Investigation of sonochemical activities at a frequency of 334 kHz: The effect of geometric parameters of sonoreactor

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Abstract
In this study, the effect of the dimensions of the bottom plate and liquid height was investigated for high-frequency sonoreactors under a vertically irradiated system. The dimensions of the bottom plate did not significantly influence sonochemical activity considering power density. However, as the bottom plate was increased in size, the hydroxyl radical generation rate decreased because of a decrease in power density. It is therefore recommended that sonoreactors with bottom-plate dimensions close to those of the ultrasonic transducer module be used. Liquid height had a significant effect on sonochemical activity, but the trend of the activity considering power density changed as the initial pollutant concentration changed. In the case of low initial concentration of As(III) (1 mg/L), the maximum cavitation yield for As(III) oxidation was observed at liquid heights of 150 mm.

1. Introduction
Studies of the ultrasonic processes have found that various parameters affect the sonochemical reactions. These parameters are categorized into ultrasonic and environmental parameters. The ultrasonic parameters include frequency, input power, and irradiation mode (continuous or pulsed mode). The environmental factors are solution characteristics (temperature, pH, dissolved gases, ionic strength), additives, and pollutant characteristics (volatility, hydrophobicity, and initial concentration) [1–8]. However, some researchers point out that the application of these results to industry has been limited because studies conducted at lab-scale sonoreactors have assumed that ultrasonic energy is homogeneously distributed in the sonoreactor [9]. Some researches have found spatial variations of sound field and cavitation intensity in the sonochemical system [10–13]. In other words, it cannot be simply presumed that ultrasonic energy is distributed homogeneously inside the sonoreactor. The type and intensity of the sound field are important parameters influencing the activity of the cavitation events and sonochemical reactions.

Recently, some researchers have found that the dimensions of sonoreactors influence the formation of the sound field [14–20]. For vertically irradiation systems, these dimensions are composed of the dimensions of the sonoreactor bottom plate and the liquid height. One study showed that, as the bottom plate changes in size, the ratio of active to non-active sonochemical sound field changes, thus affecting sonochemical activity [15]. The dimensions of the bottom plate also affect the intensity of the ultrasonic wave propagating to the sonoreactor’s side wall, which changes the amplitude of the vibration of the sonoreactor’s side wall, and the formation of the sound field changes because of the interaction between the ultrasonic wave and the wave caused by the vibration of the side wall [21]. Another dimension, liquid height, also influences the type and intensity of the active sonochemical reaction zone. The sound field can be divided into a standing wave field and a traveling wave field, and sonochemical activity is significantly influenced by the type of the sound field [22,23]. As liquid height is changed, the ratio of traveling to standing wave field changes, which in turn changes the sonochemical activity [1,16,24]. Moreover, increasing the liquid height decreases the acoustic amplitude of a stable standing field formed at the liquid–air interface, because of attenuation of the ultrasonic wave due to an increase in the irradiation distance [25,26]. Thus, it appears that various dimensions of the sonoreactor should also be included in the group of parameters considered to influence sound field formation and sonochemical activity.

Some studies have investigated the effects of the dimensions of sonoreactors on sound field generation, which influences the form of the sound field and the sonochemical reaction. Nanzai et al. suggested that the diameter of the reaction vessel is an important parameter influencing sonochemical activity under vertically
irradiated ultrasonic systems [15]. Son et al. and Asakura et al. conducted experiments at various liquid heights and found that it had a significant effect on the formation of the sound field and sonochemical activity [1,16]. Frequency influences the nature and number of cavitation bubbles and therefore the efficiency of sonochemical reaction compared to low frequencies [31–36]. However, high frequencies present limitations in that the size of the sonoreactor must be smaller because the attenuation coefficient increases with increasing ultrasonic frequency [25]. Therefore, it is necessary to research the effects of the geometric parameters of high-frequency sonoreactors on sound field formation and sonochemical reactions.

The purpose of this study was to investigate the effect of the dimensions (width and length of the bottom plate, and liquid height) of high-frequency (334 kHz) sonoreactors on the cavitation field and on the efficiency of the sonochemical reaction.

2. Material and methods

2.1. Sonoreactor

We used a rectangular standing-wave-type sonoreactor with a single ultrasonic transducer module that irradiates ultrasound vertically (Fig. 1a). The experiments for determining the effect of the irradiation distance were conducted by changing liquid height and irradiation distance (50, 100, 150, 200, and 250 mm). The ultrasonic transducer module (Mirae Ultrasonic Tech.) used consists of three piezotransducers (diameter 50 mm, Del Piezo, W 68 × L 194 mm). The frequency was 334 kHz, and maximum input power was 300 W.

