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A study of low temperature inactivation of fecal coliforms in electrolyte solutions using hot air bubbles

Xinkai Xue, Richard M. Pashley*

School of Physical, Environmental & Mathematical Sciences, UNSW Canberra, Northcott Drive, Canberra, ACT 2610, Australia, Tel. +61 425333527; email: xinkai.xue@student.adfa.edu.au (X. Xue), Tel. +61 2 62688482; Fax: +61 2 62688298; email: r.pashley@adfa.edu.au (R.M. Pashley)

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ABSTRACT

A novel method to inactivate fecal coliforms in aqueous solutions, using a stream of hot air bubbles, without heating the solution above about 50°C was studied in this work. Initially, it was found that at high salt concentrations (e.g. 0.15 M NaCl), where bubble coalescence is inhibited, modest but consistent coliform inactivation rates were obtained for a range of fecal coliform contamination levels. That is, the coliform densities drop at a rate of 4% per min over the range 550–14,000 CFU/100 mL. More importantly, an analysis of the likely mechanisms involved in the inactivation process led to the use of lower level salt concentrations, targeted specifically at a reduction in the repulsive interaction forces between typical coliforms and hot air bubbles, rather than at bubble coalescence inhibition. The results obtained support the view that surface forces can strongly influence the coliform inactivation rate and that the addition of low concentrations of, for example, $CaCl_2$, can increase inactivation levels by more than 1,000 times, without affecting bubble coalescence and bubble size.

Keywords: Thermal inactivation; Low temperature inactivation; Sewage treatment; Bubble coalescence; Surface forces; Electrical double layer forces; Van der Waals forces

1. Introduction

The development of new technologies is of importance in solving many current water purification and wastewater treatment challenges. In the water treatment industry, this often means reducing energy consumption, generating value from the wastewater, developing more flexible processes that meet varying feed water qualities, or a combination of all these objectives. Water sterilization is an integral part of these water treatment and recycling processes [1–4]. Current water inactivation methodologies used industrially often have the following limitations. For example, UV irradiation treatment can only be used in low turbidity water and high levels of color present in the water will also reduce its effectiveness [5]. Ozone and chlorine chemical oxidation, even at low concentrations, can be potentially toxic and hazardous to humans and the local environment. The work reported here is based on a study of a new, potentially safer, technology, using a bubble column process initially developed for use in on-site household sewage water treatment and recycling.

*Corresponding author.

The use of the bubble column for inactivation is based on the observation that a continuous flow of bubbles into a bubble column produces substantial evaporative cooling effects and hence hot gas bubbles rapidly transfer their heat to the solution [6]. For instance, bubble columns cool the water or salt solution to about 8°C at steady state, even with a continuous inlet air flow at 22°C. This temperature reduction is independent of air flow rate and bubble size [6,7]. A theory has been developed to explain these results, which is simply based on the steady state thermal balance created as new, warm bubbles enter the column and evaporate precisely that amount of water equivalent to the thermal energy supplied by the bubble to the (cooler) column [6]. This situation is described by the following equation:

$$\left[\Delta T \times C_p(T_e)\right] + \Delta P = \rho_V(T_e) \times \Delta H_{vap}(T_e)\left(\text{in units of } \mathrm{Jm^{-3}}\right) \quad (1)$$

When the bubble column has reached its steady state temperature (T_e), the amount of heat (and work) given by the difference (ΔT) between the inlet gas temperature (T_i) and the temperature of the gas as it exits the system (T_o) multiplied by the specific heat of the gas, at constant pressure, in units of $\mathrm{Jm^{-3}\,K^{-1}}$ is balanced by the standard enthalpy of vaporization of water at that column temperature. In the ideal situation, T_o will be equal to the steady state temperature of the column (T_e). The ΔP term accounts for the work done per unit volume of the gas entering the column due to the decrease in pressure of the gas as it passes through the column. This work is given by the pressure difference (ΔP) between the point just before the gas enters the sinter and atmospheric pressure, into which it is released as the gas leaves the column. It should be noted that in this dynamic balance of energies the work done by the reduction in volume of the gas, on cooling, is taken into account in the C_p term and the work done by the expansion of the bubbles, on absorbing water vapor, is included in the ΔH_{vap} term.

In a bubble column, air bubbles in the size range 0.5–2.5 mm rise at a limited speed of about 10–35 cm/s, in quiescent water, because of their shape oscillations which dampen rise rate [8]. Meanwhile, these oscillations also accelerate the rate of transfer of water vapor into the bubbles and thus enhance the rate of vapor collection. As a result, equilibrium vapor pressure within the bubbles is therefore attained quite quickly, within a few tenths of a second [8], which means that the heat from the bubbles produced at a sinter is transferred to the solution within a rise distance of about 5–10 cm. This suggests that using the bubbles inside a dense bubble column is a quite efficient way for heat transfer from hot air bubbles to the surrounding solution. Moreover, some interesting results were obtained with added salt (NaCl) at levels above 0.17 M, which inhibit bubble coalescence [9], and hence produces finer bubbles and cuts down the time to half for the column to reach the steady state operating temperature [6]. These observations led to the recent development of a new bubble column method to thermally inactivate microorganisms, such as fecal coliforms in water, by using a significantly lower amount of energy than the traditional method of boiling water [7].

