Quantification of sonochemical and sonophysical effects in a 20 kHz probe-type sonoreactor: Enhancing sonophysical effects in heterogeneous systems with milli-sized particles

Jongbok Choi, Younggyu Son, Jongil Choi

Department of Environmental Engineering, Kumoh National Institute of Technology, Gumi 39177, Republic of Korea
Department of Energy Engineering Convergence, Kumoh National Institute of Technology, Gumi 39177, Republic of Korea

Abstract

Even though acoustic cavitation has been widely investigated, only few researchers focused on the relationship between sonochemical and sonophysical activities and on the enhancement of sonophysical activity. In this study, sonochemical and sonophysical activities were investigated in a heterogeneous system to understand the relationship between these two activities and to suggest optimal conditions for ultrasonic desorption/extraction processes comprising milli-sized glass beads. The sonochemical activity was quantitatively analyzed using potassium iodide dosimetry in homogeneous and heterogeneous systems. Sonophysical activity was quantitatively and qualitatively analyzed using paint-coated bead desorption tests and aluminum foil erosion tests under three probe positions of “T” (1 cm below the liquid surface), “B” (1 cm above the vessel bottom), and “M” (midpoint between “T” and “B”). Three different sizes of glass beads (diameter: 0.2, 1.0, and 4.0 mm) were used in this study. The highest sonochemical activity was obtained at “B” in both homogeneous and heterogeneous systems. However, three times lower sonochemical activity was observed in the heterogeneous system than in the homogeneous system because significant attenuation and unstable reflection of ultrasound occurred in the bead layer and suspension. Higher sonophysical activity was observed, when the bead size decreased and the probe approached the bottom. However, no significant sonophysical activity was detected when the beads were attached to the bottom. Therefore, the sonophysically active region was the zone around the probe body, opposite to the ultrasound irradiation tip, and only suspended beads could undergo severe cavitation actions. This was confirmed via aluminum foil tests. Several erosion marks on the foil were observed in the area around the probe body, whereas no severe damage was observed at the bottom. Moreover, the degree of sonophysical activity did not change for various saturating gases. This might be due to the different thresholds of sonochemical and sonophysical activities.

1. Introduction

Highly concentrated energy is released in local areas, and various sonochemical and sonophysical effects can be observed in homogeneous and heterogeneous systems when cavitation bubbles collapse [1–4]. For decades, most researchers have focused on sonochemical effects, including pyrolysis inside the bubbles and radical reactions outside the bubbles in the treatment of organic and inorganic pollutants in environmental sonochemistry [5–8]. Reportedly, sonophysical effects including microstreaming, microjets, and shockwaves are induced in heterogeneous systems and have more complicated mechanisms than those in homogeneous systems [1,9].

Sonophysical effects for extraction, washing, and destruction have recently been widely studied, and novel ultrasonic processes have been suggested. Son et al. reported that various pollutants in contaminated soils, including petroleum hydrocarbons, heavy metals, and persistent organic pollutants, can be effectively removed via ultrasonic processes compared to conventional washing processes [10–15]. Some researchers have used ultrasound technology for cleaning contaminated textiles and compared them with conventional shaking and stirring technology [16–18]. Some researchers have also applied ultrasound technology for destroying and removing living organisms during disinfection processes.

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Even though acoustic cavitation has been widely investigated, only few researchers focused on the relationship between sonochemical and sonophysical activities and on the enhancement of sonophysical activity. In this study, sonochemical and sonophysical activities were investigated in a heterogeneous system to understand the relationship between these two activities and to suggest optimal conditions for ultrasonic desorption/extraction processes comprising milli-sized glass beads. The sonochemical activity was quantitatively analyzed using potassium iodide dosimetry in homogeneous and heterogeneous systems. Sonophysical activity was quantitatively and qualitatively analyzed using paint-coated bead desorption tests and aluminum foil erosion tests under three probe positions of “T” (1 cm below the liquid surface), “B” (1 cm above the vessel bottom), and “M” (midpoint between “T” and “B”). Three different sizes of glass beads (diameter: 0.2, 1.0, and 4.0 mm) were used in this study. The highest sonochemical activity was obtained at “B” in both homogeneous and heterogeneous systems. However, three times lower sonochemical activity was observed in the heterogeneous system than in the homogeneous system because significant attenuation and unstable reflection of ultrasound occurred in the bead layer and suspension. Higher sonophysical activity was observed, when the bead size decreased and the probe approached the bottom. However, no significant sonophysical activity was detected when the beads were attached to the bottom. Therefore, the sonophysically active region was the zone around the probe body, opposite to the ultrasound irradiation tip, and only suspended beads could undergo severe cavitation actions. This was confirmed via aluminum foil tests. Several erosion marks on the foil were observed in the area around the probe body, whereas no severe damage was observed at the bottom. Moreover, the degree of sonophysical activity did not change for various saturating gases. This might be due to the different thresholds of sonochemical and sonophysical activities.

