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Ozone and cavitation for water disinfection

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Abstract

Ozone is a powerful oxidant, which is used extensively for water disinfection. Although it is claimed to produce less toxic byproducts than chlorine, the mutagenicity of the aldehydes and other compounds produced as byproducts during ozonation cannot be ruled out. Due to this there is a need for additional disinfection processes, which can reduce or eliminate these toxic byproducts by reducing the usage of ozone. Moreover, higher cost of these biocides necessitates its optimum usage. Synergistic processes reduces to half or one-third the required concentration of ozone for disinfection as found in this study. Due to these factors, synergistic processes appear to be promising for water disinfection. In this study, we investigate the viability of ozonation and cavitation (hydrodynamic cavitation and ultrasonication) for the disinfection of the heterotropic plate count (HPC) bacteria and indicator microorganisms (total coliforms, faecal coliforms and faecal streptococci) in bore well water.

Keywords: Disinfection; Cavitation; Ozone; Heterotropic plate count bacteria; Total coliforms; Faecal coliforms; Faecal streptococci

1. Introduction

The combination of drugs in order to obtain an effect greater than that of any compound taken alone has been practised for generations [1]. In a similar manner, combination of two or more disinfection techniques has also been applied to water treatment. Hybrid techniques employ the combination of various oxidation techniques, which can result in the generation of sufficient hydroxyl radicals and their oxidising potential for water purification. These processes are known as the advanced oxidation processes (AOP). The OH radical is a powerful oxidising radical, second only to fluorine [2] and is therefore attractive to use in water treatment. Advanced oxidation systems generally combine ozone, hydrogen peroxide and ultraviolet radiation e.g. O_3 and H_2O_2; O_3 and UV; and H_2O_2 and UV.

A number of hybrid techniques have been reported in the literature which include the combination of UV radiation and ozonation for the treatment of humic acids [3] and low molecular weight organic compounds [4], combination of ultrasonication and ozonation for aromatic compound degradation [5], inactivation of microorganisms [6] and disinfection of water [1]. The AOP (PEROXONE) which is a combination of ozone and hydrogen peroxide has been used for disinfection of water [7]. Reports on the combination of ultrasound and chemical disinfection suggest that a synergistic phenomena between ultrasound and glutaraldehyde occurred [8]. Some microorganisms are sensitive to lower concentrations of oxidising agents when exposed to ultrasound and the combined action of UV radiation with high frequency ultrasound increases the rate of bacterial inactivation [8].

In this paper, we investigate the viability of hybrid cavitation processes involving the use of chemicals like ozone along with cavitation (ultrasonication and hydrodynamic cavitation). Previous studies have indicated that these techniques can inactivate a wide range of microorganisms. Ultrasonication [9,10] and hydrodynamic cavitation [11] which are essentially different means of generating cavitating conditions i.e. using sound and flow energies, respectively, have been particularly useful for cell disruption. Cavitation is a phenomena of formation, growth and collapse of microbubbles within a liquid. If this phenomena occurs due to the passage of high frequency sound waves, then it is called acoustic cavitation (ultrasonication) and if it occurs due to the pressure variations in the flowing liquid due to the change in the geometry of the flowing system, it is called hydrodynamic cavitation.

The mechanism by which these microorganisms are killed by ultrasound can be explained as follows: the passage of sound through a liquid produces alternating pressure changes, which at sufficient intensity can cause cavities to

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Nomenclature

C	concentration of microorganism
C_1	initial concentration of microorganism
C_2	final concentration of microorganism
CFU	colony forming units
dc/dt	rate of disinfection
HC	hydrodynamic cavitation
HPC	heterotropic plate count
k	rate constant
Rs.	rupees
t	time of treatment
US	ultrasonic

form in the liquid. This cavity formation in response to an alternating pressure (acoustic) field is called acoustic cavitation [12].

Cell disruption by ultrasound is dependent on the mechanical effects of gaseous cavitation in the liquid. It occurs due to the mechanical stresses arising from the shock waves of cavity collapse and from flows and turbulence generated by pulsating cavities. Doulah and Hammond [13] put forward a mechanism where it was assumed that eddies with scales larger than that of the cell would impart kinetic motion to it. Eddies of a scale comparable to the cell dimension would impart oscillatory motions to the cell without causing their disruption. When the kinetic energy of this oscillatory motion exceeds the wall strength, the cell will disintegrate.

For most biological systems the liquid is water, which requires sound pressures of 1–8 bar to reach the cavitation threshold. These sound pressures are easily produced in the 8–20 kHz frequency range. It has been assumed that the cells are disrupted during the cavity collapse stage [14] and that the disruption is caused by the differential pressure gradients existing rather than by the high temperatures generated during the collapse of the cavities. As a result, ultrasonication has been effectively used to release intracellular enzymes from bacteria without any temperature deactivation of the enzymes [9].

A detailed account of the mechanism of cavitation by ultrasonication and hydrodynamic cavitation has been published elsewhere [15].

In this paper, we compare the disinfection efficacy of ultrasonication, hydrodynamic cavitation, ozone and their combination. As an exploratory work, initially the disinfection studies were assessed by the heterotropic plate count (HPC) method. Since this only provides overall information on the microbial reduction, specific microorganisms were studied which are considered as indicators of pollution in potable water. Total coliforms, faecal coliforms and faecal streptococci were chosen for this study as they are frequently present in drinking water which leads to a number of waterborne diseases in human beings.

2. Materials and methods

The disinfection study was carried out on bore well water, which had a bacterial population as indicated in Table 1. The technique used to calculate the bacterial population has been described in Section 3. The observed variation in bacterial population can be attributed to seasonal variation (monsoon and non-monsoon months in Mumbai, India), which leads to a significant change in the water table level and soil porosity and percolation conditions. However, this variation in the bacterial population did not have any significant effect on the experimental results as is shown later.

The bore well water was filtered by using Whatman filter papers, size No. 1, to remove suspended particles and mud before subjecting it to the following disinfection treatment techniques.

