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# Investigations on semiconductor sonocatalysis for the removal of pathological micro-organisms in water

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ABSTRACT

Contamination of drinking water by bacterial pollutants is a major environmental problem. In the current study, the possibility of using zinc oxide-mediated sonocatalysis, as a potential advanced oxidation process for the removal of a major pollutant, i.e. *Escherichia coli*, is investigated. Critical parameters for optimum efficiency are identified. The organism deactivation is fully irreversible in the case of ZnO-mediated sonocatalysis. Scanning electron microscopy images show that morphological changes and cell-wall disruption of organisms are more in sonocatalysis compared to sonication alone. The deactivation is practically unaffected by initial pH in the range 5–9. Reactive oxygen species including *in situ*-formed free radicals play significant role in the deactivation. Sonoluminescence-induced photocatalysis is a major contributor in the disinfection process. A probable mechanism involving physical effects and semiconductor activation by ultrasound followed by the events leading to the deactivation of the bacteria is proposed.

*Keywords:* Zinc oxide; Sonocatalysis; Micro-organisms; Disinfection; Water; Hydrogen peroxide

## 1. Introduction

Semiconductor-mediated photocatalysis has been investigated extensively as a viable technique for the removal of organic and inorganic pollutants from water [1–4]. Photocatalytic deactivation of bacterial pollutants [5–7] from aqueous streams has also been reported extensively in recent years. Another advanced oxidation process under investigation in this context is sonolysis as well as sonocatalysis in which ultrasound (US) is used as the energy source in place of conventional heat or light [7–10]. Major observations in this respect up to 2003 were summarized by Piyasena [10]. US is able to inactivate bacteria and de-agglomerate bacterial clusters or flocs through a number of physical, mechanical and chemical effects arising from cavitation [11–13]. The mechanism underlying ultrasonic inactivation of bacteria involves both chemical and physical effects [12]. The chemical effects in liquid include cavitation which consists of nucleation, growth, and collapse of bubbles which result in localized supercritical condition such as high temperature, pressure, electrical discharges, and plasma effects. The gaseous contents of a collapsing cavity reach temperatures of ~5,500˚C and that of the liquid's immediately surrounding the cavity reach up to 2,100˚C. The localized pressure is estimated to be around 500 atmospheres resulting in the formation of transient supercritical water. The cavities thus serve the purpose of high-energy micro reactors. The

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consequence of these extreme conditions is the cleavage of dissolved oxygen and water molecules resulting in reactive oxygen species (ROS) such as $H^{\bullet}$, $OH^{\bullet}$, $HO_2^{\bullet}$ and $O^{\bullet}$ radicals and $H_2O_2$. These ROS can disrupt or damage various cellular functions or structures of micro-organisms and play a significant role in the cell deactivation process through DNA damage [7].

Mediation by semiconductor oxides has been proven to be effective in enhancing the rate of chemical and bacterial decontamination of water under sono and photochemical conditions [9,14–16]. However, most of these studies used titanium dioxide ($TiO_2$) as the catalyst. Earlier studies from our laboratories revealed that zinc oxide (ZnO) is an efficient sono and photocatalyst for the removal of chemical and bacterial pollutants from water [9,16]. In this paper, the application of ZnO as a sonocatalyst for the removal of a common bacterial pollutant, i.e. *Escherichia coli* (*E. coli*), a Gram negative organism, from water is investigated with special reference to the influence of various reaction parameters on the sonobactericidal effect.

## 2. Experimental and methods

*E. coli* is one of the main species of bacteria that live in the lower intestines of warm-blooded animals (including birds and mammals) and are necessary for the proper digestion of food. It is a subgroup of fecal coliform bacteria that belongs to the family of *Enterobacteriaceae* and is non-spore forming, Gram negative, straight rod-shaped, and facultative anaerobes arranged singly or in pairs. There are numerous different strains within the species, some of which can be harmful. Generally, release of these naturally occurring organisms into the environment is not a cause for alarm. However other disease-causing bacteria, which can include some pathogenic strains of *E. coli* or viruses, may also be present in these wastes and can cause clinical syndromes like diarrhea, urinary tract infection, pyrogenic infection and septicemia.

ZnO (99.5%) from Merck India Limited used in the studies was characterized by surface area, pore size distribution, particle size analysis, adsorption and scanning electron microscopy (SEM). The particles are approximately spherical in shape and porous as seen in the SEM image in Fig. 1.

