ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理 Chinese Physics B

Theoretical estimation of sonochemical yield in bubble cluster in acoustic field

Zhuang-Zhi Shen(沈壮志)

Citation: Chin. Phys. B . 2020, 29(1): 014304 . **doi:** 10.1088/1674-1056/ab6108
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Dynamics of an ultrasound contrast agent microbubble near spherical boundary in ultrasound field

Ji-Wen Hu(胡继文)[1,2], Lian-Mei Wang(王练妹)[1], Sheng-You Qian(钱盛友)[2], Wen-Yi Liu(刘文一)[1], Ya-Tao Liu(刘亚涛)[1], Wei-Rui Lei(雷卫瑞)[1]

Chin. Phys. B . 2019, 28(11): 114301 . **doi:** 10.1088/1674-1056/ab4d3f

Influence of temperature on the properties of one-dimensional piezoelectric phononic crystals

Ahmed Nagaty, Ahmed Mehaney, Arafa H Aly

Chin. Phys. B . 2018, 27(9): 094301 . **doi:** 10.1088/1674-1056/27/9/094301

Temperature rise induced by an annular focused transducer with a wide aperture angle in multi-layer tissue

Meng Qi(戚萌), Jiehui Liu(刘杰惠), Yiwei Mao(毛一葳), Xiaozhou Liu(刘晓宙)

Chin. Phys. B . 2018, 27(1): 014301 . **doi:** 10.1088/1674-1056/27/1/014301

Impact of cavitation on lesion formation induced by high intensity focused ultrasound

Pengfei Fan(范鹏飞), Jie Yu(于洁), Xin Yang(杨鑫), Juan Tu(屠娟), Xiasheng Guo(郭霞生), Pintong Huang(黄品同), Dong Zhang(章东)

Chin. Phys. B . 2017, 26(5): 054301 . **doi:** 10.1088/1674-1056/26/5/054301

Study of acoustic bubble cluster dynamics using a lattice Boltzmann model

Mahdi Daemi, Mohammad Taeibi-Rahni, Hamidreza Massah

Chin. Phys. B . 2015, 24(2): 024302 . **doi:** 10.1088/1674-1056/24/2/024302

Theoretical estimation of sonochemical yield in bubble cluster in acoustic field*

Zhuang-Zhi Shen(沈壮志)†

School of Physics & Information Technology, Shaanxi Normal University, Shaanxi Key Laboratory of Ultrasonics, Xi'an 710119, *China*

(Received 7 May 2019; revised manuscript received 10 June 2019; accepted manuscript online 12 December 2019)

In order to learn more about the physical phenomena occurring in cloud cavitation, the nonlinear dynamics of a spherical cluster of cavitation bubbles and cavitation bubbles in cluster in an acoustic field excited by a square pressure wave are numerically investigated by considering viscosity, surface tension, and the weak compressibility of the liquid. The theoretical prediction of the yield of oxidants produced inside bubbles during the strong collapse stage of cavitation bubbles is also investigated. The effects of acoustic frequency, acoustic pressure amplitude, and the number of bubbles in cluster on bubble temperature and the quantity of oxidants produced inside bubbles are analyzed. The results show that the change of acoustic frequency, acoustic pressure amplitude, and the number of bubbles in cluster have an effect not only on temperature and the quantity of oxidants inside the bubble, but also on the degradation types of pollutants, which provides a guidance in improving the sonochemical degradation of organic pollutants.

Keywords: bubble cluster models, bubble cluster dynamics, chemical kinetics, bubble temperature, strong oxidants, acoustic cavitation

PACS: 43.25.+y, 43.35.+d, 44.20.+b, 82.20.–w **DOI:** 10.1088/1674-1056/ab6108

1. Introduction

Wastewater from chemical industries, domestic lives, hospitals and/or municipal lives contains complex, hazardous organic compounds, which contaminate the fresh water bodies and might carry a large quantity of contaminants, which coexist and lead to cross reactions and have detrimental effect on human as well as aquatic life. The majority of these compounds are recalcitrant or biorefractory, *i.e.*, complete mineralization of these compounds is difficult to achieve by using biological methods.[1–3] The way of solving this problem is to develop and establish more effective and efficient waste water treatment technologies such that the complex refractory molecules degrade into simpler molecules, which is vital to combating the deteriorating water quality.[4] Advanced oxidation process (AOP) is perhaps the best choice if one desires to go for the complete mineralization of the organic component. Several AOPs have been developed in the past for effectively degrading these pollutants.[1] The advantages of AOPs basically involve the production of extremely reactive hydroxyl (·OH) radicals, which do not selectively attack the organic pollutant molecules.[3] Sonochemical oxidation by acoustic cavitation has been extensively investigated as an effective AOP for destructing a large variety of organic pollutants such as aromatic compounds. The technique of the acoustic cavitation encompasses the production of strong oxidants such as hydroxyl radicals (·OH) through the radial motion of a cavitation bubble driven by an acoustic wave.

Acoustic cavitation is a kind of micro-bubble nucleus in liquid driven by an ultrasonic wave. The bubble nuclei oscillate, grow, shrink and collapse at high speed. The collapse produces a short and ultra-high temperature release, creates a high pressure and a high-intensity electric field. Therefore, the collapse of cavitation bubbles can be likened to a "microreactor" at the moment of collapse, which is similar to a high-pressure "reaction kettle". The water vapor projected from the bulk liquid phase into the cavitation bubble splits and produces chain reactions at high temperature and high pressure, releasing highly active oxides (·HO, ·O, ·HOO, H_2O_2, $\cdot HO_2$, *etc.*). The organic contaminants inside the bubble will be combusted under both the extreme temperature and the high pressure and reacted with the oxidants[5] and supercritical water.[6]

In addition, the shock waves and microjets produced by cavitation bubbles cause oxidants to escape to the interface and aqueous solution. Clearly, this leads to rapid oxidation between the oxidants and organic pollutants in the solution. Due to the particularity of cavitation bubbles, the quantity of organic pollutants that can be degraded inside bubble is limited. Sonochemical reactions have been successfully employed for degrading the various pollutants, but the degradation degree of organic pollutants mainly depends on the concentration of strong oxidants released into the bulk solution. A great deal of previous experimental research has revealed that many factors have an effect on ultrasonic degradation, for example, the solution property, the nature of contaminant, the ultrasonic field parameter, and the driving wave formation. The solution property contains viscosity,[7] surface tension,[8] vapor pressure,[9] ambient temperature,[10] pH,[11] *etc*. The characteristics of

*Project supported by the National Natural Science Foundation of China (Grant No. 11674207).