2.1. Ozone

The ozone generator used in this study was supplied by Arshad Electronics, India Ltd. It can be operated up to a maximum current of 1.2 A. The generator produces ozone according to the corona discharge method. Dry air was used as the feed gas. The air flow rate was 28 l s^{-1}.

The ozone generator was operated at 1.2 A for all the experiments performed. At this current, it was found that the generator produces ozone at a rate of 0.2 g/h, with a concentration of 50 mg/l of ozone in the exit air. The rate of ozone generation was found by bubbling ozone for 15 min through 400 ml of a 2% potassium iodide solution. Ozone concentration was then determined by titration with sodium thiosulphate by the iodometric titration procedure as described in the Standard Methods [16].

A stock solution of ozone was prepared by passing ozone into 100 ml of sterile distilled water for a period of 24 min.

Table 1
Variation in bacterial population in bore well water

Month	HPC bacteria (CFU/ml)	Total coliforms/100 ml	Faecal coliforms/100 ml	Faecal streptococci/100 ml
January–March	2500–8000	50–200	20–100	30–200
April–June	3000–5000	60–150	30–80	40–70
July–September	1000–3000	25–60	18–30	20–50
October–November	2500–4000	125–170	20–60	30–80
November–December	6500–7500	150–200	80–100	180–200

The concentration of ozone in this solution was 50 mg/l. Appropriate amount of this ozone solution was used as the dosage for various experiments.

All the experiments were performed on 1 l of bore well water using different doses of ozone. 10, 20, 40, 60 and 80 ml of the ozone stock solution was used to achieve 0.5, 1, 2, 3 and 4 mg/l, respectively, of ozone concentration in water used in the study. The total reacting volume of water + ozone was 1 l. The treatment was carried out for a period of 15 min and the solution was kept well mixed with the aid of a magnetic stirrer.

2.2. Acoustic cavitation

Ultrasonication was carried out with an ultrasonic horn (Supersonics), which operated with a frequency of 22 kHz and an electrical power rating of 240 W. Hundred millilitres of bore well water was subjected to ultrasonication for a period of 15 min. Samples were withdrawn at regular intervals. The temperature was maintained at 35–37 °C with the aid of an ice bath as ultrasonication and the concentration of energy results in a temperature rise, which also might cause disinfection. To isolate the cavitation and temperature disinfection effect, the temperatures were maintained at the above level.

The ultrasound bath (Supersonics) used had a peak operating frequency of 20.5 kHz. The bath had an internal surface made of stainless steel (SS). The internal dimensions of the bath were 145 mm × 145 mm × 150 mm. The electrical power consumption of the bath was 120 W. Two litres of bore well water was subjected to sonication instead of 100 ml as the bath can handle larger volumes. Samples were withdrawn at regular intervals. Placing the bore well water directly in the bath meant that there was no method of cooling it during operation. To prevent the temperature from rising above 35 to 37 °C, the ultrasonic irradiation has been used intermittently, for the system to cool down during the quiet period. Incorporation of any solid body in the bath is known to change the sound field drastically, which affects the location and intensity of the cavitational effects. The bath was characterised [17] without any solid body in it and hence we have retained this configuration.

2.3. Hydrodynamic cavitation

The set-up used to induce hydrodynamic cavitation is shown in Fig. 1. The set-up essentially consisted of a closed loop circuit including a holding tank, a centrifugal pump and a valve. The holding tank has a capacity of 10 l. It has a diameter of 420 mm and height of 700 mm. The multistage centrifugal pump (KSB Pumps Ltd., India) has a power consumption of 1.5 kW and has a speed of 2800 rpm. The cavitating valve is ball type made of SS.

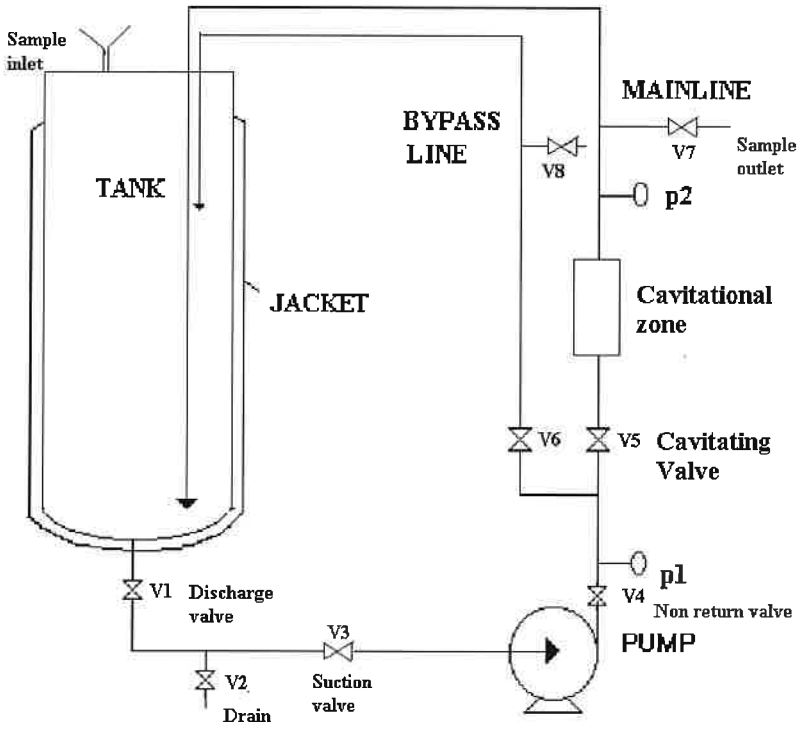

Fig. 1 Hydrodynamic cavitation set-up
V1 to V8 - Control valves
p1 and p2 - Pressure gauges

Fig. 1. Hydrodynamic cavitation set-up: V1–V8, control valves; p1 and p2, pressure guages.