The average size of the particles as computed from the image is $10 \times 10^{-2}$ μm. The Brunauer–Emmett–Teller surface area was ~12 $m^2/g$. All reagents used were AnalaR Grade or equivalent. The cell-culture medium and the irradiating solutions were prepared by standard techniques. For stock culture of *E. coli* the nutrient broth contained 5 g/L yeast extract, 5 g/L peptone (CAS No. 91076-46-8), and 5 g/L NaCl (CAS

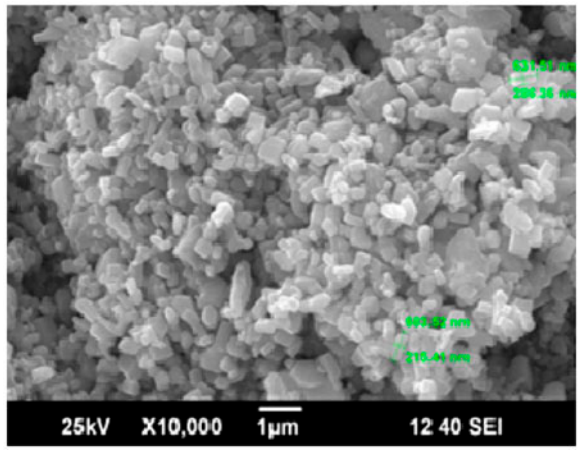


Fig. 1. Typical SEM image of ZnO.

No. 7647-14-5) in distilled water at pH 7.5. The bacterial cells were inoculated and subcultured under sterile conditions for 24 h at 37°C in 100 mL of the nutrient broth under aerobic conditions and constant agitation in a shake incubator at 140 rpm. The cells were then sedimented by centrifugation at 8,000 rpm for 15 min at 4°C. The bacterial pellet obtained was washed with sterile distilled water. It was then resuspended in sterile distilled water and the absorbance was measured at 600 nm using UV–Visible spectrophotometer. The cell suspensions were diluted with sterile distilled water in Pyrex glass beakers to the required cell density of ~$10^7$ colony forming units/mL (CFU/mL). This suspension in required volume was taken in bottles containing weighed amounts of the catalyst and irradiated using US in the dark in an ultrasonic bath operating at 40 kHz and power of 100 W. The samples were covered with aluminum foil before and after irradiation to eliminate the effects of diffused light illumination, if any. The temperature was kept at 37°C during US irradiation by circulating cooling water maintained at appropriate temperature. Sampling was done at predetermined time intervals by pipetting out 1 mL of the experimental solution into 9 mL sterile saline and was serially diluted. After mixing, 0.1 mL aliquots of each dilution were spread onto MacConkey agar plates. The cell inactivation was monitored by counting the CFU/mL after 24 h incubation at 37°C. All experiments were repeated at least thrice and the average value was taken.

## 3. Results and discussion

Disinfection of *E. coli* was examined in the presence of ZnO and US individually and in combination. As expected, no deactivation of the organisms was

observed in the absence of US irradiation, with or without catalyst. The deactivation by US alone in the absence of the catalyst is 20% while it is over 65% in presence of ZnO. The enhancing effect is not due to the aggregation or adsorption of the cells as no such reduction was observed during the incubation of the organisms in the presence of catalyst, in the absence of irradiation. The enhancement in presence of the catalyst can be attributed to the increased production of OH radicals on the surface of the ZnO particles. When US energy is supplied to the ZnO particles, excited electrons move from the valence band to the conduction band and positive holes are generated in the valence band. In the vicinity of the surface of ZnO particles, the holes react with water to produce more hydroxyl radicals [17] which provide additional disinfection effect. An ultrasonic wave is propagated throughout the vessel via the solvent so that all the particles in the vessel are expected to contribute to generating radical species. The microscale bubbles formed during the US irradiation get collapsed generating local high-temperature fields where water molecules are pyrolitically decomposed to generate more hydroxyl radicals. These radical species are moving into the intracellular portion of bacteria and destroying the metabolic pathway. Strong shear forces that rupture the cell membranes of bacteria are also generated during the collapse of the bubble [13]. SEM images of the organisms (Fig. 2(a)–(c)) before and after US irradiation show that irradiation causes morphological changes and possibly cell-wall disruption. Before illumination, the cells had cylindrical shape. After illumination many of the cells were completely damaged and the cells lost their viability, as observed from the number of CFU/mL. The damage caused by the US in presence of catalyst is significantly more than that in the absence of the catalyst under otherwise identical conditions.