The rapid transfer of heat from hot bubbles to produce water evaporation within a bubble column can be used to sterilize without raising the water temperature above 50°C. The initial report [7] was focused on using the bubble column process for highly contaminated water and did not examine the effects at lower levels, which leaves open the question of whether the process should be identified as a secondary or tertiary water treatment process. In the present study, the effects of the hot bubbles have been quantified at both high and low levels of fecal coliforms and this has been used as a basis for a detailed analysis of the mechanisms involved. In the earlier work, 0.15 M NaCl was added into the column to enhance treatment efficiency by reducing bubble size and increasing bubble density. However, in many practical situations, the use of high salt levels presents problems due to the large amounts of treated water and water recycling regulations and standards. Therefore, the need for added salts to inhibit bubble coalescence and produce finer bubbles for the coliform inactivation process has been re-examined in this study.

The present work is primarily focused on a study of the electrostatic forces between bubbles and coliforms in solutions, which is considered to be the key to an improved bubble treatment process. The surface of air bubbles in neutral water is negatively charged, apparently because the bubble surface selectively adsorbs hydroxyl ions from the surrounding water [10]. Since typical bacterial cells are also negatively charged [11], there should be a natural electrostatic repulsion between coliforms and air bubbles, which will be salt dependent, and a repulsive, short range, van der Waals force, which will be less dependent on the salt level. The natural biopolymers present on the surface of most cells [12] are also negatively charged and will also be affected by the type and level of salt in solution.

The zeta potentials of air bubbles [13,14] and coliforms [15] have been measured in various salt solutions. The zeta potentials of *Escherichia coli* (*E. coli* type: D21 g), a species of fecal coliform, have been measured in different types of electrolyte, such as KCl and $CaCl_2$, and at different concentrations [15]. Interestingly, at the same concentration, the potentials in $CaCl_2$ solutions displayed significantly reduced values compared with those in KCl solutions, which suggests that the repulsive forces between these cells and with air bubbles will be significantly reduced. It is found that only a relatively small amount of $CaCl_2$ is required to produce these effects. Zeta potential measurements can also be used to calculate the corresponding surface charge densities, which can be used to estimate the change in electrostatic surface forces between coliforms and air bubbles. In the present work, we have studied the effects of this reduction in electrostatic repulsive forces, between coliforms and bubbles, on the inactivation rate caused by the collision of coliforms with hot bubbles. The discovery that surface forces influence bubble column inactivation of coliforms will have wide ranging applications to the treatment processes for many other micro-organisms. In addition, the use of low-level additives to influence these forces offers great potential for improved water treatment efficiency.

2. Materials and methods

2.1. Materials

2.1.1. Contaminated water source

In this study, a natural water source was used for the fecal coliform feed water to more closely model the type of water expected from secondary/tertiary-treated sewage water. All samples were taken from a natural lake in a region which used to be waterfowl habitat ponds, which normally provided sufficiently high densities of fecal coliform bacteria [16], between September 2013 and January 2014 in Canberra. The samples were immediately stored at 4°C in the dark and processed within 48 h after collection. Before all experiments, the visible suspended solids in the water samples were removed by coarse filtration. Low density (550 colony-forming-units (CFU) per 100 mL) fecal coliforms were observed at mean temperatures around 25°C, during September 2013–November 2013, while medium and high densities (5,500–14,000 CFU/100 mL) were observed at greater mean temperatures, around 30°C, during November 2013–January 2014.

2.1.2. Biological water quality indicator

For monitoring and evaluating the inactivation process, fecal bacteria were chosen as water indicators because they are often used as indicators of possible sewage contamination [17]. They also indicate the possible presence or absence of pathogenic bacteria, viruses, and protozoan that also live in human and animal digestive systems [18].

2.2. A pilot bubble column process

The bubble column process used in these studies is described schematically in Fig. 1. From left to right, the air was pumped by a HIBLOW air pump, then through a dry tank containing silica-gel. In the air heater, the air was heated to maintain 150°C just above the sinter surface, where a thermometer was applied to monitor the temperature. Typically, a 40–100 μm pore size glass sinter (type 2) of 135 mm diameter was fitted to the base of the bubble column where the hot air was bubbled through the sinter into 250 mL of contaminated water. The room temperature air flow rate was typically 25 L/min, measured just prior to the heater. However, the actual flow rate of 150°C air pumped into the column was more than that due to expansion. The heated air flow rate into the solution could be calculated as: measured air flow rate $\times T_{\text{sinter surface}}/T_{\text{before heater}}$ with T in Kelvin. So the real flow rate into the sinter was almost 36 L/min, when the flow meter indicated a value of 25 L/min. However, because of the rapid cooling of the bubbles due to evaporation at the water–air interface, only the room temperature air flow rate is reported here. The actual air flow rate within the column would only be marginally greater (by about 10%) than the room temperature air inlet flow rate because of the modest temperature increase, of up to 47°C, in the column.