†Corresponding author. E-mail: szz6@163.com

© 2020 Chinese Physical Society and IOP Publishing Ltd

contaminant involve initial concentration of liquid,[12] volatility, polarity, structure of pollutant,[13] *etc*. The ultrasonic field parameter comprises ultrasonic frequency,[14–17] ultrasonic intensity,[18–20] *etc*. Driving wave formation usually utilizes simple harmonic wave, square wave and triangle wave.[21,22] In addition, the reactor shape is also one of the factors affecting ultrasonic degradation.[23–29] However, in the respect of how these factors affect the quantity of strong oxidants produced such as free radicals by the acoustic cavitation, and the quantity of strong oxidants that are released into the bulk solution from the interior of bubble, researchers focused mainly on the study of single bubble cavitation.[22,30–39] In fact, cavitation bubble always exists in the form of bubble cluster, and there are thousands of microbubbles in the cluster. For the quantity of strong oxidants produced by bubble collapse, the study of a single bubble cannot replace the study of the multiple bubbles. Up to the present time, most of attention for multi-bubble acoustic cavitation has been paid mainly on the dynamic characteristics of cavitation bubbles.[40–43] But for the dynamic characteristics of the multi-bubble acoustic cavitation, the papers on how to affect the quantity of strong oxides, and the quantity of strong oxides that are released into bulk solution from the interior of bubbles, are not reported.

Theoretical evidence of sewage degradation is solely based on experimental results published in numerous research papers. In order to explore the theoretical basis of improving the degradation effect, in this paper, the square pressure wave is used. The purpose of this paper is to predict the concentration (or quantity) of strong oxidants such as free radicals generated in bubbles when multi-bubble cavitation occurs, and to improve the methods of degrading the organic pollutants by the acoustic cavitation.

2. Mathematical models and numerical methods

2.1. Model for bubble clusters and for cavitation bubbles in cluster

To describe the dynamics of the cluster and the bubble in cluster theoretically in an acoustic field, the model to be established includes some assumptions as follows. 1) A bubble cluster is considered as a large spherical drop that contains liquid and a large quantity of microbubbles. 2) The bubble cluster and cavitation bubble in cluster oscillate spherically during expansion and compression, in the case with only radial motion but without taking into account the influence of gravity, or buoyancy or other forces on cavitation bubbles. 3) The cluster size is much smaller than the acoustic wavelength. 4) A finite volume of an unbounded slightly compressible viscous liquid and surface tension are taken into account. 5) Radiation damping is considered. 6) The scattering cross sections of the neighboring bubbles do not overlap with each other. 7) The gas pressure inside the bubbles is spatially uniform for each bubble. 8) We shall study in detail the specific case of an oxygen bubble in water at 20 °C and constant density. 9) Heat transfer, mass transfer, diffusion of water vapor, and chemical reaction inside the bubble is considered. 10) Heat transfer, the effect of chemical reaction on internal energy, is not taken into consideration. So, a simple model describing the oscillations of the cluster from Nigmatulin is used:[44]

$$R\ddot{R}+\frac{3}{2}\dot{R}^2=\frac{P_{\rm c}-P_{\rm l}}{\rho}+\frac{R}{\rho c}\left(\dot{P}_{\rm c}-\dot{P}_{\rm l}\right). \tag{1}$$

Here, $R=R(t)$ is the cluster radius, The initial cluster radius $R(t=0)=R_0$ ($=4$ mm), $P_{\rm c}=P_{\rm c}(t)$ is the liquid pressure in the cluster, $\rho=10^3$ kg/m^3 is the liquid density, $c=1500$ m/s is the sound speed in the liquid, $P_{\rm l}$ ($=P_0+P_{\rm t}$) is the driving incident pressure, $P_0=1.013\times10^5$ Pa is the static ambient pressure, $P_{\rm t}$ is the incident acoustic pressure.

The dynamic equation of cavitation bubble oscillation in the cluster is written as follows:[45–47]

$$r\ddot{r}+\frac{3}{2}\dot{r}^2=\frac{P_{\rm w}-P_{\rm c}}{\rho}+\frac{r}{\rho c}\frac{\rm d}{{\rm d}t}\left(P_{\rm w}-P_{\rm c}\right), \tag{2}$$

$$P_{\rm w}=P_{\rm g}-\frac{4\mu\dot{r}}{r}-\frac{2\sigma}{r}. \tag{3}$$

Here, $r=r(t)$ is the instantaneous bubble radius in the cluster, The initial bubble radius $r(t=0)=r_{0a}$ ($=4$ μm) is supplied as an initial condition. The $P_{\rm w}$ is the gas pressure at the bubble wall, $\sigma=0.0725$ N/m is the surface tension, $\mu=10^{-3}$ Pa·s is the liquid viscosity, $P_{\rm g}=N_{\rm tot}kT/(4\pi/3)(r^3-h^3)$ is the gas pressure inside a bubble, $k=1.38\times10^{-23}$ J/mol·K is the Boltzmann's constant, $h=r_{0a}/8.54$ is the Van der Waals hard core radius, T is the temperature inside a bubble, $N_{\rm tot}(t)$ is the total number of particles and varies with condensation and evaporation of water vapor, which is calculated from $N_{\rm tot}(t)=n_{\rm H_2O}(t)+n_{\rm O_2}(t)$, where $n_{\rm H_2O}(t)$ and $n_{\rm O_2}(t)$ are the quantity of water vapor molecules and the number of oxygen molecules inside the bubble at any time t (in the present case, we study oxygen bubbles).

Equations (1) and (2) are complemented with the following equation of conservation of liquid volume in the cluster (in this paper, the initial bubble radii in cluster are assumed to be equal to each other):

$$R^2\dot{R}=Nr^2\dot{r}, \tag{4}$$

where N is the number of bubbles in cluster.

2.2. Mass transfer across the bubble

In this paper, both oxygen and water vapor diffuse across the bubble wall during radial bubble motion.

Mass transfer of oxygen:[48]

$$n_{\rm O_2}(t+\Delta t)=n_{\rm O_2}(t)+\left.\frac{{\rm d}m}{{\rm d}t}\right|_{\rm diff}\cdot4\pi r^2\Delta t,$$

$$\left.\frac{{\rm d}m}{{\rm d}t}\right|_{\rm diff}=D_{\rm O_2}\cdot\frac{c_0-c_{\rm s}}{r}, \tag{5}$$

with

$$c_s = \frac{10^3 \rho N_A p_{O_2}}{M_{H_2O} K_B} \quad \text{and} \quad p_{O_2} = \frac{n_{O_2}}{N_{tot}} P_g,$$

where $n_{O_2}(t)$ is the number of oxygen molecules, $D_{O_2} = 1.76 \times 10^{-9}$ m^2/s is the diffusion coefficient of oxygen in liquid water, $K_B = 6.73 \times 10^9$ Pa is the Henry's constant of oxygen in water, N_A is the Avogadro number, M_{H_2O} is the molecular mass of water, c_0 is the oxygen concentration in the liquid at infinity, in this calculation, $c_0 = 0$ is assumed, c_s is the saturated oxygen concentration at bubble wall in the liquid, and P_{O_2} is the partial pressure of oxygen in the bubble in Pa.