1. Introduction

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2. Experimental methods

2.1. Chemicals

Potassium iodide (KI, 99.5%) and sodium hydroxide (NaOH, 97%) were purchased from Junsei Chemicals Co., Ltd. (Japan). Luminol (C₆H₄N₃O₂, 97%) was purchased from Sigma Aldrich (USA). All chemicals were used as received.

2.2. Experimental setup

A 20-kHz horn-type sonicator (VCX-750, Sonics & Materials Inc., USA), equipped with a threaded-end type probe and a replaceable tip of 13 mm diameter, made of a titanium alloy, was used in this study. The probe was submerged in a 500 mL circular glass vessel (a commercialized glass beaker with a slightly concave bottom). The diameter and height of the glass vessel were 85 mm and 120 mm, respectively. The probe was placed at three positions, including a low position (1 cm above the bottom of the vessel), a middle one (midpoint between the liquid surface and the bottom), and a top position (1 cm below the liquid surface). The positions were designated as B, M, and T, respectively [26,27]. The electrical energy consumption of the sonicator, termed as electrical power in this study, was measured using a power meter (HPM-300A, ADPower, Korea), equipped with a data logger. The ultrasonic energy, termed as calorimetric power in this study, was calculated using the following calorimetric equation:

\[ P_{\text{cal}} = \frac{dT}{dt} C_p \cdot M \]  

(1)

where \( P_{\text{cal}} \) is the ultrasonic/calorimetric energy, \( \frac{dT}{dt} \) represents the rate of increase of the liquid temperature, \( C_p \) denotes the specific heat capacity of the liquid (4.184 J/(g·K)) for water), and \( M \) is the mass of the liquid [26]. The input power level applied to the sonicator was set to 50%. The electrical powers were 69, 73, and 85 W, and calorimetric powers were 39.2, 44.8, and 57.9 W for B, M, and T, respectively.

Therefore, the sonophysical effects can be optimized by adjusting geometric factors such as the probe position. In this study, sonochemical oxidation and sonophysical activities were investigated to understand how sonophysical effects can be enhanced along with the interpretation of the mechanism and relationship between these activities in homogeneous and heterogeneous systems. Using a 20 kHz probe-type sonicator, one of the most common laboratory apparatuses, sonochemical oxidation (potassium iodide [KI] dosimetry) and sonophysical activity (bead desorption and aluminum foil erosion tests) were quantitatively investigated as one of the basic steps for optimizing sonophysical effects. Three probe positions and three types of millimeter-sized glass beads were used. The cavitative activity zone was visualized via luminol method. Moreover, the effect of saturating gas on sonophysical activity was investigated.

2.3. Quantification of sonochemical activity

The sonochemical oxidation was quantified using a KI solution (10 g/L KI) and visualized using a luminol solution (0.1 g/L luminol and 1 g/L NaOH) [26,31,32]. The concentration of I\(^{-}\) ions was measured using a UV–vis spectrophotometer (Vibra S60, Biochrom Ltd., UK). The ultrasound irradiation time was maintained at 3 min. All tests and measurements were repeated three to five times, and the average values are reported in this study. Sonochemical luminescence (SCL) images were obtained using a luminol solution and an exposure-controlled digital camera (DSC-RX100M7; Sony Corp., Japan) in a completely dark room. The exposure time was 20 s.