### 3.1. Effect of catalyst loading

The effect of catalyst concentration on the ultrasonic disinfection of *E. coli* was tested by keeping all

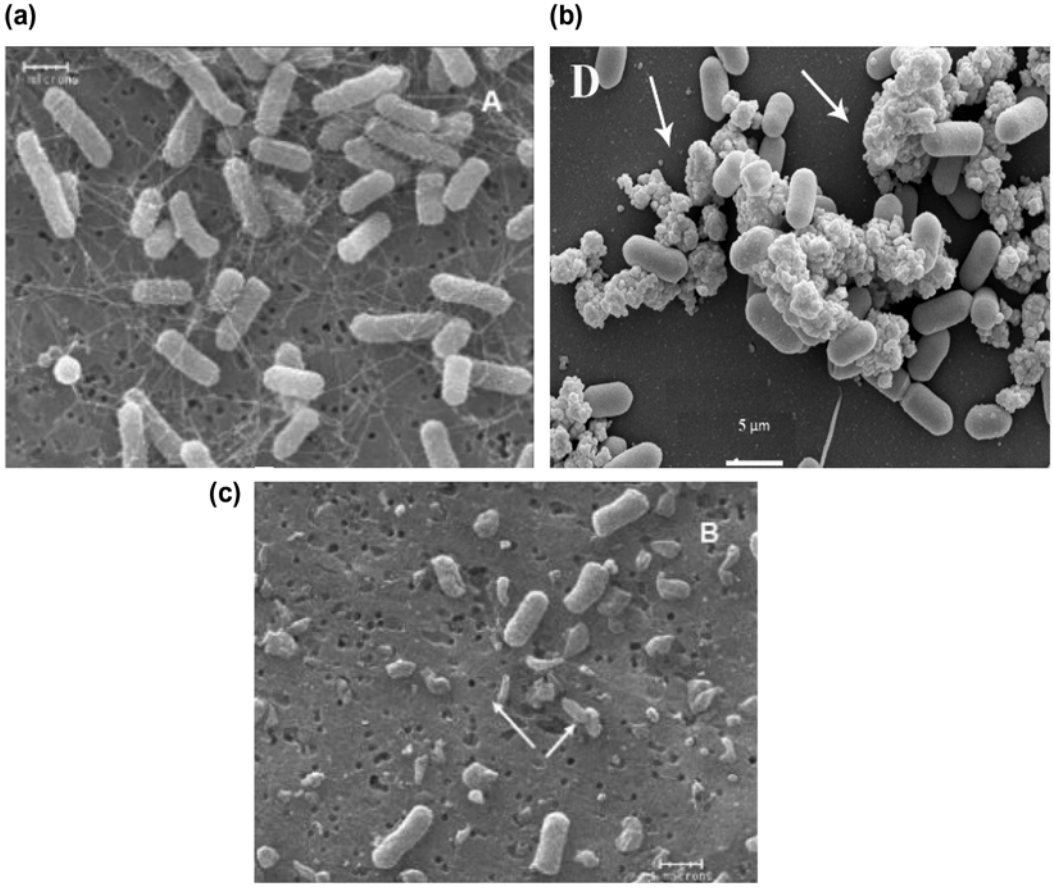


Fig. 2. SEM image of *E. coli*: (a) before US irradiation, (b) after US irradiation, and (c) after US irradiation in presence of ZnO.