The dimensions of the bottom plate of the sonoreactor are shown in Fig. 1b. The minimum dimensions of the bottom plate, referred to as the base size, were the same as those of the ultrasonic transducer module: W 68 × L 194 mm. Dimensions of the bottom plate were changed to increase width, length, and width and length simultaneously, from base size to 64 mm. To determine the effect of the dimensions of the bottom plate on sonochemical activity, experiments were conducted with a variety of sonoreactors with bottom plates of various dimensions but with the same input power (240 W) and liquid height (150 mm).

2.2. Triiodide method

A triiodide method was used to quantify the sonochemical reaction. The concentration of the potassium iodide (KI) (JUNSEI) solution was 10 g L⁻¹. When the KI solution was irradiated with ultrasound, iodine (I₂) was generated because of the reaction of iodide ions (I⁻) and reactants such as free radicals (·OH, ·H, ·OOH) and hydrogen peroxide (H₂O₂) formed by acoustic cavitation. The iodine (I₂) reacted with the iodine ions (I⁻) and generated a triiodide ion [16,37]. The concentration of the triiodide ion (I₃⁻) was measured using a UV spectrophotometer (SPECORD 40, Analytic Jena) at a wavelength of 350 nm.

2.3. Sonochemiluminescence

Sonochemiluminescence (SCL) was used to visualize the sonochemical reaction field. Luminol solution with 0.1 g L⁻¹ luminol (3-aminophthalhydrazide, Samchun) and 1 g L⁻¹ sodium hydroxide (Ducksan) was prepared for each irradiation condition. Hydroxyl radicals generated from sonolysis induce luminol molecules to transform into excited-state fluorescing 3-aminophthalate (3-APA), which then stabilize and emit visible light, known as SCL [16,38]. SCL images were recorded for an exposure time of 1 min using a digital camera (Canon EOD 400D equipped with a Tamron AF 17–50 mm lens) in a dark room.

2.4. As(III) oxidation

An As(III) oxidation experiment was conducted to simulate the sonochemical reaction in an environmental water system. As(III) solution was prepared using NaAsO₂ (94%, Sigma–Aldrich). A stock solution of 500 mg/L was prepared and diluted by adding distilled water to a concentration of 1 mg/L. At regular intervals, 5 mL samples were taken from the reaction solution. The samples were filtered using an anion-exchange cartridge (Supelclean, LCSAX solid-phase extraction 3 mL) to separate As(V) from the samples. After this step, the concentration of As(III) was analyzed using an inductively coupled plasma atomic emission spectrometer (Perkin-Elmer 7300DV).

3. Results and discussion

3.1. Effect of the bottom-plate dimensions (W × L)

The effect of the dimensions of the bottom plate of the sonoreactor on the formation of the sound field and sonochemical reaction was investigated. To discuss the sonochemical efficiency (SE) quantitatively, a triiodide method was adopted. Fig. 2 shows the I₃⁻ concentration versus time at various dimensions of sonoreactor bottom plate. Low I₃⁻ generation rates were observed with the sonoreactor with a bottom plate of large width and length. Comparing the results (Fig. 2a–c), the decrease

Fig. 1. Schematic of (a) a vertical irradiation sonoreactor and (b) various dimensions of the sonoreactor bottom plate. W × L (W 68 mm × L 194 mm) were the dimensions of the transducer module.
in the $I_3^-$ generation rate in the case of increasing bottom-plate width was greater than in the case of increasing bottom-plate length. This was because the volume of the reactor increased more when bottom-plate width increased. Reaction volume change influenced the power density. With increasing bottom-plate dimensions, the power density decreased because increasing the surface area of the bottom plate meant that the volume of the solution increased under the same liquid height and input energy.

The power density was calculated using the following equation:

$$\text{Power density} = \frac{P}{V_L}.$$  \hspace{1cm} (1)

where $P$ is the electrical power and $V_L$ is the volume of the solution. The $I_3^-$ generation rate (mg L$^{-1}$ min$^{-1}$) was observed to influence power density.