2.3. Preparation of NaCl and $CaCl_2$ solutions

In the initial studies, NaCl ($\geq$99% purity, obtained from Sigma–Aldrich) was added to the contaminated water to prepare a 0.15 M solution, in order to inhibit bubble coalescence and so produce a higher density of smaller bubbles, with a higher air/water interfacial area [4]. However, high salinity is also known to contribute to the mortality of fecal coliforms in water, caused by osmotic pressure, which can cause growth suppression in fecal bacteria [19]. Table 1 summarizes the effects of salt level on the survival rates of *E. coli*. Hence, to avoid the effects by salinity and storage time, the initial experiments used NaCl concentration levels at up to 1% salinity (i.e. 0.17 M). In addition,

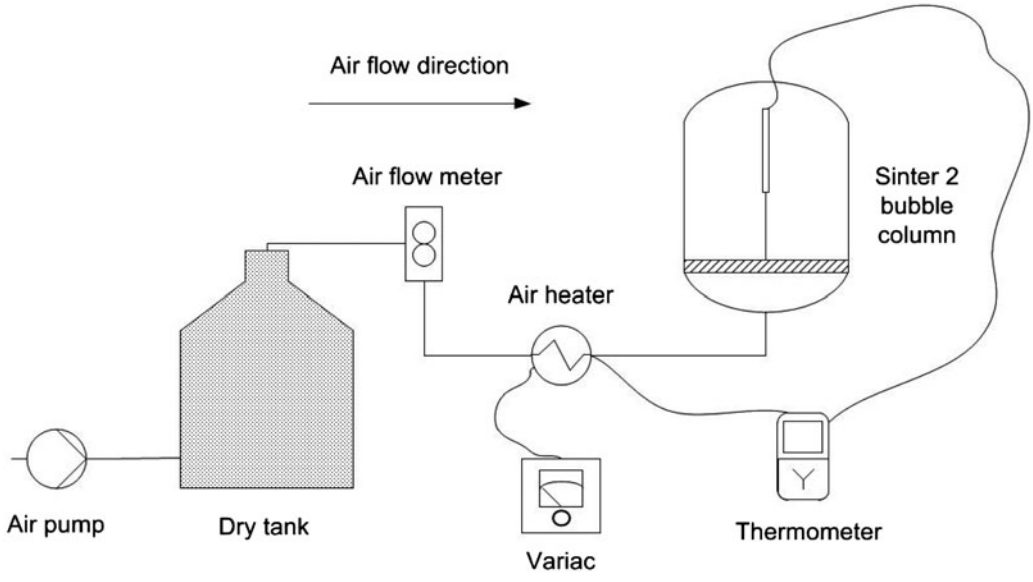

Fig. 1. A schematic pilot-scale bubble column system.

Table 1
Percent survival of *E. coli* in seawater adjusted to selected salinities [19]

Salinity (%)	Exposure (d)	Survival (%)
1	2	100.6
	5	87.6
	8	53.5
1.5	2	27.9
	5	11.7
	8	7.1
2.5	2	8.6
	5	5.1
	8	4.3
3	2	1.7
	5	0.7
	8	2

the water samples were changed every two days, in order to maintain the coliforms in a healthy condition. It should also be noted that adding these levels of NaCl has no clear detrimental influence on growing coliform colonies in the incubation process [20]. The 0.01 M $CaCl_2$ added to the experimental solutions was obtained from $CaCl_2{\cdot}2H_2O$ ($\geq 99\%$ purity) from Sigma–Aldrich.

However, using the bubble column process produces a slight increase in salt level due to the water vapor generated into the bubbles during the process. To overcome this effect in these studies, an initial NaCl concentration of 0.15 M was used in the column. Over a typical 40 min experiment with a column temperature of about 47.5°C, the total water vapor evaporated would increase the NaCl concentration to about 0.18 M. However, a considerable portion of the water vapor would typically recondense during the experiments and hence the actual water loss would be significantly less than that in the calculation. Consequently, use of 0.15 M NaCl concentration in these thermal inactivation studies should not introduce any salt effects on coliform viability.

2.4. Water quality evaluation method

The membrane filtration (MF) technique [21,22] was used to estimate fecal coliform bacteria populations in the water for all experiments. In each experiment, a required amount of water sample was collected from 10 to 15 mm above the central area of the sinter, using a sterile syringe. Typically these samples were diluted with sterilized water to optimize the fecal coliform count. These samples were filtered through sterile 47 mm gridded membrane filters made from mixed esters of cellulose with 0.45 μm pore size. The filters were then placed in petri dishes containing m-FC Agar broth with rosolic acid and incubated for a period of 24 ± 2 h at 44.5°C. The growth media was obtained from Millipore Corporation. This growth media is specifically designed to facilitate the growth of fecal coliforms and suppresses other micro-organisms [23]. Following incubation, the petri dishes were removed from the incubator and each dish was counted for fecal coliform colonies. It is important to notice that only bluish spots should be counted as

fecal coliform colonies. Those colonies with other color such as gray should not be included into the count.