other parameters constant. The results are shown in Fig. 3. The deactivation increased with increase in catalyst loading especially in the lower range 0.02–0.1 g/L. However, above 0.1 g/L, the increase was less pronounced as seen by comparing the results of 0.1 and 0.15 g/L. The optimum catalyst loading may depend on the initial cell count present in the system. The disinfection was significant in the initial stage. However, the rate decreased as time progressed. For example, at 0.1 g/L loading of ZnO the concentration of *E. coli* decreased by 65% in 2 h, while in the next 2 h the reduction effected was only an additional 20%. Increased deactivation with increase in catalyst loading may be due to increased number of active sites for interaction between the semiconductor particles and the bacterial cells in suspension together with the increased ROS production from the enhanced surface area. However, at higher loadings there is rapid saturation of the surface micro-organism encounters which result in stabilized or even decreased rate of deactivation. This saturation by the organisms or their damaged remnants on the catalyst surface also can cause the decreased rate (number of organisms deactivated per unit time, say h) of deactivation with time. The screening effect seen in photocatalysis which spatially limits the photoactive region is not seen in sonocatalysis as the ultrasonic energy is propagated throughout the entire region in the vessel. Hence, the optimum dosage is much higher in sonocatalysis compared to photocatalysis under identical conditions in reaction vessels of same size and geometry. In any case there is an optimum beyond which the activity is lower which may be due, at least partially, to the shielding effect of these overcrowded particles from the energy source. The optimum dosage of ZnO, as determined experimentally, is 0.1 g/L. Hence, all further studies on the organisms were carried out at this loading.

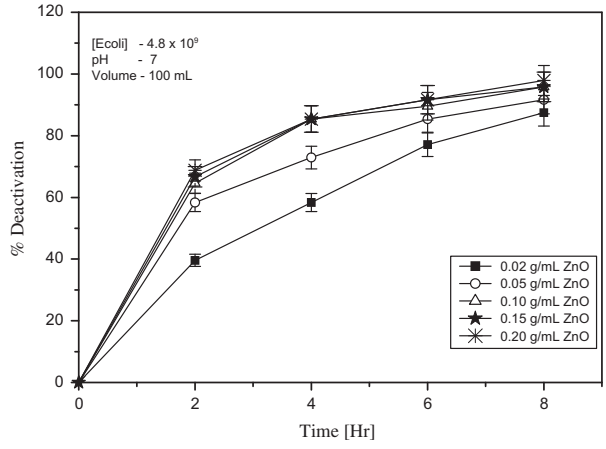


Fig. 3. Effect of ZnO loading on the disinfection of *E. coli*.

Time taken for complete deactivation of the organisms depends on their population density as well as the catalyst loading. At cell concentrations of approximately below $1.9 \times 10^3$ CFU, complete deactivation is achieved in 7–8 h while it takes more time, often >16 h (not shown here) when the initial concentration was higher. Complete deactivation can be accelerated for a particular concentration by enhancing the catalyst dosage.

### 3.2. Effect of concentration of the organism

The effect of changing concentration of the organisms on the rate of deactivation is shown in Fig. 4. The rate increased with increase in concentration and is eventually tending towards stabilization. This showed that the rate is dependent on the concentration of the organisms and the catalyst sites' availability. As the reaction progressed the effective concentration of organism decreased and the concentration-dependent deactivation rate also decreased correspondingly.

Further it is seen that at higher concentrations of the organisms ($>3 \times 10^6$ CFU/mL) and at higher catalyst loadings (>0.1 g/L) the rate is almost stabilized. The final relative cell (FRC) concentration $N/N_0$ calculated after 4 h, where $N_0$ and $N$ are the concentrations of viable cells before and after irradiation, respectively, also shows that at higher concentrations of the cells at lower catalyst loadings, the FRC concentration is more or less the same. Similarly, in the lower cell concentration range and higher catalyst loadings the FRC concentration does not change much. Hence, variation in the concentrations of the cells within these respective ranges does not make any significant changes in the rate of the disinfection under otherwise

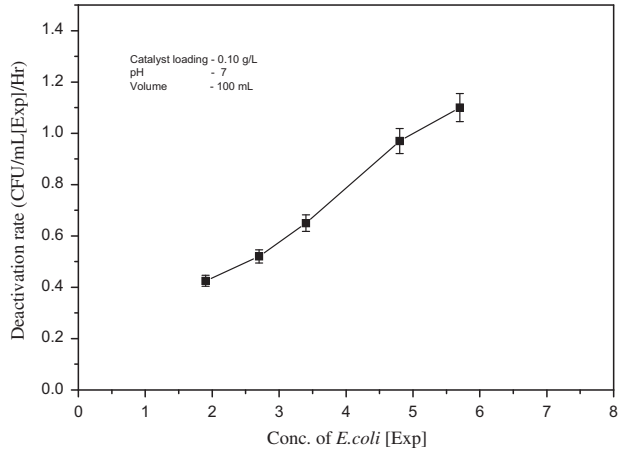


Fig. 4. Effect of concentration of *E. coli* on the disinfection rate.

identical conditions. Typical calculations are shown in Table 1. The results are in agreement with the findings of Dadjour et al. [18] who reported that in the case of $TiO_2$-catalyzed ultrasonic disinfection of *E. coli*, initial concentration of the organism has no significant effect on the process over a wide range, i.e. $1.6 \times 10^3$–$1.1 \times 10^7$ CFU/mL.