It was not sufficient to compare sonochemical activity using only $I_3^-$ concentration rate as the standard, because of the different
power densities of the sonoreactors. To consider the difference in power density, a cavitation yield was introduced. Cavitation yield was used to compare the efficiency of the sonochemical reaction practically with the amount of $I_3^-$ generated during sonication under a system of changing solution volume \[1,16\]. The equation for the cavitation yield is as follows:

$$ \text{cavitation yield} = \frac{K}{V_L} P_E $$ \hspace{1cm} (2)

where $K$ (M min$^{-1}$/C$_0$) is the triiodide ion generation rate and As(III) oxidation rate, $V_L$ (L) is the volume, $P_E$ (W) is the input power. The cavitation yield for $I_3^-$ with each sonoreactor was measured, and it was found that the cavitation yield remained virtually unchanged despite the different bottom-plate dimensions. The difference in the cavitation yields for the various bottom-plate dimensions was under 10% and was due to experimental error.

Therefore, it appears that $I_3^-$ generation rate per power density was constant with varying bottom-plate dimensions. In other words, $I_3^-$ generation rate by sonication changed linearly depending on changes in the power density caused by changing the dimensions of the bottom plate under the same input power and the same liquid height.

The activity of the cavitation events was influenced by the formation of the sound field during sonication. To visualize the active sonochemical zone at each sonoreactor, SCL images were taken using luminol solution for 334 kHz with a liquid height of 150 mm (see Fig. 3). In the images, a stripe was observed representing the standing wave field. Light of high intensity was visible within the range of the diameter of the transducers, regardless of the dimensions of the vibrating plate. It appears that the range of the diameter of the transducers was the location of the majority of the cavitation events, and therefore the bottom-plate dimensions larger than the transducer module had little effect on cavitation activity. It was observed that waves not only propagated in a straight line but also progressed toward the side wall of the reactor. The waves progressing toward the side wall generated wall vibration, which caused a reduction in the acoustic pressure amplitude and energy of the sonochemical reaction \[21\]. In the sonoreactor with a vibrating plate larger than the ultrasound source, it was expected that the bubble nuclei generated in the sound field would diffuse to the region with no sound field. These bubble nuclei dissolved without exhibiting growth, and thus the number of bubbles that underwent cavitation events decreased \[12,13,15,36,39\]. These two phenomena occur simultaneously, which may reduce and enhance the efficiency of the sonochemical reaction if the bottom-plate dimensions are large, and thus there is no significant difference between the various dimensions of the vibration plate.

Nanzai et al. used four cylindrical sonoreactors with a vibrating plate of different diameters (20, 50, 90, and 120 mm) to test sonochemical reactions \[15\]. To compare sonochemical activity, $\text{H}_2\text{O}_2$ yield by sonication and chloride ions formed from the decomposition of 1,2,4-trichlorobenzene, and the SE, in terms of yield per injected energy, was measured under fixed liquid height and a frequency of 200 kHz using an ultrasonic irradiator with a diameter of 65 mm. Nanzai et al. found that SE peaked with a sonoreactor of a diameter of 90 mm. This result suggests that a sonoreactor with a vibrating plate area larger than the sonication zone may not improve the SE. We defined SE as the value of $I_3^-$ generation rate per power density. However, the effect of bottom-plate size between Nanzai et al. study and our study differed. Their study used an indirect type of ultrasonic irradiation, whereas we directly irradiated the reaction solution.

It appears that the effect of the dimensions of the bottom plate on sonochemical reactions is not significant. However, to consider power density, it is useful to employ a sonoreactor with a bottom...
plate that is not larger than the transducer module. Considering both cavitation yield and $I_3$ generation rate, we recommend bottom-plate dimensions that are not beyond those of the transducer module.

### 3.2. The effect of the liquid height

To investigate the effect of liquid height in a sonoreactor with a vertically irradiated ultrasonic system on the efficiency of the sonochemical reaction, an iodide method was used. The experiments were conducted at various liquid heights (50, 100, 150, 200, and 250 mm) to vary the irradiation distance. The effect of the liquid height on $I_3$ generation rate was investigated (see Fig. 4a) under a vertically irradiated system. A significant decrease in the $I_3$ generation rate was found with increasing irradiation distance. With increasing liquid height under the same input power, power density decreased because the increasing liquid height, and irradiation distance, caused the volume of the solution to increase. It was observed that the $I_3$ generation rate influenced power density.

However, it is not sufficient to compare $I_3$ generation rates directly between systems with differing liquid heights, because of the difference of the power density. Therefore, cavitation yield for $I_3$ was used to compare sonochemical activity (see Fig. 4b).