The mass transfer of water vapor is calculated from the following equation[39]

$$\begin{aligned} n_{H_2O}(t+\Delta t) &= n_{H_2O}(t) + 4\pi r^2 D_{H_2O} \Delta t \frac{\partial C_{H_2O}}{\partial r} \\ &= n_{H_2O}(t) + 4\pi r^2 D_{H_2O} \Delta t \left(\frac{C_{w0} - C_w}{l_{diff}} \right), \end{aligned} \quad (6)$$

where $n_{H_2O}(t)$ is the number of water vapor molecules inside the bubble, D_{H_2O} is the diffusion coefficient of water vapor, C_{w0} is the equilibrium concentration (number density) of water vapor at the bubble wall, C_w is the actual concentration (number density) of water vapor inside the bubble.

$$l_{diff} = \min \left(\sqrt{\frac{r D_{H_2O}}{|\dot{r}|}}, \frac{r}{\pi} \right)$$

is the instantaneous diffusive penetration depth.

2.3. Heat transfer across the bubble[39]

$$\frac{dQ}{dt} = 4\pi R^2 \lambda_{mix} \frac{T_0 - T}{l_{th}}, \quad l_{th} = \min \left(\sqrt{\frac{r\chi}{|\dot{r}|}}, \frac{r}{\pi} \right). \quad (7)$$

Here, λ_{mix} is the effective thermal conductivity of mixed gas or vapor, l_{th} is the thermal diffusion length, χ is the thermal diffusivity of oxygen-vapor mixture in the bubble, T_0 is the temperature of bulk liquid, and T is the temperature inside the bubble.

2.4. Temperature inside bubble[39]

The temperature inside the bubble satisfies the following equation:

$$C_{V,mix} \frac{dT}{dt} = \frac{dQ}{dt} - P_g \frac{dV}{dt} + (h_{H_2O} - U_{H_2O}) \frac{dn_{H_2O}}{dt}. \quad (8)$$

The parameter meaning of the above equation is described in Refs. [1,49].

2.5. Chemical kinetics inside bubble[31,32,50]

The substances inside the bubble will react to each other chemically at high temperature, and thus produce a series of strong oxidants such as free radicals. The concentration of radicals and the concentration of other oxidants are calculated by using chemical kinetic model. In order to illustrate the model, the water molecule is split and thus produces ·H and ·OH at an extremely high temperature and pressure under micro-bubble cavitation conditions. Here is an example:

$$H_2O \Leftrightarrow \cdot H + \cdot OH, \quad (9)$$

$$\frac{d[\cdot OH]}{dt} = \sum \text{production} - \sum \text{destruction}, \quad (10)$$

where $[\cdot OH]$ is the concentration of hydroxyl radicals (in units of mol/m^3).

Reaction (9) in the forward direction (from left to right) produces ·OH, and therefore contributes to the first sum in Eq. (10) (production $= A_f T^{b_f} \exp(-C_f/T)[H_2O]$). On the other hand, the backward process (from right to left) corresponds to a consumption of ·OH and thus contributes to the second term in Eq. (10) (destruction $= A_b T^{b_b} \exp(-C_b/T)[\cdot H][\cdot OH]$). Because the cavitation bubble is oxygen bubble, the important chemical reactions related to oxygen in the bubble are shown in Table 1. The parameters (*e.g.*, A_f and A_b) in Eq. (10) are described in Refs. [32,50].

Table 1. Important reactions inside bubble.

Chemical reaction	Chemical reaction	Chemical reaction	Chemical reaction
$H_2O + M = OH + H + M$	$O_2 + M = O + O + M$	$H_2O + O = OH + OH$	$OH + M = O + H + M$
$H + OH = O + H_2$	$H_2O + H = OH + H_2$	$HO_2 + H = OH + OH$	$OH + OH + M = H_2O_2 + M$
$O + OH = H + O_2$	$H + H = H_2$	$H_2O + OH = H_2O_2 + H$	$H + O_2 + M = HO_2 + M$
$H_2O_2 + H = H_2 + HO_2$	$HO_2 + OH = H_2O_2 + O$	$O + O_2 + M = O_3 + M$	$OH + O_2 = O_3 + H$
$OH + O_2 = O + HO_2$	$H + O_3 = O + HO_2$	$H + O_3 = OH + O_2$	$HO_2 + O = OH + O_2$
$H_2O + HO_2 = H_2O_2 + OH$	$O_2 + O_2 = O_3 + O$	$H_2 + HO_2 = H_2O_2 + H$	$HO_2 + HO_2 = H_2O_2 + O_2$
$HO_2 + H = H_2 + O_2$			

M denotes any third body molecules regarded as a catalyst in the reaction.

2.6. Numerical simulation

The mathematical model forms a set of coupled, highly nonlinear and stiff differential equations. Therefore, these equations are solved by using the Runge–Kutta method with help of Matlab.

3. Results and discussion

3.1. Behavior of bubble cluster and cavitation bubbles in cluster in acoustic field

Ultrasonic degradation of organic pollutants requires chemical reactions, but they must occur on the basis of acoustic cavitation background. During the collapse of acoustic cavitation bubbles, the strong acoustic effects such as transient high temperature and pressure in the bubbles, acoustic microjets and shock waves outside the bubbles are formed. These strong acoustic effects occur mainly inside the cavitation bubble and near the bubble wall.[51] These strong sound effects are related to the dynamic behavior of the cavitation bubble, so the understanding of the dynamic behavior of acoustic cavitation bubbles is helpful in exploring the ways to improve the degradation of organic pollutants by acoustic cavitation. Figure 1 shows the behavior of a bubble cluster and cavitation bubbles in a cluster at a frequency of 50 kHz and an acoustic pressure amplitude of 1.5 atm (The unit 1 atm = 1.01325×10^5 Pa). The initial cluster radius (R_0) is 1 mm, the number of the cavitation bubbles is $N = 300$, and the initial cavitation bubble radius (r_{0a}) in the cluster is 4 μm. In this paper, the driving waveform is the square wave signal ($P_{\rm us}\,{\rm sign}(\sin(2\pi ft))$). In Fig. 1(a), bubble cluster radius (R) is shown as a function of time. Under the action of driving acoustic pressure ($P_{\rm t}$), the cluster radius changes very little. But, at collapse of a bubble cluster, the liquid pressure ($P_{\rm c}$) in cluster increases suddenly up to 14.9 times the static ambient pressure, followed by small oscillations due to the very small bounces of cluster radius (see Fig. 1(b)). The oscillation of liquid pressure in cluster also causes the cavitation bubbles in cluster to oscillate (see Fig. 1(c)). The dash-dotted line (left scale, in Fig. 1(c)) represents the relationship between the radius of the cavitation bubble and time. It shows that the radius of cavitation bubble is almost unchanged in the positive half (0–10 μs) of the first acoustic cycle (20 μs). In the negative half cycle (10–20 μs), cavitation bubble begins to expand till its maximum value. Then, in the positive half of the second acoustic cycle, the bubble is compressed and collapsed rapidly, and then expanded and collapsed repeatedly. In this period, it produces high temperatures in the previous collapse stages, and soon afterwards the temperature is negligible because the collapse process is relatively weak as shown with the solid line (right scale). In Fig. 1(d), the number of molecules inside a bubble is shown as a function of time. The solid line represents the total number of molecules inside a bubble, the dash-dotted line denotes the number of water vapor molecules ($n_{\rm H_2O}$) inside a bubble, and the dashed line refers to the number of oxygen molecules ($n_{\rm O_2}$) inside a bubble. On the one hand it is seen from Fig. 1(d) that the $n_{\rm H_2O}$ changes drastically with time due to the evaporation and condensation. At the slow expansion phase in bubble oscillation, $n_{\rm H_2O}$ increases drastically due to the evaporation because the partial pressure of water vapor ($p_{\rm v}$) in the bubble decreases considerably (see Fig. 1(e)). On the other hand, at the collapse of a bubble, $n_{\rm H_2O}$ decreases drastically due to the condensation because $p_{\rm v}$ increases significantly.[31] The number of oxygen molecules does not change. Because the time scale for diffusion of oxygen is $\sim r_{0a}^2/D_{\rm O_2}$ where r_{0a} is the initial bubble radius (4 μm) and $D_{\rm O_2}$ is the diffusion coefficient of oxygen in water (10^{-9} m^2/s). The time scale for oxygen diffusion is 0.01 s, which is far higher than the time scale of bubble dynamics (1/50 kHz = 20 μs), therefore the transport of oxygen across the bubble can be ignored. In Fig. 1(e), the partial pressure of water vapor ($p_{\rm v}$) in the bubble is shown as a function