The ideal sample volume of wastewater for coliform testing should yield 20–80 colony-forming units or CFU per filter. For example, if the colony counts per plate were either under 20 CFU or over 80 CFU in one plate, this dish would be regarded as having an unacceptable count [17], either because the numbers are too low or too high, where individual colonies would inevitably become combined.

For the low fecal coliform density experiments, the same volume and same fecal coliform density were studied, with 150°C of hot dry inlet air at 25 L/min flow rate, and different operation times. Around 100 mL of treated water was collected in each experiment and analyzed using the MF procedure. The water samples used for these experiments were collected from the lake at the same time and used within two days, because the reproducibility within samples was good, but sample to sample reproducibility was variable. Then, all of the individual experimental results were combined to produce averaged data. By comparison, for medium and high coliform densities, typically, only 2 mL samples were required with the MF procedure, to make sure that there were reasonable and sufficient coliform numbers in each dish.

2.5. Experimental instruments

Electrical conductivity and pH values of water samples were measured using a EUTECH PC700 instrument. Turbidity values were obtained using a HACH 2100AN Turbidimeter.

Solution particle counting was carried out using a Spectrex laser particle counter Model PC-2300. In this case, the number of particles in the lake water samples exceeded the maximum countable number for this instrument. In order to avoid coincident counts, ideally, one measurement should aim at less than 1,000 particles per mL [24]. Therefore, the lake water samples were diluted with commercial bottled water (drinking), which was used because this water had a very low background particle count (of about 5 particles greater than 1 μm per mL).

The photographs of the bubbles in the column were taken with a Pentax K-5 II camera with a shutter speed of 1/8,000 s. The size range of the bubbles could be measured from high speed photographs taken with this camera, since a 1 mm diameter bubble would only move around 3% of its diameter at a mean rise velocity of 25 cm/s [8].

A Millipore single chamber incubator was used to process the petri dishes at 44.5°C for about 24 ± 2 h.

3. Results and discussion

3.1. Characterization of the water source

The basic physical parameters of the collected water were measured and are summarized in Table 2. Conductivity and pH were monitored before the experiment, as showed as Table 2. The turbidity values for all collected samples were between 20 and 30 NTU. The natural water particle number varied, depending on weather conditions and collection location. The particles ranged from 1 to 100 μm in diameter. Similar results for natural lake water were also reported [25].

3.2. Bubble column coliform inactivation in NaCl solutions

3.2.1. Experimental study of bubble column coliform inactivation in NaCl solutions

Initially, a study was carried out on the effect of bubble column coliform inactivation with added NaCl to produce maximum bubble coalescence inhibition (which occurs at 0.17 M) in the low coliform density experiments using a continuous flow of hot air, at 150°C, at a flow rate of 25 L/min, with different treatment times. A combination of all sub-experiments' results is shown as Fig. 2. The results of lake water with added 0.17 M NaCl showed that each separate experiment followed a reproducible order with time, even with such low CFU/100 mL values. In other words, the system gave stable and reproducible results, even for low coliform densities.

To exclude any possible effects of increasing salinity in the columns, during water vapor loss, as mentioned in Section 2, the added salt concentration was slightly reduced. A series of experiments with low contamination level water, with and without added NaCl (at 0.15 M), were carried out. The results obtained are also summarized in Fig. 2, which shows the effect on coliform inactivation rate, with and without added 0.15 M salt, at 25 L/min flow rate of 150°C inlet air. The results obtained indicate that the fecal coliform survival rate in the solution with 0.15 M NaCl was quite similar to that in 0.17 M NaCl, but was much less than without added salt, especially within the first 20 min, when the solution temperature within the column was around 45°C.

It has been established that an inhibitory influence on metabolism and growth in non-fecal coliforms occurs at 44.5°C, but fecal coliforms are essentially unaffected [26]. Therefore, these results demonstrate that the lethal effect on the fecal coliforms was not the warm environment in the column, but the transient heat transferred from the hot bubbles during collisions.