While increasing the irradiation distance over 50 mm, the cavitation yield for $I_3$ decreased. The results show that a significant decrease in the efficiency of the sonochemical reactions occurred with decreasing liquid height. However, there was a difference in the effect of liquid height on sonochemical reactions between the study by Son et al. and our study [16]. They found a significant improvement in the efficiency of the sonochemical reaction based on cavitation yield as the liquid height increased in low-frequency (36 and 108 kHz) sonoreactors. It appears that the difference occurs because formation of the sound field is significantly dependent on ultrasonic frequency. The bubbles should oscillate stably to collapse, radiating intensive energy. The bubbles in the traveling wave field formed near the ultrasonic irradiator were transferred to a standing wave field formed near the surface of the liquid. The bubbles in the standing wave field were trapped in the antennas so that they were able to grow to an active size range. The bubbles in the traveling wave field underwent a transient cavitation event and had a short life cycle. However, the bubbles in the standing wave field underwent stable cavitation with hundreds of acoustic cycles [16,22,23,26,40,41]. Therefore, the ratio of the traveling to the standing wave field was an important factor in the sonochemical reactions. Lee et al. report that the standing wave field percentage changes with changing frequency [13]. In addition, SCL images of some studies show that the proportion of the averaged standing wave under low frequency changes greatly with changing irradiation distance, whereas the majority of the sound field is composed of standing waves under high frequency. It seems that these differences were due to the differences of the irradiation distance on sonochemical activity acquired by high- and low frequency.

Asakura et al. tested four frequencies (45, 129, 231, and 490 kHz) to measure SE at different liquid heights [1]. They found a relationship between the liquid height for the peak value for sonochemical reactions and the applied frequency:

$$h_{\text{peak}} = \frac{23,400}{f} - 22.9,$$  \hspace{1cm} (3)

where $h_{\text{peak}}$ [mm] is the liquid height at the peak of the cavitation yield value and $f$ [kHz] is the ultrasonic frequency. It is difficult to apply this equation to every system, but the equation fits well with similar studies. The $h_{\text{peak}}$ for our study calculated with Eq. (3) is 47 mm, similar to 50 mm. The $h_{\text{peak}}$ value may explain the decrease observed in the cavitation yield as the liquid height increased.

It was found that a sound field where a standing wave field was formed more dominantly was generated at the liquid surface [26,41]. As mentioned above, the bubbles in the standing wave field may grow through hundreds of ultrasonic cycles and cause cavitation events actively. Cavitation events occurred more violently in the region close to the liquid surface than in the region near the transducer because of that stable standing field. Therefore, the sound field at the liquid surface where the ultrasound can be reflected is important. The ultrasonic intensity of the sound field at the liquid surface was affected by stability of the surface and the intensity of the propagated sound wave. Tuziuti et al. report that light intensity observed in a SCL image for a sonoreactor with Teflon particles that were able to cover and fix the liquid surface were brighter than that without Teflon particles [26]. This suggests that the liquid surface ripples disturbed the formation of a stable standing wave and caused cavitation events less violently. A liquid height of less than $h_{\text{peak}}$ causes an unstable liquid surface because of the high ultrasonic intensity under a vertical irradiation sonoreactor. This unstable liquid surface may explain the decrease of sonochemical activity at the liquid height of 30 mm. However, as liquid height, and ultrasonic irradiation distance, increased, intensity of the propagated sound wave decreased:

$$I = I_0 \exp(-2\pi d).$$  \hspace{1cm} (4)

where $I$ is the ultrasonic intensity at some distance, $d$, from the source, $I_0$ is the ultrasonic intensity at source of the ultrasound, and $\alpha$ is the attenuation coefficient. Ultrasonic intensity decreased

![Fig. 4](image-url). The effect of the liquid height and irradiation distance on cavitation yield for $I_3$. The dimensions of the bottom plate of the sonoreactor were W 100 × L 226 mm². Input power and frequency were fixed at 240 W and 334 kHz, respectively. Fig. 4a is the effect of the liquid height, Fig. 4b is the effect of cavitation yield.
by scattering because of bubbles of ultrasound and attenuation as the irradiation distance increased. Therefore, a sound wave with low ultrasonic intensity was formed when the liquid level was high. On the other hand, the increase in the hydrostatic pressure acted as a compressive pressure on the cavitation bubbles with increasing liquid height. The growth of the bubbles was suppressed by the extra compressive pressure.