### 3.3. Effect of pH

The effect of initial pH of the reaction system on the sonocatalytic deactivation of *E. coli* is investigated and the results are shown in Fig. 5. In the absence of catalyst, ~20% decrease in the bacterial population was observed under US irradiation at neutral pH which increased in both highly acidic (pH 3) and alkaline pH (pH 11). The disinfection is negligible in the absence of US irradiation either in the presence or absence of the catalyst at all pHs indicating the tolerance of the organisms to acidic and alkaline conditions. Even in the presence of catalyst and US irradiation, the inactivation was independent of the initial pH value in the range 4–9. However, as irradiation progressed the deactivation became fully independent of pH. Earlier studies on the photocatalytic deactivation of *E. coli* in presence of $TiO_2$ showed that the deactivation is followed by a decrease in the pH of the system. In the current study also decrease in pH is observed, though to a much lesser extent, from 7 to 6.5. The relative stability of the bacteria in the otherwise lethal acidic pH in the absence of US irradiation is due to the presence of acid-induced proteins that protect the cells from an acid shock and the tolerance of acid-adapted cells towards osmotic stress [19]. However, in presence of the high-energy US radiation, such protection will be ineffective making the influence of pH less visible in the wider of range.

Table 1
Effect of concentration of *E. coli* vs. catalyst loadings on the FRC concentration

| Concentration (CFU/mL) | Catalyst loading (g/L) | FRC ($N/N_0$) |
|---|---|---|
| $1.9 \times 10^3$ (L) | 0.1 (H) | 0.26* |
| $1.9 \times 10^3$ (L) | 0.02 (L) | 0.50 |
| $2.7 \times 10^5$ (L) | 0.1 (H) | 0.23* |
| $2.7 \times 10^5$ (L) | 0.02 (L) | 0.54 |
| $3.4 \times 10^7$ (H) | 0.10 (H) | 0.14 |
| $3.4 \times 10^7$ (H) | 0.02 (L) | 0.35** |
| $4.8 \times 10^9$ (H) | 0.10 (H) | 0.11 |
| $4.8 \times 10^9$ (H) | 0.02 (L) | 0.37** |

Notes: H: High; L: Low.
*Indicate comparable rates of disinfection.
**Indicate comparable rates of disinfection.

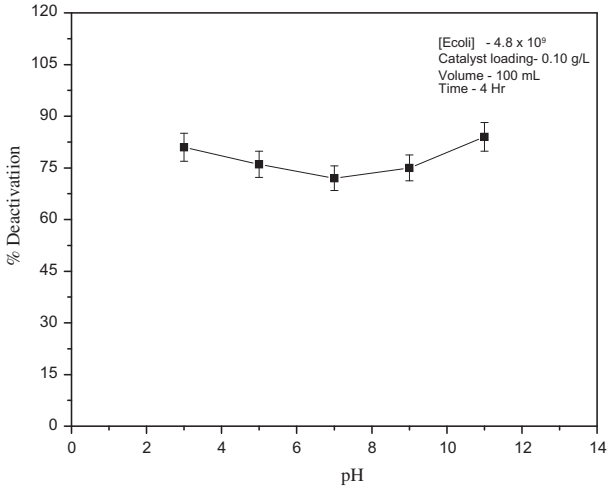


Fig. 5. Effect of pH on the disinfection of *E. coli*.