Table 2
Basic properties of the lake water feed

Electric conductivity (μs/cm)	pH value	Turbidity (NTU)	Particle numbers (per mL)
178 (±20)	7.32 (±1)	20–30	0.2–0.8 million

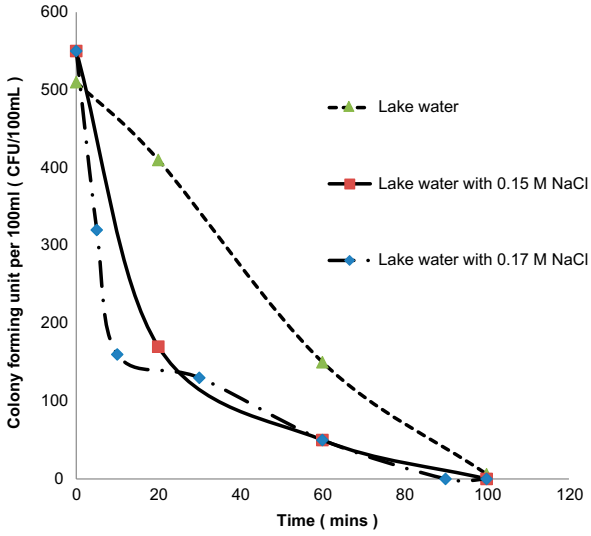

Fig. 2. Sum of individual experiments of the changes in colony forming units per 100 mL with operating time for a (sinter type 2) bubble column containing 250 mL raw lake water without and with added 0.17 and 0.15 M NaCl, using 150°C dry air inlet at a flow rate of 25 L/min.

In addition, any effects due to flotation and dispersed coliforms adhering to the column walls were tested in a "blank" experiment using unheated, room temperature, air flow, over the same time, and at the same flow rate. The results obtained showed that the number of coliforms remained the same following the cool air flow process, which indicated that the bubbling process itself did not contribute to the coliform inactivation.

It should be noted that unlike raw lake water experiment, the presence of added salt leads to bubble coalescence prevention and increased bubble density in the bubble column (Fig. 3(a) and (b)). This enhances the effective and rapid transfer of heat from the smaller and more numerous air bubbles (Fig. 3(a)) to the surrounding water, and so improves the disinfect rate, as illustrated in Fig. 2.

3.2.2. Proposed theory of bubble column coliform inactivation in NaCl solutions

Shahid et al. [7], reported a similar decrease in fecal coliform densities using much more heavily

(a) Raw lake water with 0.15M NaCl

(b) Raw lake water

(c) Raw lake water with 0.01M $CaCl_2$

Fig. 3. Photographs of (sinter type 2) bubble columns containing 250 mL under different solution conditions, with 150°C dry air inlet at a flow rate of 25 L/min.

contaminated water ($\geq 1.0 \times 10^5$ CFU/100 mL). Treatment at these contamination levels more closely approximates to secondary sewage treatment [1]. Generally, each type of treatment has different disinfecting rates and working capacities. Therefore, several different treatment types are generally combined, so

that the harmful micro-organisms can be disinfected almost completely and hence the final product can meet the necessary regulations and standards. However, this inactivation process, even for low-level contaminated water with added salt, is still as effective, which is unusual. It is reasonable to say that the bubble column process may be a useful new method to combine secondary and tertiary treatment, due to its wide working range.

Two hypothetical theories of bubble column coliform inactivation efficiency, with added 0.15 M NaCl, were developed based on the low fecal coliform densities study and the previously published [7] data. In the following equations, the density of the fecal coliforms, after t min bubble column treatment, is given by N_t.

(1) A fixed rate theory: based on a fixed rate of inactivation per min, is shown as:

$$N_t = N_{t-1} \times 0.96 \tag{2}$$

(2) A probability of inactivation theory: where the rate of inactivation will depend on the coliform density:

$$N_t = \left(1 - \left(N_{t-1} \times 10^{-6}\right)\right) \times N_{t-1} \tag{3}$$

Comparison of these models with the observed inactivation rates in medium and high densities leads to the conclusion that the fixed inactivation rate model is more consistent with the observed behavior, such as that shown in Figs. 4 and 5. These figures show that in the range of initial densities 5,500–14,000 CFU/100 mL in saline water, the empirical results were in close agreement with the fixed inactivation rate model at a rate of 4% per min.

In addition, the rate of coliform inactivation with time followed an exponential decay, as shown in Fig. 6, and suggests that the fecal coliform inactivation rate is consistent over a range of densities.

3.3. Analysis of heat transfer process

In this bubble column process, the initially hot air bubbles must produce a thin layer of heated water around the surface of the bubbles. The transient collisions between these heated water layers and the coliforms appear to be the fundamental mechanism of the coliform inactivation. This is likely to be related to the heating of membrane lipids. At temperatures over 70°C, phospholipids, the main component of cell membranes become more fluid, disrupting the integrity of the cellular membrane, and making the cell leaky. In addition to this, the membranes also play a

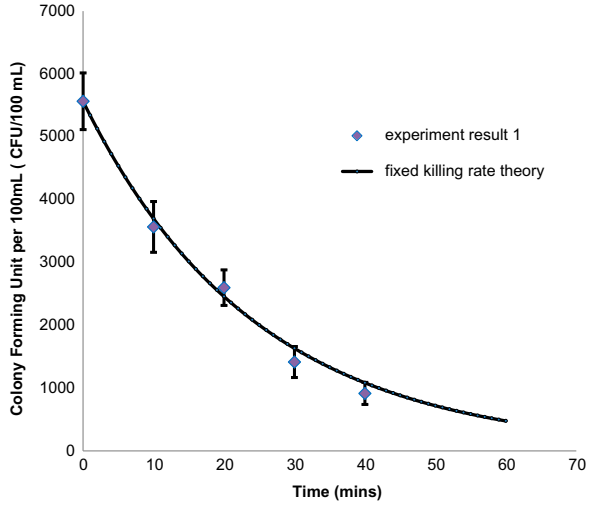

Fig. 4. Comparison of the fixed rate theory with experimental results on medium level contaminated salty water (at 0.15 M NaCl). The error bar at each data point reflects the standard deviation of three measurements.