The suction side of the pump is connected to the bottom of the tank. V1 is the discharge valve, V2 the drain valve which is kept closed during operation and V3 is the suction valve. During operation, V1 and V3 are kept open. The discharge from the pump branches into two lines. A non-return valve V4 is provided to ensure the flow of liquid in the correct direction. The main line consists of a valve V5 (ball valve) which acts as a cavitating device due to its ability to throttle the flow. A hard glass tube has been provided next to this valve which makes the visual observation easier. A bypass line is provided (V6) to control the liquid flow through the main line. Valves V7 and V8 are provided as sample outlet valves. The holding tank is provided with cooling jacket to control the temperature of the circulating liquid. Pressure gauges are provided to measure the inlet pressure (p1) and the fully recovered downstream pressure (p2) which in most of the cases was atmospheric.

Ten litres of bore well water was fed into the holding tank. Initially, both the mainline valves and the bypass valve were left open and the water was allowed to circulate for a period of 1 h after which it was allowed to stand as such for another hour. This initial run was carried out before every experiment in order to obtain a nearly constant starting value of the bacterial population. This was done to minimise the variations obtained in the blank reading of the samples treated.

For the actual experiment, the bypass valve was left open till the pump reached its maximum speed and then partially or totally closed. The second valve (bypass line) was then throttled to obtain the required pump discharge pressure. Experiments were carried out at pump discharge pressures of 1.72, 3.44 and 5.17 bar. Samples were withdrawn at regular time intervals from the outlet valve. Cooling water was passed in the jacket only after the temperature in the holding tank was about 2–3 °C higher than the cooling water temperature (30 °C).

2.4. Hybrid techniques

2.4.1. Acoustic cavitation and ozone

0.5, 1, 2, 3 and 4 mg/l of ozone was added to bore well water just before subjecting it to ultrasonication in the ultrasonic horn and bath as described in Section 2.2.

2.4.2. Hydrodynamic cavitation and ozone

0.5, 1 and 2 mg/l of ozone were added to bore well water just before subjecting it to hydrodynamic cavitation as described in Section 2.3.

2.5. Ozone decomposition studies

Aqueous ozone concentration was determined using an iodometric method [18]. This method has been reported in the literature for ozone determination [19–21]. The iodometric method is based on the liberation of free iodine from potassium iodide (KI) solutions by reaction with ozone [18]. The liberated iodine is titrated with a standard solution of sodium thiosulphate using starch as an indicator. The titration is performed at a pH of 3–4 since the reaction is not stoichiometric at a neutral pH due to the partial oxidation of thiosulphate to sulphate. The chemical reactions of the iodometric method are

$$O_3 + 2I^- + H_2O \rightarrow 2OH^- + O_2 + I_2 \quad (1)$$

$$2S_2O_3^{2-} + I_2 \leftrightarrow S_4O_6^{2-} + 2I^- \quad (2)$$

The iodometric method can be used to determine ozone concentrations above 1 mg/l. The procedure of the potassium iodide reaction and titration with sodium thiosulphate was performed as recorded in Standard Methods [18].

2.5.1. Ozone decomposition in the absence of ultrasound

Ozone was bubbled through 100 ml of sterile distilled water for a period of 24 min to give initial ozone concentration of 50 mg/l. Twenty-five millilitres of this solution was withdrawn at regular intervals and added to 400 ml of 2% KI, acidified with 0.1 N sulphuric acid and titrated with 0.005 M potassium thiosulphate. Thus the residual ozone concentration of ozone remaining at different time intervals was calculated as stated in the Standard Methods [18].

2.5.2. Ozone decomposition in the presence of ultrasound

Ozone was bubbled through 100 ml of sterile distilled water for a period of 24 min. This solution was then subjected to ultrasonication by the ultrasonic horn. Twenty-five millimetres of this solution was withdrawn at regular intervals and added to 400 ml of 2% KI, acidified with 0.1 N sulphuric acid and titrated with 0.005 M potassium thiosulphate. Thus the concentration of ozone remaining at different time intervals was calculated as stated in the Standard Methods [18].

Similar experiment was carried out in the case of the ultrasonic bath. However, the ozone solution was not subjected to ultrasonication directly in the bath, but a beaker containing the ozone solution was place in the ultrasonic bath.

3. Method of analysis

The disinfection efficacy of the techniques described above was assessed by the number of microorganisms present before and after treatment. Enumeration of bacteria was done by plate count method (pour plate technique) as recommended by the American Public Health Association, 1985 [16]. This method of analysis has been used for the estimation of the overall reduction in the colony forming units (CFUs). For this purpose, plate count agar (Hi-media) was used as the growth medium. The samples before and after treatment were suitably diluted so that the count was between 30 to 300 colonies per plate. 0.1 ml of treated water was introduced into each petridish and 10 ml of plate count agar media was added and mixed. The agar was allowed to set and these petridishes were then inverted and incubated

at 35 °C for 48 h. The colonies developed were counted using Image-plus, image analysis system and expressed as CFU/ml. Duplicate plates as recommended in Standard Methods, were prepared for each sample and the results were averaged. A media control plate was always prepared to eliminate error due to media contamination.

In addition to the overall CFU/ml, the decrease in the number of indicator microorganisms (total coliforms, faecal coliforms and faecal streptococci) was also assessed. The enumeration of these microorganisms were also carried out as per the American Public Health Association, 1985 [16] using the M-Endo Agar LES, M-FC Agar Base and the K F Streptococcal Agar (Hi-media), respectively.

4. Results and discussions

4.1. Percentage killed/extent of disinfection

4.1.1. Ozone

Ozone has disinfection properties due to its oxidising effect on the microorganisms. It oxidises the organic compounds in the cell membranes of the microorganisms, which result in the rupture of the membranes, affecting the cell viability and thus disinfection is achieved. When a known quantity of water is treated with a known amount of ozone, it is observed that as the time of treatment is increased the number of microorganisms killed also increases. From Table 2, it can be seen that, in the case of HPC bacteria, for 0.5 mg/l of ozone dosage, 46% disinfection is achieved in the first 15 min of treatment, which in turn increases to 82% at the end of 60 min. The same trend is observed when other ozone concentrations like 1, 2, 3 and 4 mg/l are used. This effect is due to the increase in the contact time between the organism and ozone as the time of treatment is increased. Although the sampling for all the experiments were carried out at every 5 min interval, significant effect was seen only at 15 and 60 min interval. Due to this, only these results have been presented in Table 2.