2.4. Quantification of sonophysical activity

Three types of beads with mean diameters of 0.2, 1.0, and 4.0 mm were used in this process. For the desorption tests, the beads were coated with red paint using oil-based spray paint and exposed to ultrasound irradiation in water, with a bead ratio of 5:1 [11]. The turbidity induced by the paint desorption was measured using a UV–vis spectrophotometer (Vibra S60, Biochrom Ltd., UK). The irradiation time was kept at 3 min.

Aluminum foil erosion tests were conducted using aluminum foil and a cylindrical frame with three diameters of 45, 62, and 80 mm. The frame was used to avoid moving the foil using ultrasound and ultrasound-induced liquid flow. The aluminum foil with a thickness of 16 μm was wrapped around the frame. The irradiation time was 30 s. Afterward, the damaged foil was dried, scanned, and analyzed visually.

3. Results and discussion

3.1. Sonochemical activity in heterogeneous systems

Reportedly, sonochemical oxidation activity can vary greatly depending on the probe immersion depth of a 20 kHz sonicator in a homogeneous system (only liquid) [26,27]. Herein, sonochemical and sonophysical activities were investigated to understand the cavitation phenomena in a heterogeneous system (liquid and solid) under various probe positions. KI dosimetry was used to quantitatively analyze the sonochemical oxidation in a heterogeneous system including KI solution and glass beads (diameter: 0.2, 1.0, 4.0 mm). The probe was placed at positions T, M, and B with a weight-based solid:liquid ratio of 1:5. As
shown in Fig. 1, approximately six to eight times higher oxidation activity was observed at position B compared to that at T and M in the homogeneous system. Sonochemical oxidation activity is reported to be highly enhanced when the probe is placed very close to the reactor bottom because of the intensification and expansion of the cavitation active zone, which is induced by the strong reflection of ultrasound at the bottom and then at the liquid surface [26]. The SCL images (no beads) of Fig. 2 show the evolution process of the cavitational active zone from a small area just below the emitting tip to a circular-shaped large area covering most of the whole liquid volume.

In the presence of glass beads, the highest sonochemical activity was also obtained at B despite considerably lower values compared to that of no beads condition. Moreover, the lowest activity was obtained for the 1 mm beads, and the highest activity was obtained for the 0.2 mm beads for all applied probe positions. The differences in sonochemical activity, depending on the presence and size of the glass beads, can be explained by the following reasons with the real and SCL images in Fig. 2: 1) bead movement induced by ultrasound irradiation; the 0.2 mm beads, the lightest beads, moved vigorously, and more beads were suspended for the higher probe position. In contrast, the larger beads (4 mm) moved slightly to the vessel wall and rotated at their position because of their heavy weight. Relatively small movements and suspensions were observed for the 1 mm beads at T and M positions. Wang et al. also reported that a larger suspension and violent mixing could be achieved when the probe was placed adjacent to the liquid surface owing to enhanced acoustic streaming [33]; 2) attenuation and reflection of ultrasound due to the presence of the beads; the main reason for the significant change in the cavitation active zone in the presence of beads was attributed to different characteristics of ultrasound attenuation and reflection. The top layer of the beads reacted as an ultrasound reflector, whereas the flat bottom of the vessel reacted as a reflector in the absence of beads. The layer of the beads at the bottom could shorten the irradiation distance between the probe tip and the reflector compared to the no beads condition. Some parts of ultrasound could be transmitted into the bubbles layer, and large attenuation might occur because no activity and weak activity were observed in the dense layer of the 0.2 mm beads and the less dense layer of the 1.0 mm and 4.0 mm beads, respectively [34,35]. In addition, the rough and uneven surface of the bead layer could induce diffuse reflection of ultrasound. The reflected ultrasound was scattered at the top layer of the beads and was not parallel to the incident ultrasound. Consequently, a stable and large active zone was not formed in the presence of beads. For position B, a strong sonochemical activity could be observed only in the small region just above the top layer for the heavier beads (1 mm and 4 mm beads). The suspended 0.2 mm beads might induce large attenuation of ultrasound, and a considerably low intensity of the active zone above the top layer was observed compared to that for 1 mm and 4 mm beads, even though the active zone for the 0.2 mm beads expanded due to the suspended beads; 3) promoted nucleation for cavitation due to the presence of the beads, and the largest active zone was observed for the 0.2 mm beads at all probe positions. This could be attributed to the suspension of the light beads and promoted nucleation for cavitation at the bead surface [34,36]. The expansion of the active zone appeared most clearly at “B,” and the order of the degree of the suspension was as follows: T >
This indicates that strong reflection of ultrasound at position B might be crucial to form large active zone than large suspension of the 0.2 mm beads at position T. Notably, enhanced nucleation might occur at the top layer of 1 mm and 4 mm beads, despite no evident observation due to strong activity adjacent to the bead layer in this study. Consequently, a more stable reflector condition was formed at the 4 mm beads layer because of their heavy weight, and enhanced nucleation for cavitation occurred via the suspension of the 0.2 mm beads. Because of these phenomena, higher sonochemical oxidation was obtained for the 4 mm (stable reflector condition) and 0.2 mm (beads suspension condition) beads than for the 1.0 mm beads (less stable reflector and less suspension condition). However, significant attenuation and relatively unstable reflection of ultrasound, induced by the presence and suspension of the beads, resulted in considerably lower sonochemical activity, particularly at position B, in heterogeneous systems than in the homogeneous systems.