The sonocatalytic disinfection, as explained earlier, is caused by the direct action of US as well as attack by the reactive oxidative species generated on ZnO during the US irradiation.

$$\mathrm{ZnO} \xrightarrow{\mathrm{US}} \mathrm{ZnO}\ (h^+)\ (\text{valence band}) + \mathrm{ZnO}\ (e^-)\ (\text{conduction band}) \quad (1)$$

$$H_2O + h^+\ (\mathrm{ZnO}) \longrightarrow {}^{\cdot}OH + H^+ \quad (2)$$

$$\text{Bacterial organisms in water} \xrightarrow[{}^{\cdot}OH \text{ and other ROS}]{\text{Sono and resultant photo and sonophotocatalytic reactions}} \text{Aliphatic acids} \quad (3)$$

where ROS are the oxygenated species generated during the sonocatalytic- and the sonoluminescence-induced photo and sonophotocatalytic process [20].

### 3.4. Effect of $H_2O_2$

$H_2O_2$ is an important intermediate as well as end product in the sono and photocatalytic degradation of organic pollutants in water. Though $H_2O_2$ by itself induces the disinfection, it did not show any extra enhancing effect in presence of ZnO and US irradiation. In fact the disinfection in presence of $H_2O_2$, catalyst, and US irradiation together was less than the sum of infection achieved individually by (i) $H_2O_2$ and (ii) US + ZnO. Hence, added $H_2O_2$ does not

contribute to any extra effect or synergy as in the case of sonophotocatalytic deactivation of chemical contaminants [9]. Though $H_2O_2$ is a metastable molecule of high redox potential (1.77 V), its disinfecting properties are derived mostly from the free radicals formed in presence of catalysts. $H_2O_2$ enhances the sensitivity of bacteria to heat, light, or sound. However, the benefits of added $H_2O_2$ are not reflected in the sonocatalytic system possibly because $H_2O_2$ formed *in situ* in the sonocatalytic system is already enhancing the rate of decontamination making the added $H_2O_2$ superfluous. We have earlier reported that both the formation and decomposition of $H_2O_2$ takes place concurrently in sonocatalytic systems leading to oscillation in its concentration [9,16]. Hence, the concentration of $H_2O_2$ either formed *in situ* or externally added cannot increase beyond a critical limit, thereby restricting the enhanced detrimental effect on bacterial organisms.

## 4. Re-emergence

One of the major problems associated with environment-friendly deactivation of bacterial agents by solar energy is its re-emergence, once the source of energy is discontinued. The possibility of such re-emergence of *E. coli* deactivated by sonication and sonocatalysis is examined by measuring the bacterial concentration after the sonication has been put off. The deactivation continued for some more time after the US is put off, possibly because the free radicals generated in the process continue to be active for some more time until they are totally consumed by various processes taking place. In the case of sonocatalysis no re-emergence is noticed even after 16 h. Hence, the destruction can be considered complete and irreversible in this case. This is in contrast with the bacterial deactivation by sunlight or other softer techniques where a sizeable population of the bacteria re-emerge once the source of irradiation is off. The regrowth occurs as not all of the bacteria have been deactivated by the "soft" process. In such cases the bacteria may have entered a viable but non-culturable stage and then recovered their culturability after a period of more favorable conditions.

## 5. Mechanisms of disinfection

During sonocatalysis, the disinfection can occur both in the bulk phase and at the catalyst surface. In the bulk phase, the bacterial cells were inactivated by the micro jet shear stress and the OH radicals generated under US irradiation. At the surface, the *E. coli* were deactivated by the OH radicals generated by sonocatalytic excitation of the semiconductor. The amount of OH radicals produced in the presence of semiconductor was significantly greater than the amount generated by US alone [21].

In aqueous phase sonolysis, there are four potential sites for sonochemical activity [22]:

(i) The gaseous region of the cavitation bubble where volatile and hydrophobic species are easily degraded through pyrolytic reactions as well as reactions involving the participation of hydroxyl radicals with the latter being formed through water sonolysis:

$$H_2O \longrightarrow H^{\cdot} + {}^{\cdot}OH \tag{4}$$

(ii) The bubble—liquid interface where hydroxyl radicals are localized and therefore radical reactions predominate although pyrolytic reactions also may occur to a lesser extent.

(iii) The liquid bulk where secondary sonochemical activity may take place mainly by free radicals that escaped from the interface and migrated to the liquid bulk.

(iv) Catalyst–liquid interface where OH radicals initiate reaction.