Considering a constant initial CFU/ml, when the concentration of ozone is increased, it is observed that the time required to obtain a certain level of disinfection (% reduction in CFU/ml) is less at higher ozone concentrations. From Table 2, it can be seen that, in the case of HPC bacteria, it takes 15 min to achieve 93% disinfection, when the concentration of ozone is 4 mg/l, but it takes 60 min in the case of ozone concentration of 2 mg/l and for ozone concentration of 0.5 mg/l at the end of 60 min, only 82% disinfection has been achieved.

Having studied the effect on the HPC bacteria present in the bore well water which only gives the overall effect expressed as CFU/ml, it was also necessary to study the effect on specific microorganisms. These experiments indicated that the number of microorganisms killed increased as the dosage of ozone was increased. Thus, similar trends were obtained in the case of the indicator microorganisms.

4.1.2. Acoustic cavitation

In the case of both the ultrasonic equipment, the bath and the horn, there was an increase in the % disinfection with

Table 2
Percentage disinfection obtained for various techniques

Disinfection technique	HPC bacteria		Total coliforms		Faecal coliforms		Faecal streptococci	
	15 min	60 min	15 min	60 min	15 min	60 min	15 min	60 min
0.5 mg/l O_3	46 ± 5	82 ± 20	73 ± 15	90 ± 20	68 ± 15	92 ± 10	53 ± 8	83 ± 5
1 mg/l O_3	52 ± 10	88 ± 15	68 ± 10	92 ± 10	75 ± 5	95 ± 8	69 ± 5	94 ± 10
2 mg/l O_3	60 ± 15	93 ± 10	60 ± 14	94 ± 8	78 ± 14	100 ± 20	74 ± 8	97 ± 12
3 mg/l O_3	82 ± 10	–	96 ± 20	–	100 ± 20	–	97 ± 5	–
4 mg/l O_3	93 ± 20	–	100 ± 25	–	10 ± 20	–	100 ± 20	–
US-horn	50 ± 5	–	55 ± 5	–	47 ± 5	–	50 ± 10	–
US-bath	57 ± 5	–	75 ± 16	–	89 ± 12	–	80 ± 15	–
US-horn + 0.5 mg/l O_3	99.9 ± 25	–	99.2 ± 25	–	98.6 ± 25	–	97.3 ± 8	–
US-horn + 1 mg/l O_3	99.9 ± 20	–	99.2 ± 25	–	98.6 ± 20	–	97.7 ± 8	–
US-horn + 2 mg/l O_3	99.9 ± 20	–	99.6 ± 18	–	99.3 ± 22	–	98.4 ± 9	–
US-horn + 3 mg/l O_3	100 ± 20	–	100 ± 20	–	100 ± 25	–	100 ± 10	–
US-horn + 4 mg/l O_3	100 ± 15	–	100 ± 20	–	100 ± 28	–	100 ± 25	–
US-bath + 0.5 mg/l O_3	95 ± 16	–	96 ± 18	–	95 ± 30	–	95 ± 10	–
US-bath + 1 mg/l O_3	96 ± 30	–	96 ± 12	–	96 ± 30	–	96 ± 8	–
US-bath + 2 mg/l O_3	97 ± 25	–	98.3 ± 15	–	97 ± 25	–	97 ± 5	–
US-bath + 3 mg/l O_3	97.3 ± 20	–	98.3 ± 15	–	97.3 ± 15	–	97.3 ± 6	–
US-bath + 4 mg/l O_3	98 ± 20	–	99 ± 20	–	98 ± 12	–	98 ± 8	–
Hydrodynamic cavitation at 1.72 bar	47.5 ± 15	81 ± 15	57 ± 10	77 ± 6	44 ± 5	68 ± 6	28 ± 4	53 ± 5
Hydrodynamic cavitation at 3.44 bar	52.5 ± 10	85 ± 15	58 ± 10	80 ± 5	45 ± 5	70 ± 20	37 ± 2	61 ± 4
Hydrodynamic cavitation at 5.17 bar	56 ± 12	87.5 ± 10	66 ± 12	83 ± 12	57 ± 8	76 ± 15	40 ± 4	65 ± 5
Hydrodynamic cavitation at 5.17 bar + 0.5 mg/l O_3	60 ± 15	89 ± 5	70 ± 16	80 ± 8	80 ± 10	85 ± 20	64 ± 5	86 ± 8
Hydrodynamic cavitation at 5.17 bar + 1 mg/l O_3	63 ± 20	91 ± 12	77 ± 15	85 ± 6	78 ± 10	88 ± 12	72 ± 8	94 ± 6
Hydrodynamic cavitation at 5.17 bar + 2 mg/l O_3	66 ± 10	92 ± 20	80 ± 20	94 ± 10	88 ± 20	100 ± 25	74 ± 4	97 ± 8

treatment time for HPC bacteria as well as indicator microorganisms (Table 2). This is because increasing the time of exposure to ultrasound increases the probability of a cell or a microorganism coming into contact with a collapsing cavity, which would lyse it. The results obtained here are consistent with our earlier work [15].

4.1.3. Hydrodynamic cavitation

From Table 2, it can be seen that, when the pump discharge pressure used was 1.72 bar, only 81% reduction in the CFU concentration was obtained in 1 h for the disinfection of HPC bacteria. When the pump discharge pressure was increased, the disinfection efficiency also improved and 85–88% reduction in the CFU concentration was obtained in the same time period. At very high pump discharge pressures (5.17 bar), the time required to achieve a certain level of disinfection is less as compared to that at lower pressures. Thus it can be seen that the % disinfection is greater at higher discharge pressures for the same time of treatment. The increase in the pump discharge pressure increases the cavitational intensity i.e. the pressure intensity generated during cavity collapse [22], this in turn will be more effective in destroying the microbe. This observation is consistent with the dynamics of the cavity as predicted and measured earlier [22].

