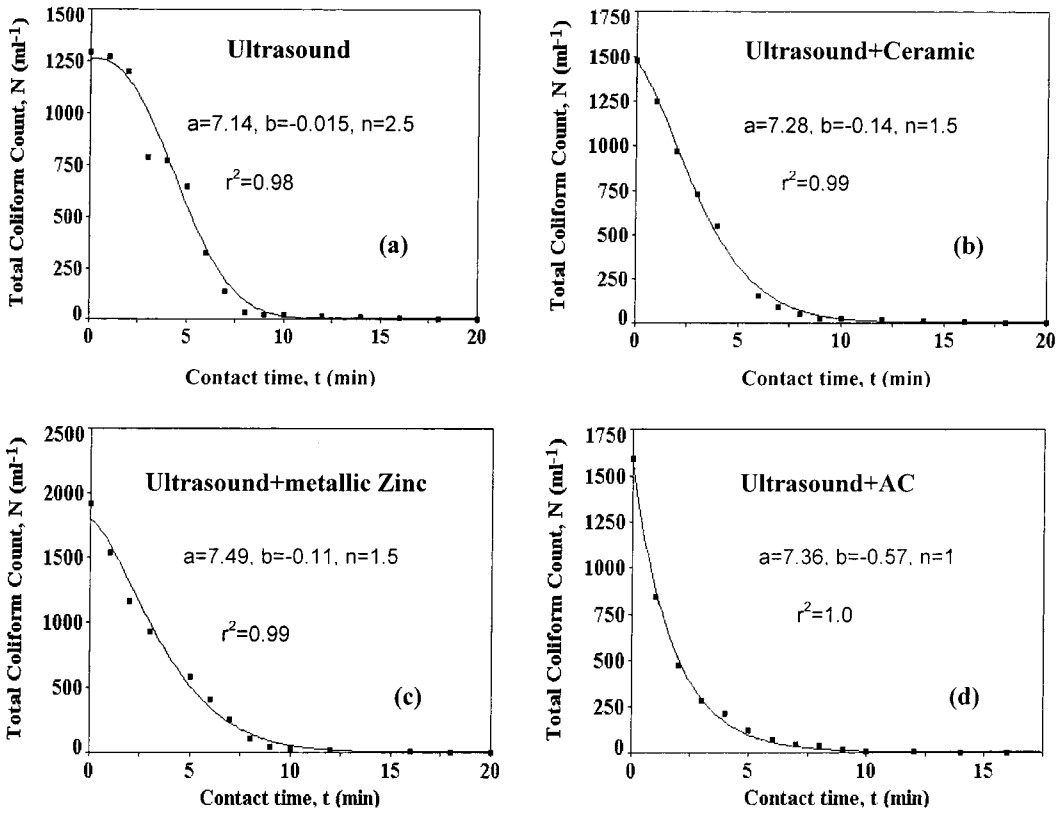

FIGURE 3. Comparative kinetics of bacterial destruction with (a) ultrasound, (b) ultrasound + ceramic, (c) ultrasound + zinc, and (d) ultrasound + activated carbon. Solid lines represent fitted curves to the model equation $\ln(N) = a + bt^n$; where t is the contact time; and a, b, and n are estimated values of model parameters.

increased contact, but they were not as fine as those of activated carbon. Particles of metallic zinc were the least brittle, and though dispensed into smaller size, they did not turn into powder form within the specified test period.

The fast rate of bacterial reduction in the presence of AC is also due to its specially manufactured surface properties, which are further activated by power ultrasound to increase its adsorptive capacity. Thus, in the presence of solids, particularly that of AC, bacterial inactivation was thought to have proceeded via two simultaneous pathways: (i) destruction by enhanced mechanical effects of ultrasound; and (ii) inactivation by adsorption processes.

To investigate the contribution of adsorptive removal on the overall reduction of *E. coli*, filtered suspensions of spent AC were washed and dried, and incubated in the nutrient agar for 24 h. No bacterial growth was detected on the agar at the end of the incubation period, signifying that adsorption on carbon surface was not a significant removal pathway for bacteria when they are simultaneously exposed to ultrasonic irradiation. The test was repeated with the spent AC granules in one of the control experiments during which the ultrasonic power was off. Incubation resulted in 70% reactivation, showing that adsorption was the principal removal pathway in the absence of ultrasound. Hence, we concluded that in a combined medium of activated carbon and ultrasonic vibrations, surfaces of AC act mainly as sites for bubble formation, and bacterial cells are inactivated directly via cavitational effects. Even if some of the cells or colonies are attached on the solid−liquid interface to undergo adsorption, the lack of bacterial growth in suspensions of the spent powders revealed that they are readily detached and destroyed by simultaneous effects of cavitation at the interfacial area or at solid surfaces.