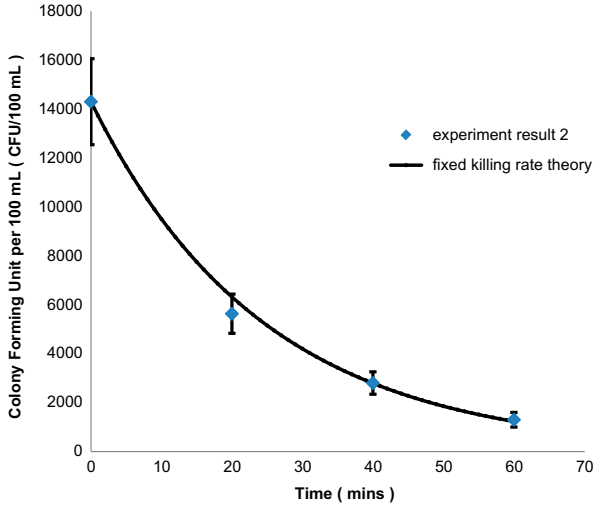

Fig. 5. Comparison of the fixed rate theory with experimental results on high level contaminated salty water (at 0.15 M NaCl). The error bar at each data point reflects the standard deviation of three measurements.

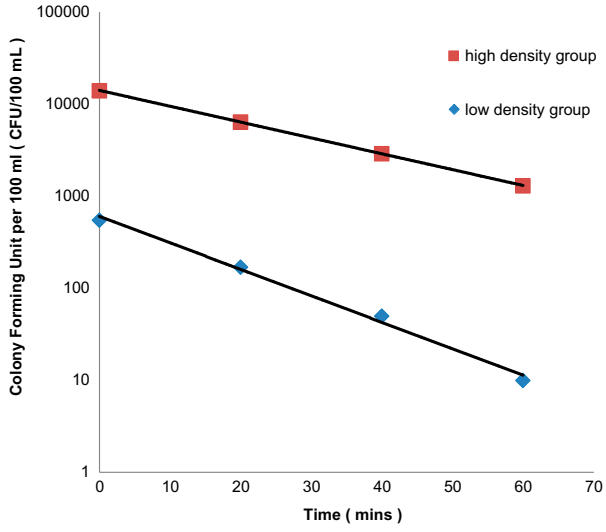

Fig. 6. Exponential decay of fecal coliform densities with time in the bubble inactivation process for two different initial contamination levels.

crucial role in cellular transport systems for moving materials into and out of the cells. Experimental results based on thermal lysis of bacterial membranes have been reported by Ray and Brock [27]. They pointed out that the destruction of the cell's membrane ultimately leads to cell inactivation.

In the column, for a 1 mm bubble, we can estimate the layer of water heated to, say, 80°C by bubbles with an initial temperature of about 150°C. Compared with the air bubbles, the size of coliforms is quite tiny, at about 0.5–2 μm [15]. The volume of a layer of (small) thickness z around a bubble is given by $4\pi r^2 \times z$. Hence, the cooling of the bubble by ΔT must determine the thickness z, in the Eq. 4:

$$C_p \Delta T V = C_{\text{water}} \Delta t 4\pi r^2 \rho_w \times z \tag{4}$$

where C_p, C_{water} are air and water heat capacities, respectively, and ρ_w is the liquid water mass density. Δt is the transient temperature increase in the water layer.

For bubbles cooling 100°C, the maximum heated water layer thickness, heated from 20 to 80°C, is about 67 nm. This estimate is consistent with the assumption that the fecal coliforms appear to be killed by heat exchange with hot air bubbles during collisions. However, both surfaces of air bubbles and coliforms are negatively charged, as mentioned before, which will create a repulsive interaction force and hence will oppose contact. This repulsive force will tend to prevent bubbles and coliforms approaching, but the extent of this effect will be determined by the range and strength of this repulsive force. Thus, the coliforms may be prevented from contacting the surface of the bubbles but they may still approach close enough, in which the distances is less than 67 nm, to be thermally inactivated. This analysis suggests that these repulsive forces will play an important role in this bubble column process. It would also be expected that the high salt levels (e.g. 0.15 M NaCl) used to prevent bubble coalescence will also reduce the repulsive electrostatic forces between bubbles and coliforms.