Similar trends were obtained in the case of the indicator microorganisms (Table 2).

4.1.4. Acoustic cavitation and ozone

It was observed that the disinfection efficiency of acoustic cavitation was increased (95–100%) when ozone was added. From Table 2, it can be observed that the results obtained with respect to time of treatment were similar to the results of only acoustic cavitation.

Although the sampling for all the experiments were carried out at every 5 min interval, significant effect was seen only at 15 and 60 min interval. Due to this, only these results have been presented in Table 2.

4.1.5. Hydrodynamic cavitation and ozone

Reduction obtained only with cavitation in the first 15 min of treatment is between 47.5 and 56% of the starting value of CFU/ml depending upon the discharge pressure used (Table 2). Similarly the reduction obtained in the first 15 min of treatment is between 46 and 93% depending on the concentration of ozone used (Table 2). However, when ozone (2 mg/l) is used in combination with cavitation in the first 15 min of treatment, the CFU count reduces 66% (5.17 bar) of the starting value of CFU/ml (Table 2) as against 60% with ozone alone. Thus there is a significant effect on the efficacy of the hydrodynamic cavitation in the presence of ozone.

4.2. Ozone decomposition studies

4.2.1. Ozone decomposition studies in the absence of ultrasound

When the ozone stock solution was studied for decomposition, it was observed that ozone decomposes gradually over a period of 20 min. Fifty-five percent decomposition was observed at the end of 15 min (Fig. 2).

4.2.2. Ozone decomposition studies in the presence of ultrasound

When the ozone stock solution was subjected to ultrasonication in the ultrasonic bath/horn, it was observed that ozone decomposes faster in the presence of ultrasound. Thus only 55% decomposition of ozone was observed at the end of 15 min when ozone stock solution was allowed to stand in the absence of ultrasound. However, when the ozone stock solution was subjected to ultrasonication, then 75% decomposition and 80% decomposition of ozone was observed in the case of the ultrasonic horn and the ultrasonic bath, respectively (Fig. 2).

This clearly points out the fact that acoustic cavitation accelerates the decomposition of ozone which accounts for

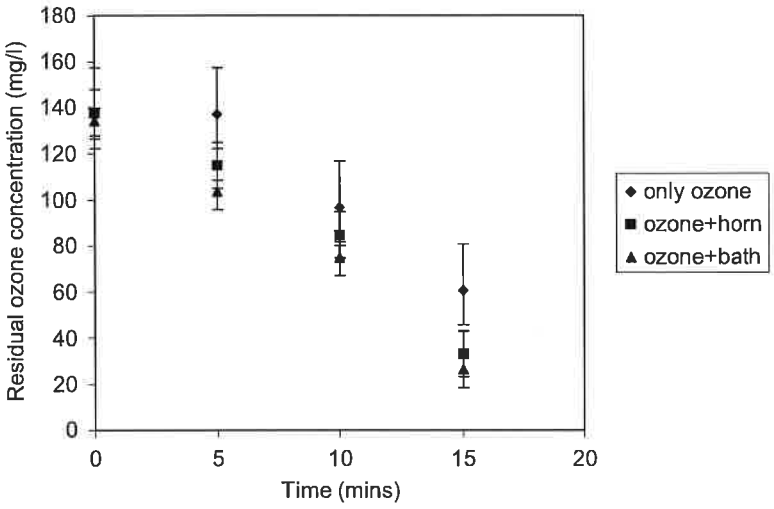

Fig. 2. Decomposition of ozone with and without sonication.

the higher disinfection efficacy of the hybrid techniques discussed above. The cavitation could also increase the permeability of the nascent oxygen through the microbial cell wall and increase the disinfection efficiency of the ozone.

4.3. Rate of disinfection

4.3.1. Estimation of rate of disinfection

A sample calculation has been shown below, which was used for estimating the rate of disinfection:

Case: Disinfection using 2 mg/l O_3 dissolved concentration
Initial CFU/ml = 3000 CFU/ml
CFU/ml at the end of 15 min of treatment = 1200 CFU/ml

Rate = no. of CFU killed/s,

$$-\frac{dc}{dt} = kC \text{ (assuming first order dependence [14])} \quad (3)$$

$$\therefore -\int_{C_1}^{C_2} \frac{dc}{C} = k\int_0^t dt \quad (4)$$

$$\therefore \ln\frac{C_1}{C_2} = kt \quad (5)$$

$$\therefore k = \frac{\ln(C_1/C_2)}{t} \quad (6)$$

$$k = \frac{\ln(3000/1200)}{900} = 1.018 \times 10^{-3}\ s^{-1} \quad (7)$$

$$C_{avg} = \frac{C_1 + C_2}{2} \quad (8)$$

$$C_{avg} = \frac{3000 + 1200}{2} \quad (9)$$

$C = 2100$ CFU/ml
Vol. = 1000 ml

$$\text{Thus rate of disinfection} = -\frac{dc}{dt} = kC_{avg}\ (\text{CFU/ml s}) \quad (10)$$

Rate of disinfection $= 1.018 \times 10^{-3} \times 2100 = 2.138$ (CFU/ml s)

$$\text{Overall rate of disinfection} = -\frac{dc}{dt} = k \times C_{avg} \times \text{vol. (CFU/s)}$$
$$= 1.018 \times 10^{-3} \times 2100 \times 1000$$
$$= 2138\ \text{CFU/s} \quad (11)$$

Thus, all the values of the rate constants have been calculated by estimating the slope over a small time interval of the $\ln(C_1/C_2)$ V/s time plots and then the overall rates of disinfection have been calculated as above with C_{avg} estimated over the range C_1–C_2 in that time interval.