To confirm the sonochemical reaction region, SCL images were obtained after 1 min of sonication (Fig. 5). Bright stripes were observed representing a standing wave field formed at all liquid heights. A difference between the high-frequency and low-frequency sonoreactors was that, as liquid height changed, the ratio of standing wave field to traveling wave field significantly changed in the low-frequency sonoreactor, whereas the ratio remained virtually unchanged in the high-frequency sonoreactor. It appears that the standing wave field was dominant at all liquid heights under high-frequency ultrasonic processes. At lower liquid height, high-intensity SCL was observed near the liquid–air interface. A more active cavitation zone was formed at small liquid height than at large liquid height.

A triiodide method was used to quantify sonochemical activity. However, the concentration of KI solution for the triiodide method was 10 g L\(^{-1}\), which had a high ionic strength compared to a real environmental water system. Changes in ion concentration influenced the specific chemico physical properties such as viscosity, surface tension, and gas solubility. In highly viscous liquid, attenuation of the ultrasonic wave increased, the region of active cavitation events decreased, and there was an increasing collapse pressure of the cavitation bubbles. The collapse pressure of the cavitation bubbles increased with increasing surface tension of the solution. With decreasing gas solubility, internal pressure inside the cavitation bubbles decreased, which allowed the violent collapse of the cavitation bubbles [42,43]. The results of \(I_3^-\) generation studies using triiodide methods and sonochemiluminescence showed that the liquid’s height in reactor is much more important than its dimension. Also, the result obtained from the triiodide method may be used as a reference for sonochemical activity, but it is not sufficient to predict sonochemical activity in a real environmental water system. Therefore, an As(III) oxidation experiment was conducted to investigate the effect of liquid height on sonochemical activity in a real environmental system.

Fig. 6 shows changes in the As(III) concentration at various liquid heights when the initial concentration was 1 mg L\(^{-1}\). As(III) oxidation rate is shown in Fig. 6a. A significant decrease in the As(III) oxidation rate was found when liquid height increased, similar to the results obtained by the triiodide method, at all initial concentrations of As(III).

However, as mentioned above, it is not sufficient to consider the As(III) oxidation rate on its own when comparing sonochemical activity. To consider the variation in power density at differing liquid heights, the cavitation yield for As(III) oxidation at 60 min was used (Fig. 6b).

A difference was observed between the trend of the cavitation yield for \(I_3^-\) generation and that of As(III) oxidation. The maximum cavitation yield for As(III) oxidation was obtained at the liquid height of 150 mm. This difference may be due to the change in the attenuation coefficient with differing ionic concentrations. At higher initial concentration, viscosity of the solution increased [42,43]. The attenuation coefficient, \(\alpha\), in Eq. (5) increased as viscosity of the solution increased [25]:

\[
\alpha = \frac{2\pi^2f^2}{\rho \nu^3} \left( \frac{4}{3} \eta_s + \frac{(\gamma - 1)\kappa}{C_p} \right),
\]

where \(f\) is frequency, \(\rho\) is the density of the solution, \(\nu\) is the sound velocity, \(\eta_s\) is the shear viscosity of the solution, \(\gamma\) is the heat capacity ratio \((\gamma = C_p/C_v\)), where \(C_p\) is the heat capacity at constant pressure, and \(C_v\) is the heat capacity at constant volume, and \(\kappa\) is thermal conductivity. As Eq. (5) indicates, an increase in the viscosity of the solution, \(\eta_s\), would increase the attenuation coefficient. This means that the amount of ultrasonic intensity loss with increasing irradiation distance was greatly increased when the solution was of a high ionic concentration. As shown in Fig. 6b, liquid height for the maximum cavitation yield for As(III) oxidation was higher than that for the maximum cavitation yield for \(I_3^-\) generation.
As(III) oxidation was observed at a liquid height of 100 mm. This result indicates the possibility of applying ultrasonic oxidation processes at large liquid heights.

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References


Fig. 6. (a) Oxidation of As(III) at various liquid height and (b) the effect of the liquid height on cavitation yield for As(III) oxidation at 60 min. Initial As(III) concentration was 1 mg L\(^{-1}\). The dimensions of the bottom plate of the sonoreactor were W 100 × L 226 mm. Input power and frequency were fixed at 240 W and 334 kHz, respectively.