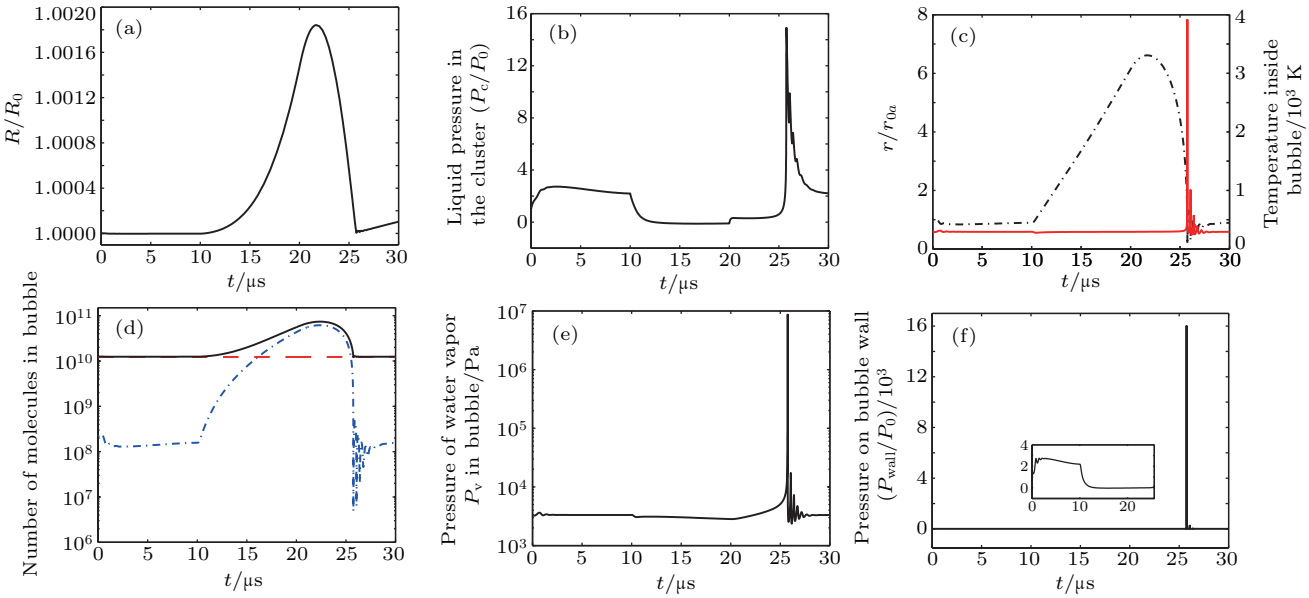


Fig. 1. Dynamic behavior of acoustic cavitation bubble *versus* time over one cycle of acoustic, when acoustic frequency is 50 kHz, acoustic pressure amplitude is 1.5 atm, number of the cavitation bubbles in cluster is 300, driving waveforms is square wave, duty cycle is 50%, bubble cluster radius is 1 mm, and initial cavitation bubble radius is 4 μm.

of time with logarithmic vertical axis. At the slow expansion phase in a bubble oscillation, the pressure of water vapor inside the bubble is 3.35×10^3 Pa, it is the saturated vapor pressure at 20 °C. On the other hand, at the collapse of cavitation bubble, the p_v increases suddenly up to 8.62×10^6 Pa, which is 3 orders of magnitude larger than the saturated vapor pressure at 20 °C, followed by small oscillation due to the small bounces of bubble radius. Its change reflects the variation of the quantity of water vapor inside a bubble (see Fig. 1(d)). Figure 1(f) shows the liquid pressure at the bubble interface as a function of time. At the slow expansion phase in a bubble oscillation, the pressure (P_{wall}) at bubble wall is almost identical to the liquid pressure (P_c) (see the inset in Fig. 1(f)) in the cluster. On the other hand, at collapse of a bubble, the pressure (P_{wall}) increases dramatically up to 1.6×10^9 Pa, followed by small oscillations due to the small bounces of bubble radius (see Fig. 1(c)).

3.2. Effect of acoustic frequency on yield of oxidants inside bubble

In order to explore the effect of acoustic frequency on the behavior of cavitation bubbles and the quantity of strong oxidants produced such as free radicals inside bubbles, in this subsection, the temperature characteristics inside the bubble and variation characteristics of the quantity of strong oxidizing substances produced by the strong acoustic effect are considered, when acoustic pressure amplitude is 1.5 atm, the number of the cavitation bubbles in the cluster is 300, and the acoustic frequencies are 25 kHz, 50 kHz, and 100 kHz, respectively. Equation (10) is a modified Arrhenius formula, which shows that the higher the temperature, the higher the reaction rate is. Acoustic cavitation accelerates chemical reactions due to the high temperature produced by the collapse of cavitation bubbles. So, it is necessary to compare the temperature characteristics of cavitation bubble under the action of different acoustic frequencies.