4.3.2. Discussion of experimental results

Based on this, the results obtained for various techniques studied in this paper have been discussed. Table 3 gives the overall rate of disinfection for the HPC bacteria and the indicator microorganisms at the end of 15 min of treatment for all the techniques employed in this study.

When different doses of ozone were used, it was observed, that as the ozone dose was increased, the overall rate of disinfection also increased. It is known that ozone is a powerful oxidant. This oxidising property is because of the nascent oxygen that is formed during the decomposition of ozone. This nascent oxygen can attack organic compounds in the

Table 3
Overall rate of disinfection (no. of microorganisms killed/s) at the end of 15 min of treatment

Disinfection technique	HPC bacteria	Total coliforms	Faecal coliforms	Faecal streptococci
0.5 mg/l O_3	1490 ± 100	0.73 ± 0.05	0.42 ± 0.01	0.44 ± 0.02
1 mg/l O_3	1508 ± 95	0.83 ± 0.06	0.39 ± 0.02	0.55 ± 0.02
2 mg/l O_3	2138 ± 120	0.85 ± 0.06	0.46 ± 0.01	0.66 ± 0.04
3 mg/l O_3	3345 ± 150	1.85 ± 0.1	1.08 ± 0.09	1.42 ± 0.1
4 mg/l O_3	4673 ± 150	2.55 ± 0.2	1.08 ± 0.08	1.65 ± 0.1
US-horn	402 ± 50	0.13 ± 0.08	0.02 ± 0.001	0.02 ± 0.001
US-bath	9461 ± 200	3.85 ± 0.1	1.01 ± 0.07	0.92 ± 0.04
US-horn + 0.5 mg/l O_3	1982 ± 80	1.35 ± 0.09	0.72 ± 0.05	0.62 ± 0.02
US-horn + 1 mg/l O_3	2209 ± 90	1.51 ± 0.09	0.72 ± 0.06	0.75 ± 0.04
US-horn + 2 mg/l O_3	2366 ± 90	1.53 ± 0.06	0.84 ± 0.04	0.89 ± 0.03
US-horn + 3 mg/l O_3	2471 ± 100	1.72 ± 0.05	1.02 ± 0.02	1.13 ± 0.05
US-horn + 4 mg/l O_3	2471 ± 100	1.72 ± 0.05	1.02 ± 0.02	1.13 ± 0.06
US-bath + 0.5 mg/l O_3	11391 ± 1000	5.16 ± 0.2	1.62 ± 0.03	2.35 ± 0.09
US-bath + 1 mg/l O_3	12739 ± 1000	5.55 ± 0.1	1.85 ± 0.08	2.84 ± 0.08
US-bath + 2 mg/l O_3	14220 ± 1050	5.54 ± 0.3	1.85 ± 0.08	2.84 ± 0.06
US-bath + 3 mg/l O_3	12403 ± 1050	3.71 ± 0.09	1.07 ± 0.06	1.69 ± 0.06
US-bath + 4 mg/l O_3	13300 ± 2000	3.71 ± 0.08	1.07 ± 0.05	1.69 ± 0.08
Hydrodynamic cavitation at 5.17 bar + 0.5 mg/l O_3	57013 ± 2500	8.82 ± 0.2	5.36 ± 0.1	5.43 ± 0.1
Hydrodynamic cavitation at 5.17 bar + 1 mg/l O_3	59939 ± 2000	10.34 ± 0.3	5.66 ± 0.1	5.92 ± 0.2
Hydrodynamic cavitation at 5.17 bar + 2 mg/l O_3	65664 ± 2025	10.72 ± 0.4	6.59 ± 0.2	6.63 ± 0.1

cell membranes of the microorganisms, which result in the rupture of the membranes, affecting the cell viability and thus disinfection is achieved. As the concentration of O_3 increases, the nascent oxygen formed also increases which in turn increases the rate of disinfection. For the HPC bacteria and the indicator microorganisms, disinfection studies were carried out using 0.5, 1, 2, 3 and 4 mg/l O_3 and highest rate of disinfection was obtained with 4 mg/l O_3.

From Table 3, it can be observed that the rate constant in the case of the ultrasonic bath is more than the ultrasonic horn for the HPC bacteria and the indicator microorganisms. This is because the cavitational zone in the case of the ultrasonic horn is restricted to the tip of the horn and hence only those microorganisms present around the tip get killed, whereas in the case of the bath the cavities are formed uniformly over the entire liquid volume.

When ozone is added to water before subjecting it to ultrasonication in the bath or the horn, the overall disinfection rate obtained is higher than that obtained when only the horn or the bath is used. This can be explained as follows:

1. The most common explanation for the influence of ultrasonics is the theory of the disaggregation of flcs of microorganisms. This concept has been accepted by various authors [1,2].
2. Another hypothesis is that of Kryszczuk (1962) in [1] who reports a transient rupture of chemical bonds between molecular components of cellular membranes which results in an increase in permeability of substances in general [1].
3. Boucher et al. [23] assume ultrasonic acceleration of diffusion allowing more rapid penetration of the toxic gas molecule into the microorganism.
4. Dahi [1] states that the disinfectant and oxidant of ozonation are the free radicals which are produced when ozone decomposes. Ultrasonic treatment increases the ozone decomposition and the activity of free radicals in water. When the activity of free radicals is attained, a very rapid inactivation of bacteria is observed.