3.4. The effect of added $CaCl_2$ on inactivation rate

3.4.1. Analysis of the interaction theory with added $CaCl_2$

Assuming surface electrostatic interaction forces are important to bubble inactivation, the addition of $CaCl_2$ salt might be expected to have a significant effect even at low concentrations, where it will not affect bubble coalescence. This is due to the fact that the presence of divalent cations can significantly affect the surface potential and counterion distribution at negatively charged surfaces. For example, relatively small amounts of divalent ions substantially lower the magnitude of the surface potential more effectively than increasing the concentration of monovalent salt, such as NaCl, at constant surface charge density [28]. In general, calcium cations may not neutralize the surface completely but its effects on reducing surface potentials and lowering surface charge densities is substantial. For example, Kim and Walker observed a significant decrease in magnitude of the zeta potential on the surface of *E. coli* in 0.01 M $CaCl_2$ solution [15].

Increased salt concentrations produce shorter Debye lengths. Eq. 5 is reasonably accurate for low ψ_0 values, of less than 25 mV. The Debye length $(\kappa)^{-1}$ is the distance from the surface where the surface potential (ψ) has fallen to $1/e$ of its surface value (ψ_0) [11].

$$\psi(x) = \psi_0 \exp(-\kappa x) \tag{5}$$

The lake water samples used in this study had an average electrical conductivity of 178 μs/cm, from Table 2, which corresponds to less than 10^{-3} M 1:1 electrolyte, such as NaCl. This also corresponds to a Debye length greater than 10 nm. By comparison, the Debye length of 0.01 M $CaCl_2$ solution is about 1.8 nm, hence the addition of this salt will both reduce the surface potentials (or shear plane potential) and the Debye length and hence significantly reduce the electrical double layer repulsive forces.

In these experiments, the bubble sizes (average size of around 1.5 mm) were almost 1,000 times larger than coliforms. To simplify the analysis, it was assumed that the air bubbles could be considered as flat surfaces, compared with the coliforms. Hence, the double layer interaction forces could be modeled as sphere-flat interactions.

Using the Derjaguin approximation [11,28] and a precise numerical solution [29] to the Poisson–Boltzmann equation [11,28] for electrical double layer interactions, the surface interaction forces between bubbles and coliforms in different solutions were estimated from known values of the Debye lengths and surface potentials in the contaminated lake water and in 0.01 M $CaCl_2$ solution (Fig. 7). In addition to repulsive electrical double layer forces, this calculation also included van der Waals forces for this system, which are also repulsive and of short range. These results, which were calculated for the 45°C temperature in the bubble column, clearly demonstrate that the barrier to coliforms approaching bubbles is much reduced by adding 0.01 M $CaCl_2$. It was also found that the increased temperature has only a small effect on the Debye length for a given salt concentration and only a slight effect on the magnitude of the double layer interaction, through the decrease in static dielectric constant and reduced osmotic pressure.

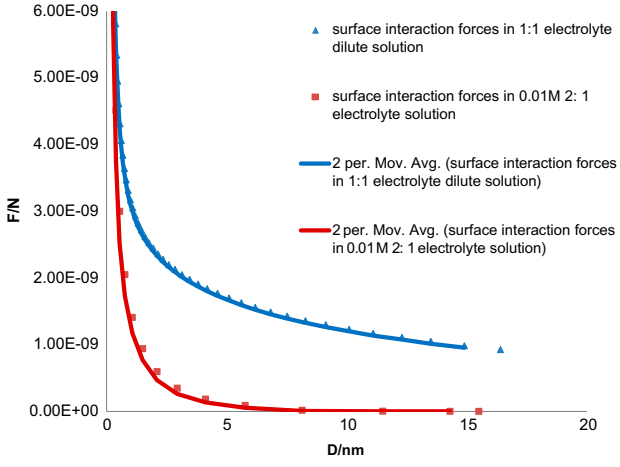

Fig. 7. The relation between surface interaction forces and separation distances between bubbles and coliforms in different electrolyte solutions, at 45°C, assuming constant surface charge densities. Upper line: surface interaction forces in 1:1 electrolyte dilute solution, such as lake water with a Debye length of 50 nm and surface charge density of −0.003 per cm^2. Lower line: forces in 0.01 M 2:1 electrolyte solution, such as $CaCl_2$ solution, with a Debye length of 1.7 nm and surface charge of −0.01 per cm^2. In both cases, the Hamaker constant was estimated to be -2×10^{-21} J, which corresponds to the hydrocarbon/water/air system [28].