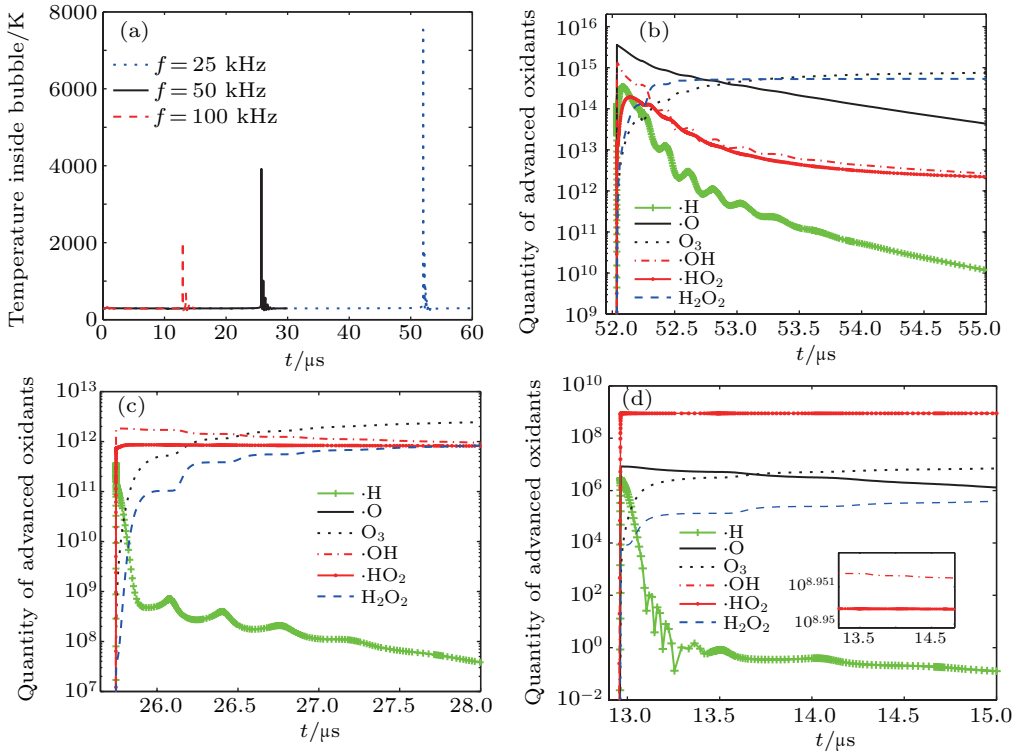


Fig. 2. Time-dependent temperature inside bubble (a) at three different acoustic frequencies (25 kHz, 50 kHz, and 100 kHz) and (b) for different oxidants inside bubble at acoustic frequency 25 kHz, and (c) and (d) time-dependent quantity of advanced oxides in different time ranges at acoustic frequencies of (c) 50 kHz and (d) 100 kHz, when acoustic pressure amplitude is 1.5 atm, number of cavitation bubbles in cluster is 300, and duty cycle is 50%.

Figure 2(a) shows the time-dependent center temperatures at 25 kHz (dotted line), 50 kHz (solid line), and 100 kHz (dash line). It is clear that the maximum center temperatures are 7537.1 K (25 kHz), 3913.5 K (50 kHz), and 2025.6 K (100 kHz), respectively. These results show that the higher the acoustic frequency, the lower the temperature generated by the collapse of cavitation bubbles is. The variations of the number of molecules inside bubble with time are shown for ·O, ·H, ·OH, $\cdot HO_2$, H_2O_2, and O_3 during one acoustic cycle at 25 kHz in Fig. 2(b), 50 kHz in Fig. 2(c), and 100 kHz in Fig. 2(d). These oxidants play a major role in sonochemical reaction. The change of the quantity of oxidants inside a bubble reflects the change of the quantity of oxidants released into surrounding solution from the interior of bubble. It can be seen from the three figures that the higher the frequency, the less the quantity of strong oxidants produced inside the bubble

is. It is also shown from the above figures that the number of molecules of each oxidant inside the bubble is nearly constant before the end of the first half of the second acoustic cycle. In other words, the quantity of strong oxidants inside the bubble does not change any more after ending all the collapse phases during over one acoustic cycle. Another common feature is that the strong oxidants produced at the collapse are not released into the bulk solution substantially, which results in the degradation of organic pollutants in the bulk solution, which is dependent on the nature of the organic matter. When the pollutants are volatilized, they will turn into the bubbles during the expansion of the cavitation bubbles. On the one hand, they will be burned off due to high temperature and pressure inside the bubbles. On the other hand, they will be reacted with strong oxidizing substances generated in the bubble, and also, a small part will be reacted with supercritical water generated by the gas–liquid interface. For non-volatile organic compounds (non-vocs), it mainly depends on the quantity of the oxidizing substances released into the bulk solution. So, compared with volatile organic compounds (vocs), the degradation effect of non-vocs is very poor, and the experiment also confirms this theoretical evidence.[9,18,52] By contrast, at 25 kHz, the number of ·H, ·O, ·OH, and $\cdot HO_2$ radicals inside bubble decrease, and the quantity and species of oxides dissolving into the surrounding liquid from the interior of the bubble are more than those at 50 kHz and 100 kHz, In conclusion, non-vocs in the bulk liquid are easily degraded at 25 kHz, and vocs are easily degraded at 50 kHz and 100 kHz. Table 2 shows the quantity of oxidants inside the bubble at different frequencies.

Table 2. Quantities of oxidants inside bubble at different frequencies.

Species	$f = 25$ kHz		$f = 50$ kHz		$f = 100$ kHz	
	Initial value	Stable value	Initial value	Stable value	Initial value	Stable value
·OH	1.31×10^{15}	2.66×10^{12}	1.82×10^{12}	3.7×10^{11}	8.95×10^{8}	$8.\ 94 \times 10^{8}$
·O	3.6×10^{15}	4.35×10^{13}	2.87×10^{12}	9.5×10^{11}	8.3×10^{6}	1.3×10^{6}
·H	3.5×10^{14}	1.17×10^{10}	3.64×10^{11}	3.80×10^{7}	2.9×10^{6}	0.0
HO_2	1.9×10^{14}	2.2×10^{12}	7.2×10^{12}	8.1×10^{11}	8.9×10^{8}	8.92×10^{8}
H_2O_2	1.14×10^{9}	5.34×10^{14}	1.2×10^{7}	8.3×10^{11}	8.0×10^{3}	3.9×10^{5}
O_3	2.83×10^{9}	7.48×10^{14}	1.35×10^{7}	2.45×10^{12}	2.0×10^{2}	7.0×10^{6}

3.3. Effect of acoustic pressure amplitude on strong oxidants inside bubbles

In Fig. 3(a), we present the changes of temperature inside the bubble for oxygen bubble in water at a frequency of 25 kHz and acoustic pressure amplitudes of 1.2 atm (dash line), 1.5 atm (solid line), 1.7 atm (dotted line). The maximum central temperatures reach 4405.9 K (1.2 atm), 7537.1 K (1.5 atm), and 9557.8 K (1.7 atm), respectively, and the first collapse times are 46.89 μs, 52.03 μs, and 54.66 μs, respectively. Clearly, with the increase of acoustic pressure amplitude, the collapse time delays even at the same frequency. Figures 3(b)–3(d) show the curves for the quantity of strong oxidants inside the bubbles as function of time for pressure amplitudes of 1.2 atm, 1.5 atm, and 1.7 atm, respectively. In Fig. 3(b), due to the small amplitude of acoustic pressure and low temperature inside bubble, the quantity of strong oxidants inside bubble is also small. The number of $\cdot HO_2$ radicals does not change, the numbers of H_2O_2 and O_3 inside bubble increase, whereas the number of ·O and ·OH radicals slightly decrease, and only ·H radicals are released in large quantity into the bulk solution. All these indicate that it is easy to degrade vocs.