In the case of HPC bacteria as well as indicator microorganisms, the overall rate of disinfection at the end of 15 min of treatment increases with an increase in the concentration of ozone up to 3 mg/l ozone concentration and then remains constant. Thus the rates obtained at 3 and 4 mg/l ozone concentration are same. However, synergism (i.e. overall disinfection rates are higher than additive) is observed only up to 2 mg/l ozone. At 3 and 4 mg/l dosage of ozone, the rates obtained for the hybrid process (horn + ozone and bath + ozone) are less than additive (Table 3). The disinfectant and oxidant from ozonation are the nascent oxygen atoms which are produced when ozone decomposes. Ultrasonic treatment increases the ozone decomposition and the activity of nascent oxygen atoms in water. When the activity of free radicals is increased, a very rapid inactivation of bacteria is observed. This is evident from the increase in the rate of disinfection obtained for the hybrid process with an increase in the ozone concentration. However, the overall rate of disinfection obtained when only ozone is used at a concentration of 3 and 4 mg/l, itself is very high. Due to this, at 3 and 4 mg/l dosage of ozone, the rates obtained for the hybrid process (horn + ozone and bath + ozone) are less than additive.

In the case of the HPC bacteria, maximum synergism is observed for horn + 1 mg/l ozone (Table 3). The rate obtained for horn + 1 mg/l ozone is similar to the rate obtained with only 2 mg/l ozone alone (Table 3). This means that, by employing the hybrid process of horn and ozone, the concentration of ozone required for disinfection can be reduced by half.

Similar results were obtained in the case of the indicator microorganisms. The overall disinfection rate of more than additive was obtained, and this increase over additive is almost same for 0.5, 1 and 2 mg/l of ozone. At 3 and 4 mg/l ozone, the rates obtained for the hybrid process of horn and ozone are less than additive (Table 3). The rate obtained for horn + 1 mg/l ozone is similar to the rate obtained with only 3 mg/l ozone alone in the case of the total coliforms and faecal coliforms (Table 3). For faecal streptococci, the rate obtained for horn + 1 mg/l ozone is similar to the rate obtained with only 2 mg/l ozone (Table 3). Here, again, by employing the hybrid process of horn and ozone, the concentration of ozone required for disinfection can be reduced by half or one-third depending upon the type of microorganism.

Similar results were obtained in the case of the hybrid process of ultrasonic bath and ozone. In the case of the HPC bacteria, maximum synergism is observed for bath + 2 mg/l ozone (Table 3) and in the case of the indicator microorganisms, maximum synergism is observed for bath + 1 mg/l ozone (Table 3).

Again in the case of hydrodynamic cavitation the overall rate of disinfection is increased when ozone is added. The explanation for this is similar to that given for ultrasonication. Here also it was observed that the overall disinfection rates obtained for the combination of hydrodynamic cavitation and ozone was more than additive in the case of the indicator microorganisms and the HPC bacteria.

From Table 3, it can be seen that the values of the overall rate of destruction differ slightly for each of the microorganism studied even though the trend remains the same for all. This can be attributed to the difference in the cell wall structure of these microorganisms, which in turn affects their susceptibility to the techniques studied in this work.

4.4. Energy effiiency and cost of treatment

Table 4 gives the energy effiiency and the cost of the disinfection techniques. The method employed to calculate these values have been discussed earlier [15]. According to the United States Public Health Services (USPHS), the

Table 4
Energy efficiency and cost of treatment [a]

Disinfection technique	Microorganism	Extent of disinfection based on electrical energy consumption (CFU killed/J)	Extent of disinfection based on actual energy dissipated (CFU killed/J)	Cost (US$/l)
2 mg/l O_3	Total coliforms	–	–	9×10^{-7}
	Faecal coliforms	–	–	9×10^{-7}
	Faecal streptococci	–	–	9×10^{-7}
Ultrasonic horn	Total coliforms	$5.09 \pm 0.1 \times 10^{-4}$	$1.67 \pm 0.1 \times 10^{-2}$	0.035
	Faecal coliforms	$7.40 \pm 0.1 \times 10^{-5}$	$2.43 \pm 0.1 \times 10^{-3}$	0.25
	Faecal streptococci	$7.40 \pm 0.4 \times 10^{-5}$	$2.43 \pm 0.4 \times 10^{-3}$	0.25
Ultrasonic horn + 2 mg/l O_3	Total coliforms	$2.3 \pm 0.2 \times 10^{-3}$	$7.9 \pm 0.2 \times 10^{-2}$	0.008
	Faecal coliforms	$1.3 \pm 0.3 \times 10^{-3}$	$4.7 \pm 0.3 \times 10^{-2}$	0.014
	Faecal streptococci	$1.7 \pm 0.4 \times 10^{-3}$	$5.9 \pm 0.4 \times 10^{-2}$	0.010
Ultrasonic bath	Total coliforms	$2 \pm 0.1 \times 10^{-2}$	$5.71 \pm 0.1 \times 10^{-2}$	0.0006
	Faecal coliforms	$8.14 \pm 0.5 \times 10^{-3}$	$2 \pm 0.5 \times 10^{-2}$	0.0022
	Faecal streptococci	$1.8 \pm 0.3 \times 10^{-2}$	$4.62 \pm 0.3 \times 10^{-2}$	0.0008
Ultrasonic bath + 2 mg/l O_3	Total coliforms	$2.1 \pm 0.4 \times 10^{-2}$	$7.2 \pm 0.4 \times 10^{-2}$	0.0008
	Faecal coliforms	$8.8 \pm 0.6 \times 10^{-3}$	$2.9 \pm 0.6 \times 10^{-2}$	0.002
	Faecal streptococci	$1.2 \pm 0.5 \times 10^{-2}$	$4.1 \pm 0.5 \times 10^{-2}$	0.001
Hydrodynamic cavitation (5.17 bar)	Total coliforms	$2.9 \pm 0.6 \times 10^{-3}$	$3.2 \pm 0.6 \times 10^{-3}$	0.006
	Faecal coliforms	$1.7 \pm 0.3 \times 10^{-3}$	$1.9 \pm 0.3 \times 10^{-3}$	0.010
	Faecal streptococci	$2.3 \pm 0.2 \times 10^{-3}$	$2.5 \pm 0.2 \times 10^{-3}$	0.008
Hydrodynamic cavitation (5.17 bar) + 2 mg/l O_3	Total coliforms	$5.9 \pm 0.5 \times 10^{-3}$	$6.4 \pm 0.5 \times 10^{-3}$	0.003
	Faecal coliforms	$3.2 \pm 0.1 \times 10^{-3}$	$3.5 \pm 0.1 \times 10^{-3}$	0.005
	Faecal streptococci	$3.8 \pm 0.1 \times 10^{-3}$	$4.2 \pm 0.1 \times 10^{-3}$	0.004