3.2. Sonophysical activity in heterogeneous systems

To investigate whether sonophysical activity could also be enhanced under the condition where sonochemical activity was increased, the same experimental conditions including the probe positions (T, M, and B) and the bead sizes (0.2 mm, 1.0 mm, and 4.0 mm) were applied for the desorption tests using the oil paint-coated beads. As shown in Fig. 3, a drastic variation in sonophysical activity, expressed as the turbidity in the aqueous phase induced by the ultrasonic desorption of red paint particles from the coated beads was observed in this study. As the bead size decreased and the probe approached the bottom (or bead layer), higher desorption occurred. The highest sonophysical activity was observed for the 0.2 mm beads at B, and extremely low desorption occurred for the 4 mm beads even at B. No conspicuous color change was visually detected for positions T and M, whereas the solution color for B turned red, as shown in the inset of Fig. 3. Notably, the partial red color in the liquid phase for the 0.2 mm beads at T and M was not due to paint desorption but due to the suspension of the paint-coated beads.

It is established that ultrasonic desorption/extraction can occur via violent sonophysical effects, including shear forces, microjets, microstreaming, and shock waves [1,11,37]. Therefore, the reason behind the highest sonophysical activity for the 0.2 mm beads at position B was attributed to the following observations as discussed above: 1) the strongest cavitation activity could be obtained at B; 2) nucleation for cavitation could be enhanced at the surface of the suspended beads, and violent desorption can occur among the suspended beads. Desorption might also occur via particle-to-particle collisions and scrubbing induced by ultrasonic violent mixing of the suspended beads. However, no significant desorption occurred for the 0.2 mm beads at position T where the highest mixing degree could be obtained. In addition, scrubbing between heavy (non-suspended) beads at the bead layer might result in paint desorption because the heavy beads rotated at their positions and scrubbed each other. However, no significant desorption occurred for the 4 mm beads at position B where the most bead rotation occurred.

![Fig. 3. Sonophysical desorption activity for three kinds of glass beads at positions T, M, and B. The inset represents real images during ultrasound irradiation.](image-url)

![Fig. 4. Real images for glass beads before and after ultrasound irradiation for free and attached bead conditions. The probe was placed at position B.](image-url)
To further understand the sonophysical activity under the condition of no movement of the beads including suspension and rotation, the desorption tests were conducted at position B under the condition in which the paint-coated beads were attached to the vessel bottom. A relatively large sonophysical activity was expected because direct contact occurred between strong ultrasound and the paint-coated beads, and large cavitational activity was observed at B. Interestingly, contrary to expectations, no meaningful sonophysical desorption activity was observed for all beads, as shown in Fig. 4. The turbidity of the attached beads was 0.013, 0.023, and 0.037 for 4 mm, 1 mm, and 0.2 mm, respectively. Notably, the turbidity for 0.2 mm was only 5% of the turbidity for the free beads. This indicated that there was no direct interaction between strong ultrasound and the beads with a very short irradiation distance; however, the movement of the beads, such as the suspension, was required to achieve large desorption in this study. The desorption mechanism for the suspended beads will be discussed later.