Process Analysis. The bacterial survival-time data generated with the four test conditions using ultrasound were analyzed by nonlinear regression techniques to establish the representative process kinetics. It was found that the concentration profile in both homogeneous and heterogeneous solutions is described by the following equation:

$$\ln N = a + bt^n \tag{1}$$

where N is the total coliform number in unit volume, t is the contact time (min), and a, b, and n are the model parameters. The predicted model is indeed the integrated form of a rate expression proposed for chlorination kinetics (*19*):

$$\frac{dN}{dt} = kNt^m \tag{2}$$

where: dN/dt is the time rate of change in bacterial number per unit volume, k is the observed rate coefficient in $[\text{time}]^{-(m+1)}$, and m is an empirical constant. The integration of eq 2 between the limits N_0 at $t = 0$ and N at t yields

$$\ln N = N_0 + \frac{k}{m+1}t^{m+1} \tag{3}$$

The predicted model in eq 1 and the integrated expression in eq 3 are identical, so that the parameters a, b, and n of the former are exchangeable with the constants of the latter, i.e., $\ln(N_0)$, $k/(m+1)$, and $m+1$, respectively. The similarity of the predicted model and that suggested for chlorination kinetics is of significance, for it suggests a similarity in the destruction mechanisms as well. The implication is that the contribution of secondary biocides (e.g. H_2O_2 and OH radicals) should be accounted for in the overall process analysis.

The results of regression analysis and curve fitting are presented in Figure 3 in a panel chart. The model parameters b and n corresponding to each curve were substituted into

TABLE 1. Model Prediction of Initial Test Conditions and Coefficients of Process Kinetics

test condition	prediction of N_0[a] $\{\ln(N_0) = a\}$	kinetic coefficients	
		k	m
ultrasound: $N_0 = 1290$ mL^{-1}	1286.9 ($\pm$25.7) ml^{-1}	-0.035 min$^{-5/2}$	3/2
ultrasound/ceramic: $N_0 = 1475$ mL^{-1}	1450.1 ($\pm$25.9) ml^{-1}	-0.203 min$^{-3/2}$	1/2
ultrasound/zinc: $N_0 = 1915$ mL^{-1}	1790.1 ($\pm$69.7) ml^{-1}	-0.165 min$^{-3/2}$	1/2
ultrasound/AC: $N_0 = 1590$ mL^{-1}	1571.8 ($\pm$40.0) ml^{-1}	-0.570 min^{-1}	0

[a] Numbers in parentheses are 95% confidence intervals.

TABLE 2. Comparative Process Performance for Constant Ratios of Bacterial Kill

process	kill time, min			
	25%	50%	95%	99.9%
ultrasound	3.35	4.76	10.16	11.95
ultrasound + zinc	1.90	3.41	12.06	15.80
ultasound + ceramic	1.62	2.90	12.26	13.45
ultrasound + AC	0.50	1.21	8.08	12.12

$k = b(m + 1)$ and $m = n$-1, respectively, to evaluate the kinetic coefficients, listed in Table 1, where the input of *E. coli* is presented as part of the test condition to allow comparison with the predicted value associated with the model parameter a. The calculations show that solids reduce the value of the overall reaction order, represented by the coefficient m, and the process is described by a pseudo-first-order kinetic model in the presence of activated carbon. The similarity of ceramic- and zinc-catalyzed kinetics is in agreement with the survival profiles presented in Figure 2. The slightly larger rate coefficient with ceramic is due to its relatively higher particle diminution capacity, as discussed in the previous section. Because the reaction orders and the units of k were different in the other three cases, comparative evaluation of all process performance was made in accordance with the time requirements for 25, 50, 95, and 99.9% kill rates, as presented in Table 2.

The results show that the effect of solid catalysts is more pronounced at high concentrations of bacteria, as obvious from the relative time requirements for 25% kill ratios. With prolonged sonication and lower bacterial concentrations, catalytic effects become less prominent, and process efficiencies approach that of individually applied ultrasonic irradiation. The declination of solid effects with time may be attributed to a variety of reasons. At high concentrations during early exposure, the probability of bacterial contact with the solid−liquid interface (where cavity formation is largest) is also high, but the chances get lower as the survival ratio is reduced. At appreciably low concentrations, therefore, the rate of kill is limited by the number of cavity bubbles in the bulk solution — a condition which is typical of non-catalyzed systems. In addition, catalytic effects may fade away by vibrational erosion of solid surfaces, the extent of which is related to the structure and surface properties of solid particles. Finally, it should be kept in mind that the rate of degassing in heterogeneous solutions is faster han that in homogeneous solutions because of a larger number of cavitation events, which rapidly reduce the availability of dissolved gases during the formation stage.

Since 100% bacterial removal by any system is technically unfeasible, and declination of solid effects by ultrasound may be minimized (by proper selection of particle size and crystalline properties, and effective control of dissolved gases), we believe that ultrasonic technologies with heterogeneous catalysis will emerge as promising alternatives for disinfecting aqueous systems. Consequently, our current study is focused specifically on physical/chemical properties of solid surfaces, significance of particle size and density, effect of gas addition, and optimization of the process for large-scale applications.

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