Comparing with Fig. 3(b), the quantities of oxidants in Figs. 3(c) and 3(d) are clearly increased, because the temperature inside bubble is increased several times. The figures show that the numbers of H_2O_2 and O_3 molecules also increase inside bubbles, and the numbers of ·H, ·O, ·OH, and $\cdot HO_2$ radicals decrease significantly. This trend shows that plenty of oxidants are released into the ambient liquid from the interior of the bubble, which is helpful in degrading the non-vocs. Especially the hydroxyl radical has high activity and has no selectivity to decompose organic pollutants.[3]

The initial and stable quantities of advanced oxidants can be compared with each other at different acoustic pressures as shown in Table 3. The theory shows that the higher the acoustic pressure amplitude, the better the degradation effect is, but the experimental result is not like that.[53] Perhaps, as the acoustic power increases, a large number of extra bubbles will be created in bulk liquid, and when the bubble number increases to a certain extent the bubbles will cause an acoustic screen effect and affect the degradation effect.[53] Therefore, when the acoustic frequency is fixed and the physic–chemical properties of pollutants are also considered, it is necessary to choose an optimal acoustic pressure amplitude to avoid too low or too high an acoustic pressure, thereby affecting the treatment effect.

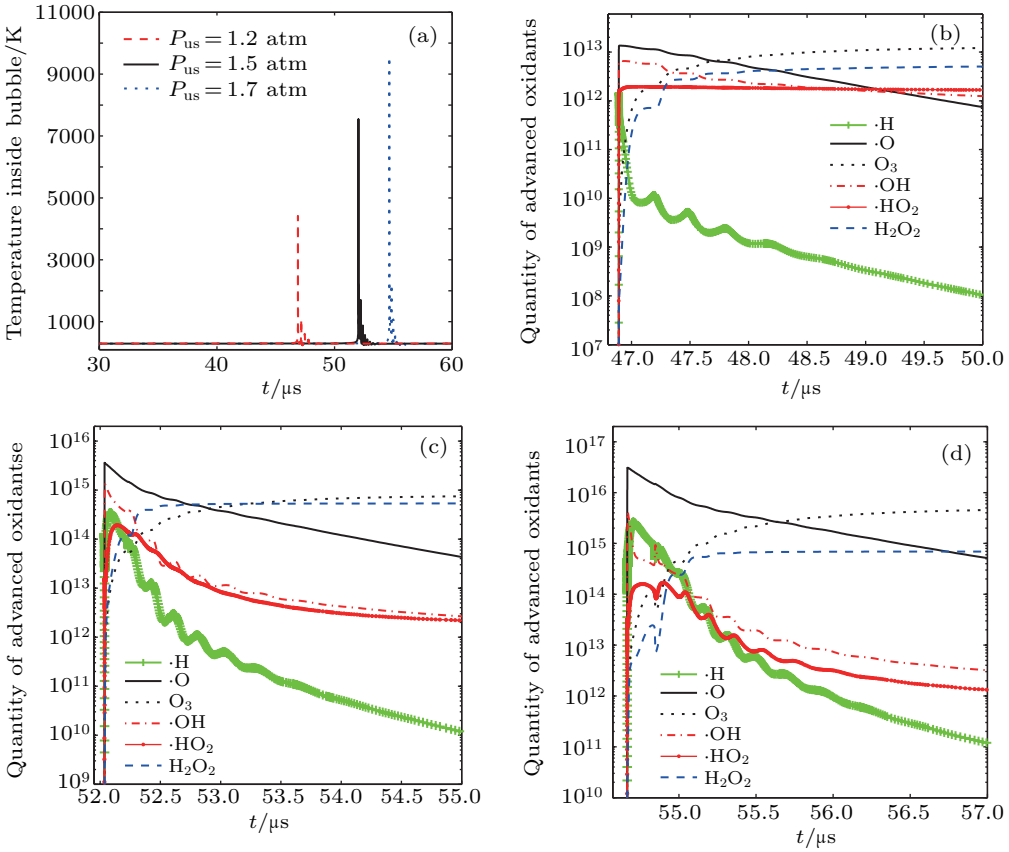


Fig. 3. (a) Variations of temperature with time at different acoustic frequencies (1.2 atm, 1.5 atm, and 1.7 atm), and variations of quantity of advanced oxidants inside bubble with time at (b) 1.2 atm, (c) 1.5 atm, and (d) 1.7 atm quantity for different oxidants, when acoustic frequency is 25 kHz, number of cavitation bubbles in cluster is 300, and duty cycle is 50%.

Table 3. Quantities of oxidants inside bubble at different acoustic pressure amplitudes.

Species	$P_{us} = 1.2$ atm		$P_{us} = 1.5$ atm		$P_{us} = 1.7$ atm	
	Initial value	Stable value	Initial value	Stable value	Initial value	Stable value
·OH	6.65×10^{12}	1.24×10^{12}	1.31×10^{15}	2.65×10^{12}	4.16×10^{15}	3.2×10^{12}
·O	1.35×10^{13}	7.44×10^{11}	3.6×10^{15}	5.0×10^{13}	3.7×10^{16}	5.15×10^{14}
·H	1.4×10^{12}	1.03×10^{8}	3.5×10^{14}	1.15×10^{10}	2.64×10^{15}	1.20×10^{11}
HO_2	1.6×10^{12}	1.67×10^{12}	1.9×10^{14}	2.2×10^{12}	1.6×10^{14}	1.3×10^{12}
H_2O_2	5.0×10^{7}	5.05×10^{12}	8.0×10^{11}	5.35×10^{14}	5.0×10^{11}	6.93×10^{14}
O_3	5.1×10^{9}	1.2×10^{13}	9.1×10^{11}	7.5×10^{14}	4.0×10^{12}	4.53×10^{15}