3.4.2. Bubble column inactivation with added $CaCl_2$

The coliform inactivation results summarized in Fig. 8 show that adding 0.01 M $CaCl_2$ has a significant effect on the rate and is more effective than without added salt, increasing the inactivation rate from approximately 29.0 to 99.9% during 40 min treatment. The results also demonstrated that the coliform inactivation in 0.01 M $CaCl_2$ solution was far more efficient than that observed in a higher level of NaCl solution, which will, in addition, also significantly reduce bubble coalescence. It should be noted that this level of added $CaCl_2$ does not affect bubble coalescence [9]. This is further supported by visual observations of the bubble columns. The photographs (Fig. 3) were taken during these experiments and clearly demonstrate that the bubbles in both raw lake water with and without $CaCl_2$ (Fig. 3(b) and (c)) are larger and of lower density than in 0.15 M NaCl solution (Fig. 3(a)), within the bubble column. In short, these results suggest that adding $CaCl_2$ produces more effective and efficient fecal coliform inactivation, due to its effect on reducing the repulsive surface forces between the bubbles and coliforms. By comparison, no change in fecal coliform density was observed when 0.01 M $CaCl_2$ was added to lake water samples and heated to 45°C for 2 h.

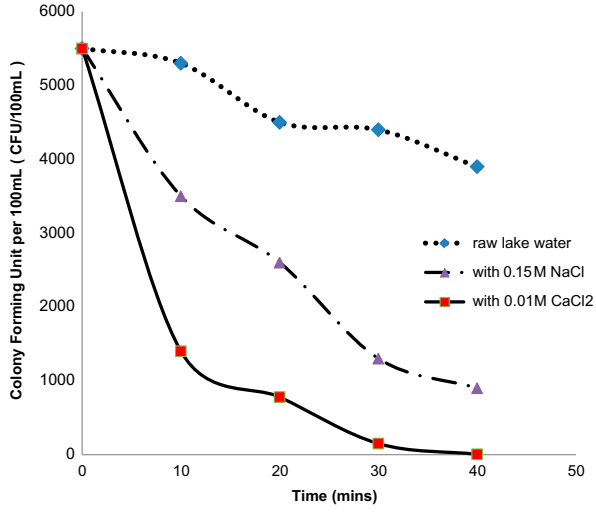

Fig. 8. Fecal coliform densities with time for (sinter type 2) bubble columns containing 250 mL raw lake water with 0.01 M $CaCl_2$, 0.15 M NaCl and without added salts, using 150°C dry air inlet at a flow rate of 25 L/min.

3.5. Effect of bubble size

It is interesting also to consider the effects of larger bubble size on treatment efficiency. The pressure (ΔP) within a bubble can be easily calculated from the *Young Laplace equation*:

$$\Delta P = 2\gamma/r \quad (6)$$

where γ is the water surface tension (at 45°C) and r is the bubble radius. For 0.01 M $CaCl_2$ solution, the mean value of the bubble radius was around 0.75 mm, which is almost twice than that observed in 0.15 M NaCl solution. Thus, the pressure inside the bubbles will be significantly lower in 0.01 M $CaCl_2$ solution and so the bubble surfaces would be less rigid and surface waves more easily produced. Such enhanced interface fluctuations might also explain, in part, some of the additional improvement observed in 0.01 M $CaCl_2$ solutions in terms of the coliform inactivation rate.

These results also imply that further improvements in the coliform inactivation rate might be achieved by other solutes, even more effective at reducing the interaction forces between bubbles and coliforms, such as $FeCl_3$ and alum and low molecular weight multivalent polymers, such as polydadmac. It may even be possible to produce suitable conditions to create an attractive electrical double layer force between bubbles and coliforms.

4. Conclusions

The novel bubble column inactivation process was found to have a wide range of operating capacities and a consistent disinfection rate, with added 0.15 M NaCl to inhibit bubble coalescence, which was used to develop an understanding of the mechanisms involved. A model of coliform inactivation was developed and this led to a study of the expected interaction forces between the bubbles and coliforms, which was then used to develop a more efficient process at lower salt levels. Low concentrations of added $CaCl_2$ substantially reduce the expected electrostatic repulsive force between coliforms and bubbles. This facilitates the approach between hot gas bubbles and the coliforms, thereby thermally inactivating the coliforms. Additionally, this level of added $CaCl_2$ did not affect the degree of bubble coalescence within the columns but significantly increased the inactivation by a factor of at least 1,000. These results indicate that other solutes may be even more effective at increasing the efficiency of the bubble column inactivation process, at even lower salt levels, extending the range of applications for this novel coliform disinfection process.

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Symbols

ΔT	—	the difference between the inlet gas temperature and the steady state temperature
C_p	—	the heat capacity of the air
T_e	—	the steady state temperature of the column
Δp	—	the pressure difference between the point just before the gas enters the sinter and atmospheric pressure
ρ_v	—	the saturated water vapor density in air at that temperature
ΔH_{vap}	—	the enthalpy of vaporization of solution
N_t	—	the coliform density at t min
N_{t-1}	—	the coliform density at $(t-1)$ min
V	—	the bubble volume
C_{water}	—	the heat capacity of water
Δt	—	the transient temperature increase in the film around the initial hot bubbles
r	—	the radius of the bubble
ρ_w	—	the liquid water mass density
z	—	the thickness of bubble layer
ψ	—	the electrical potential
ψ_0	—	the surface potential
κ	—	the reciprocal of the Debye length
Δp	—	the pressure difference between the inside bubble and solution
γ	—	the water surface tension

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