[a] Cost of O_3 used has not been considered as it is negligible (approx. 9×10^{-7} US$).

raw water supply containing coliforms not in excess of 5000/100 ml can, with modern water treatment processes, produce potable water meeting the bacterial standards. Drinking water thus produced should not contain more than 1 coliform/100 ml. According to the EEC Guidelines, 1975, the maximum permissible limit for drinking water is 1000 count/100 ml at 37 °C. Total coliforms/100 ml, faecal coliforms/100 ml and faecal streptococci/100 ml should be zero. Hence, 100% disinfection was selected as the criteria for calculation. A sample calculation is shown in Appendix A.

From Table 4, it can be seen that the ultrasonic bath is more energy efficient as compared to the ultrasonic horn. Addition of ozone increases the energy efficiency in the case of the bath and the horn because the rate of disinfection has increased i.e. greater number of microorganisms are killed for same amount of energy utilised. Similarly, in the case of hydrodynamic cavitation at 5.17 bar, addition of 2 mg/l of ozone increases the energy efficiency by almost twice that obtained with only hydrodynamic cavitation at 5.17 bar. Again it can be seen from Table 4, that the ultrasonic bath is the most energy efficient in terms of CFU killed per joule of power consumed among the various physical techniques used in this study and the hydrodynamic cavitation set-up operating at 5.17 bar in combination with ozone appears to be the second best. The method of estimation of the energy is based only on the electrical energy consumption and the equipment's electrical to mechanical efficiency has not been considered. However, in terms of actual energy dissipated which accounts for the energy dissipation efficiency of the concerned equipment (transformation of electrical to mechanical) is considered then the order of efficacy of a method could be different. Thus when large-scale physical water treatment is desired, hybrid techniques will be an economical choice in terms of energy consumption compared to ultrasonication alone which appears to be suitable on a relatively small scale.

Cost plays a vital role in the selection of a suitable disinfection technique, which in turn would affect the overall economics of a water treatment scheme. An ideal disinfection technique is one, which is able to bring down the bacterial population to the desired level, and is also economical. Hybrid methods like the use of hydrodynamic cavitation + ozone and acoustic cavitation + ozone appear to be one such technique. However, the cost of treatment is considerably more as compared to the use of ozone alone (Table 4). Costing for all the equipment studied in this paper is done on the basis of actual electrical energy, considering cost of electricity as Rupees (Rs.) 3/kWh ($ 1.00 ≅ Rs. 45). Cost of ozone has been calculated by considering the cost as Rs. 20/kg and the dosage as 2 mg/l. Chemical disinfection techniques i.e. treatment with ozone is cheaper by one or two orders of magnitude than the hybrid methods described in this paper. However, the disadvantages associated with chemical treatment such as the formation of toxic byproducts could be reduced or altogether eliminated by

these hybrid methods, although this is not assessed in this paper.

In most of the treatment plants, water is available at considerable hydrostatic heads or pressures, which is then reduced using pressure reduction stations to make it suitable for chemical treatment such as chlorination or ozonation. The design of these pressure reduction stations can be changed so as to make them work in a hydrodynamic cavitation mode, without the supply of any additional energy. This is likely to reduce the treatment cost and also the quantity and the cost of the chemicals used in the treatment. Thus, hydrodynamic cavitation if used in a hybrid mode, shows a considerable promise.

5. Conclusions

1. From the studies carried out in this work, it can be observed that hybrid techniques are far superior for treating water as compared to any individual physical treatment technique. Thus the combination of hydrodynamic cavitation, and ozone proved to be an effiient method of water disinfection.
2. The hybrid technique described in this paper not only reduces the HPC bacteria (CFU/ml) but also reduces the total coliforms, faecal coliforms and faecal streptococci, which are considered as the indicators of pollution in drinking water.
3. In terms of energy effiiency, which is an important criteria for large-scale water disinfection, the above-mentioned hybrid process appears to be very attractive.
4. Employing such hybrid techniques can also reduce the dosage of the chemical disinfectant required. Thus by using the combination of ultrasonic horn and ozone or hydrodynamic cavitation and ozone, the concentration of ozone required for disinfection was reduced to half or one-third depending upon the type of microorganism.

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Appendix A. Calculation of energy efficiency and cost of treatment of total coliforms by ultrasonic horn as reported in Table 4

- Energy effiiency:
  Time of treatment = 15 min (900 s)
  Volume = 100 ml
  Electrical consumption = 240 W
  Initial microbial count = 200 total coliforms/100 ml
  At the end of 15 min, microbial count = 90 total coliforms/100 ml
  ∴ Total coliforms killed in 15 min = 110 total coliforms/100 ml
  Total coliforms killed/W of power consumed = 110 CFU total coliforms killed/100 ml/240 W = 0.458 total coliforms killed/100 ml/W
  ∴ Total quantum coliforms killed/J of power consumed = 0.458 total coliforms killed/100 ml/W × 100 ml/900 s = 0.458 total coliforms killed/100 ml/J s × 100 ml/900 s = 5.09×10^{-4} total coliforms killed/J
- Cost of treatment:
  Energy effiiency = 5.09×10^{-4} total coliforms killed/J
  To reduce total coliforms from 100/100 ml to 0/100 ml
  Energy required = $100/5.09 \times 10^{-4}$ = 196463.65 J/100 ml = 1964636.5 J/l = $1964636.5 \times 2.7778 \times 10^{-7}$ kWh/l
  Considering 1 kWh = \$ 0.066 = $1964636.5 \times 2.7778 \times 10^{-7} \times$ \$ 0.066/l = \$ 0.035/l

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