3.4. Effect of number of cavitation bubbles in cluster on strong oxidants inside bubbles

In Fig. 4(a), the calculated temperature inside bubble is shown as a function of time during the collapse phase. Included in this figure are the plots of bubble temperature versus time for the number of the cavitation bubbles in cluster $N = 500$ (dotted line), $N = 1000$ (solid line), and $N = 3000$ (dash line), respectively. Their maximum central temperatures reach 5320 K ($N = 500$), 3547.4 K ($N = 1000$), and 1706.4 K ($N = 3000$), respectively, and their first collapses occur at 52.26 μs, 52.63 μs, and 53.58 μs, respectively. Clearly, with the increase of the number of cavitation bubbles in cluster, the occurrence of collapse delays even at the same frequency and acoustic pressure amplitude. The possible reason is that the larger the number of cavitation bubbles with the fixed cluster radius, the greater the limitation of expansion and compression of the bubbles will be, which results in the delay of the collapse time of the bubbles and the temperature dropping inside each bubble.[54]

Figures 4(b)–4(d) show the quantities of strong oxidants inside bubble for the three different numbers of cavitation bubbles ($N = 500$, $N = 1000$, and $N = 3000$), respectively. It can be seen from the three curves that the higher the number of the cavitation bubbles in cluster, the less the quantity of oxidants (such as free radicals) produced inside bubble is. A large quantity of the oxidants are created at the collapse because the bubble temperature increases up to 5320 K (for the case $N = 500$), while relatively a small quantity of oxidants

are created because the bubble temperature increases only up to 1706 K ($N = 3000$). It is seen that the quantity of the oxidants created inside bubble is correlated with the bubble temperature at collapse. The three figures show that the numbers of H_2O_2 and O_3 molecules also increase inside bubble, while the number of $\cdot HO_2$ radicals becomes nearly constant, only ·H radical is released in large quantity into the bulk solution. In Fig. 4(b), the number of ·O and ·OH radicals inside bubble decrease slightly, while the number of ·O and ·OH radicals in bubble are nearly unchanged as indicated in Figs. 4(c) and 4(d). By compare with Fig. 3(c), it can be seen that the smaller the number of cavitation bubbles in cluster, the more the quantity and species of the oxidants released into the bulk liquid is and the better the degradation of non-vocs.

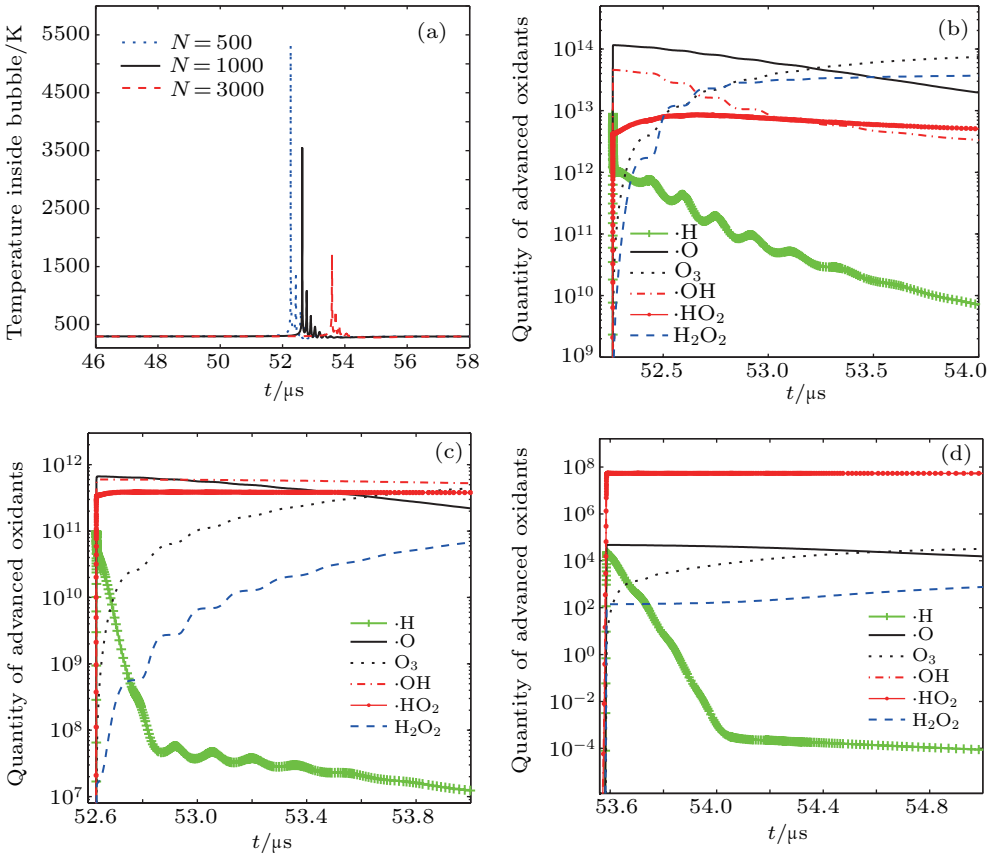


Fig. 4. Variations of temperature inside bubble with time for three different numbers of cavitation bubbles in cluster (500, 1000, and 3000), and variations of quantity of advanced oxidants with time for (b) 500, (c) 1000, and (d) 3000 cavitation-bubbles in cluster, when acoustic frequency is 25 kHz, acoustic pressure amplitude is 1.5 atm, and duty cycle is 50%.

4. Conclusions

Taking the weak compressibility of liquid into consideration, the model that directly couples the dynamics of a bubble cluster and cavitation bubbles (oxygen bubbles) in cluster and the chemical kinetics in an acoustic field is used. We can conclude that the change of external driving pressure leads to the small expansion or compression of the cluster radius. At the moment of the compression collapse of bubble cluster, the liquid pressure in the cluster increases dramatically, and then decreases gradually. In the meantime, the change of this pressure also causes the expansion or compression of cavitation bubbles in the cluster. The cavitation bubble collapse is accompanied by releasing the high temperature at the moment of compression collapse. The number of water vapor molecules inside the bubble increases with the slow expansion of the cavitation bubble and decreases rapidly with the instantaneous collapse. This process will occur repeatedly due to the bounces of bubble. But the number of oxygen molecules in the bubble remains constant throughout the expansion or compression stage. However, the number of free radicals and the number of other oxidant molecules inside the bubble depend on the temperature produced during the collapse of the cavitation bubble, and the internal temperature within the bubble is also affected by some factors, such as acoustic frequency, acoustic pressure, the number of cavitation bubbles in cluster, *etc*. This is a complex engineering system. In order to improve the effect of ultrasonic degradation of organic pollutants, it is necessary to consider the role of all factors comprehensively. In this article, when the acoustic pressure amplitude (1.5 atm) is constant, the driving waveform is square wave, the duty cycle is 50%, the number of cavitation bubbles is 300, and the acoustic frequencies are 25 kHz, 50 kHz, and 100 kHz, respectively. The number of oxidant molecules inside the bubble de-

creases with the acoustic frequency increasing. The acoustic wave of 25 kHz is more suitable for the degradation of non-volatile organic pollutants, while the acoustic wave of 50 kHz and 100 kHz are suitable for the degradation of volatile organic pollutants. When the acoustic frequency is 25 kHz, the acoustic pressure amplitudes are 1.2 atm, 1.5 atm, and 1.7 atm, respectively. The quantity of oxidants inside the bubble increases with the increase of acoustic pressure amplitude. The acoustic pressure of 1.2 atm is more suitable for the treatment of vocs, while the acoustic pressure of 1.5 atm and 1.7 atm are more suitable for the degradation of non-vocs. However, too high an acoustic pressure will cause an acoustic shielding phenomenon, which affects the treatment effect. This should be noticed. Finally, for the number of cavitation bubbles in cluster, when the acoustic frequency is 25 kHz, the acoustic pressure is 1.5 atm, the quantity of oxidants inside the bubble decreases with the increase of the number of cvatiation bubbles in cluster. This suggests that within a fixed bubble cluster, the number of bubbles should be as small as possible.