OH radicals can recombine to produce $H_2O_2$ which may in turn interact with hydrogen to generate OH radicals:

$${}^{\cdot}OH + {}^{\cdot}OH \longrightarrow H_2O_2 \tag{5}$$

$$H_2O_2 + H^{\cdot} \longrightarrow H_2O + {}^{\cdot}OH \tag{6}$$

Reactions initiated by ·OH radicals primarily in the liquid bulk as well as the bubble interface and the catalyst surface may be the dominant deactivation pathway.

The catalyst particles, in addition to promoting the OH radicals, may also stabilize the reactive species resulting in more intensive disinfection. Further, sonocatalysis leads to the formation of $H_2O_2$ which also acts as a ROS. The photocatalytic characteristics of ZnO induced by the US-initiated sonoluminescence caused by the implosion of bubbles, also will result in disinfection. It is known that flashes of single bubble sonoluminescence (SBSL) involve intense UV light which can activate ZnO photocatalytically [18]. The semiconductor particles can also lead to strong jet streams and physical stresses in the ultrasonic system which can affect the cell structure as well as the cell

membrane of the organisms [7,21]. US can also increase catalyst surface area producing more active sites for reactions with target species. Further, smaller catalyst particles may enter the bacterial cells which may have already damaged cell membranes and cause additional damage to intracellular components. Sonication itself can also cause greater intracellular damage in damaged bacterial cells. Other factors leading to disinfections include pressure and pressure gradients resulting from bubble collapse causing cell damage due to mechanical fatigue and shear forces induced by microstreaming. Intrinsic oxygen vacancies on the catalyst surface can also lead to more cavitation [23].

The photocatalytic disinfection of *E. coli* in water has been modeled with kinetic equations based on a simplified reaction mechanism which consists of three different stages; i.e. (i) initial delay or smooth decay at the beginning of the reaction, usually called "shoulder," (ii) a log-linear disinfection region that covers most part of the reaction, and (iii) a deceleration of the process at the end of the reaction, usually called "tail" [24]. Kinetic constant, pseudo-adsorption constant, and inhibition coefficient were the three key parameters used in the model. It was seen that the inhibition coefficient is not influenced by the experimental conditions while the other two are most sensitive. The presence of different inorganic anions and cations in water strongly influences the efficiency of the disinfection process as has been observed in our laboratory as well. The effect is also dependent on the concentration of the ions. This indicates the possibility of different mechanisms for the disinfection and thus different values of kinetic and pseudo-adsorption constants depending on the water characteristics. However, the model cannot be applied as such in the current instance of sonocatalytic deactivation because the "shoulder" is not observed here. The log-linear inactivation region that covers over 50% of the reaction and the "tail" are observed here as well. Hence in sonocatalysis, the physical and chemical effects of sonolysis may be the dominant driving forces of disinfection initially. As the reaction proceeds, the SBSL sets in making the disinfection a complex process involving a combination of sonolysis, sonocatalysis, photocatalysis, and possibly sonophotocatalysis.

## 6. Future outlook

The advantage of sonocatalysis in wastewater treatment compared with conventional techniques lies in processing safety, reduction in the amount of secondary waste, and irreversibility in the bacterial decontamination. However, appropriate reactor design and relatively high operating costs of the sonoreactor are impediments in the large-scale commercial application of the process at present [25]. Fundamental research on the origin of extreme conditions created by acoustic cavitation in complex fluids is required to optimize the sonochemical-processing applications. The effect of frequency of US and the presence of suspended solid particles, dissolved solids and gases, ionic species, etc in water on the efficiency of the process should be studied at different operating scales. The economy of the process, compared to other processes can be ascertained only after identifying all relevant parameters including engineering data required to improve sonoreactor design and scale-up. Large-scale commercial application of the technique may have to wait until some of these issues are resolved.

## 7. Conclusions

Sonocatalysis as a means of bacterial decontamination of water is investigated using ZnO as the catalyst. The influence of various parameters on the rate of sono-deactivation of *E. coli*, is evaluated. The rate of deactivation increases with increase in catalyst loading and with increase in concentration of the organism. Externally added $H_2O_2$ does not accelerate the deactivation as expected probably because the *in situ*-formed $H_2O_2$ may have already played the role. The deactivation is independent of the initial pH, though at higher acidic and alkaline range, slight enhancement in the deactivation is observed. The ZnO-induced sono-deactivation is irreversible. The study reveals conclusively that ZnO-mediated sonocatalysis has the potential to be used an effective tool for the irreversible decontamination of bacterial organisms in water.

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