References

[1] Sivasankar T and Moholkar V S 2008 *Chemosphere* **72** 1795
[2] Malani R S, Khanna S and Moholkar V S 2013 *J. Hazard. Mater.* **256–257** 90
[3] Sasi S, Rayaroth M P, Devadasan D, Aravind U K and Aravindakumar C T 2015 *J. Hazard. Mater.* **300** 202
[4] Gogate P R, Pandit A B 2004 *Adv. Environ. Res.* **8** 501
[5] Henglein A and Kormann C 1985 *Int. J. Radiat. Bio.* **48** 251
[6] Hua L, Hochemer R H and Hoffmann M R 1995 *J. Phys. Chem.* **99** 2335
[7] Gutierrez M and Henglein A 1988 *J. Phys. Chem.* **92** 2978
[8] Suzuki Y, Maezawa A and Uchida S 1999 *Chem. Eng. Technol.* **22** 507
[9] Okuno H, Yim B, Mizukoshi Y, Nagata Y andMaeda Y 2000 *Ultrason. Sonochem.* **7** 261
[10] Ku Y, Chen K Y and Lee K C 1997 *Water Res.* **31** 929
[11] Jiang Y, Pétrier C and David Waite C 2002 *Ultrason. Sonochem.* **9** 163
[12] Visscher A D, Langenhove H V and Eenoo P V 1997 *Ultrason. Sonochem.* **4** 145
[13] Zhao B B and Wang L 2000 *Chem. Eng.* **6** 21
[14] Drijvers D, Baets R D, Visscher A D and Langenhove H V 1996 *Ultrason. Sonochem.* **3** S83
[15] Entezari M H, Kruus P and Otson R 1997 *Ultrason. Sonochem.* **4** 49
[16] Petrier C and Francony A 1997 *Ultrason. Sonochem.* **4** 295
[17] Cum G, Galli G, Gallo R and Spadaro A 1992 *Ultrasonics* **30** 267
[18] Bhatnagar A and Cheung H M 1994 *Environ. Sci. Technol.* **28** 1481
[19] Price G J, Matthias P and Leoz E J 1994 *Process Saf. Environ.* **72B** 27
[20] Terese M O and Philippe F B 1994 *Water Res.* **28** 1383
[21] Chen W C 2014 *Acoustic Cavitation Physics* (Beijing: Science Press) p. 269
[22] Sun J, Shen Z Z andMo R Y 2019 *Chin. Phys. B* **28** 014301
[23] Gogate P R, Sutkar V S and Pandit A B 2011 *Chem. Eng. J.* **116** 1066
[24] Gogate P R, Mujumdar S and Pandit A B 2003 *Adv. Env. Res.* **7** 283
[25] Hodnett M, Choi M J and Zeqiri B 2007 *Ultrason. Sonochem.* **14** 29
[26] Hua I, Hochemer R H and Hoffmann M R 1995 *Envrion. Sci. Technol.* **29** 2790
[27] Berlan J and Mason T J 1992 *Ultrasonics* **30** 203
[28] Gogate P R 2003 *Ultrason. Sonochem.* **10** 325
[29] Kumar A, Gogate P R and Pandit A B 2007 *Ultrason. Sonochem.* **14** 538
[30] Yasui K 1997 *J. Phys. Soc. Jpn.* **66** 2911
[31] Kamath V and Prosperetti A 1993 *J. Acoust. Soc. Am.* **94** 248
[32] Yasui K, Toru T, Sivakumar M and Iida Y 2005 *J. Chem. Phys.* **122** 224706
[33] Merouani S, Hamdaoui O, Rezgui Y and Guemini M 2014 *Ultrason. Sonochem.* **21** 53
[34] Stricker L and Lohse D 2014 *Ultrason. Sonochem.* **21** 336
[35] Kerboua K and Hamdaoui O 2018 *Ultrason. Sonochem.* **41** 449
[36] Sivasankar T, Vijayan and S M 2008 *AIChE J.* **54** 2206
[37] Cuiling G and Douglas P H 1998 *J. Acoust. Soc. Am.* **104** 2675
[38] Brian D S and Andrew J S 2000 *Proc. R. Soc. Lond. A* **456** 1685
[39] Toegel R, Gompf B and Pecha R 2000 *Phys. Rev. Lett.* **85** 3165
[40] Behnia S, Zahir H and Yahyavi M 2013 *Nonlinear Dyn.* **72** 561
[41] Chong K J Y, Quek C Y, Dzaharudin F and Ooi A 2010 *J. Sound Vib.* **329** 687
[42] Wang Y C and Christopher E B 1999 *J. Fluid Eng.* **121** 872
[43] Yasui K, Iida Y, Tuziuti T and Kozuka T 2008 *Phys. Rev. E* **77** 016609
[44] Nigmatulin R I, Sh I, Vakhitova N K and Sh E 2000 *AIP Conf. Proc.* **524** 455
[45] Sh E and Sh I 2005 *Acoust. Phys.* **51** 705
[46] Tervo J T, Mettin R and Lauterborn W 2006 *Acta Acust. United Ac.* **92** 178
[47] Nasibullaeva E S and Akhatov I S 2013 *J. Acoust. Soc. Am.* **133** 3727
[48] Yasui K 1996 *A new formulation of bubble dynamics for sonoluminescence*, National Institute of Advanced Industrial Science and Technology, Japan
[49] Sivasankar T and Moholkar V S 2009 *Chem. Eng. J.* **149** 57
[50] Yasui K, Tuziuti T, Iida Y and Mitome H 2003 *J. Chem. Phys.* **119** 346
[51] Suslick K S, Hammerton D A and Cline R E Jr 1986 *J. Am. Chem. Soc.* **108** 5641
[52] Shemer H and Narkis N 2005 *Ultrason. Sonochem.* **12** 495
[53] Findik S, Gunduz G and Gunduz E 2006 *Ultrason. Sonochem.* **13** 203
[54] Shen Z Z and Wu S J 2012 *Acta Phys. Sin.* **61** 244301 (in Chinese)