Therefore, the active area for desorption was suggested as the zone around the probe body, opposite to the direction of ultrasound irradiation. From the SCL images at position B in Fig. 2, it could be assumed that extremely strong ultrasound did not induce any significant cavitation events [38,39], and the strong activity just above the bead layer was formed by the reflected ultrasound, which was weaker than the incident ultrasound. However, this assumption is controversial, and further research is required to confirm it.

After completing ultrasound desorption for the free beads, it was observed that uniform desorption occurred for the whole 0.2 mm beads, which moved violently. In contrast, the color of the 0.2 mm beads generally faded slightly. However, for the 1 mm and 4 mm beads, the paint was completely desorbed for some of the beads, whereas no desorption occurred for others. This indicated that the desorption of the heavy beads occurred only in the limited area, and it was confirmed that no significant movement of the beads was induced in the 1 mm and 4 mm bead layers in this study.

3.3. Aluminum foil tests

Aluminum foil erosion tests were conducted without the beads to investigate the sonophysical activity around the probe body. Aluminum foil erosion tests have been used for the quantitative analysis of acoustic cavitation in previous research, and three-dimensional erosion analysis has been rarely reported [15,40-43]. A cylindrical aluminum foil tube with three diameters of 45, 62, and 80 mm was inserted in the vessel, and the ultrasound was applied at positions T, M, and B. As shown in the planar figures in Fig. 5, evident erosion on the aluminum foil was observed for the diameters of 45 and 62 mm at position B where the highest sonochemical and sonophysical activities were observed as discussed above. No significant erosion was observed at the position T and M and for the diameter of 80 mm (even at position B). The reason for the absence of damage on the foil could be explained by the formation of a cavitational active zone, as visualized in the SCL images in Fig. 5. No cavitational activity was observed in the area where the flawless foil was present. Therefore, it could be confirmed that the desorption of the 0.2 mm beads primarily occurred for the suspended beads around the probe body and the desorption was induced by micro-scale sonophysical effects such as microjets. In addition, there is no lack of sonophysical activity in the bottom area because a small but certain level of sonophysical erosion could be obtained on the foil placed at the vessel bottom, as shown in Fig. 6. The threshold of the sonophysical effects for the target materials should also be considered to better understand the mechanism of ultrasonic desorption, washing, and extraction [41].

Saturating gases, including Ar and O<sub>2</sub>, can reportedly affect the severity of cavitation by changing the environmental conditions inside

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Fig. 5. Aluminum foil erosion images for three foil tube diameters of 45, 62, and 80 mm at positions T, M, and B. The yellow lines represent the end position of the emitting tip. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Aluminum foil erosion images for three diameters of 45, 62, and 80 mm at T, M, and B. The foil was placed at the bottom of the vessel.
the cavitation bubbles \cite{32,44–46}. Previous studies have reported the effectiveness of Ar/O\textsubscript{2} gas mixtures for sonochemical oxidation reactions \cite{44,45,47}. Herein, the effect of saturating gas on the sonophysical activity was investigated using air, O\textsubscript{2}, N\textsubscript{2}, and Ar in the aluminum foil erosion tests, as shown in Fig. 7. Interestingly, no big differences were observed for the four gases at B, and considerably high activity was obtained for N\textsubscript{2}. Relatively low sonochemical activity has been reported in N\textsubscript{2} saturated gas conditions compared to those in Ar, O\textsubscript{2}, air, and mixtures \cite{48,49}. The violent mixing action by the ultrasound irradiation of the 20 kHz probe might induce the degassing of excessive N\textsubscript{2} and the gassing of O\textsubscript{2} from the atmosphere, and the saturating gas characteristics might be changed. However, no significant change in the saturating gas condition was observed owing to the short irradiation time (30 s), and no enhancement was observed for Ar and O\textsubscript{2}. Therefore, saturating gas evidently had no significant effect on the degree of sonophysical activity in this study unlike that of sonochemical activity in previous research as mentioned above. There might be differences between the thresholds of sonochemical and sonophysical activities, translating into no observed differences for aluminum foil erosion under various saturating gas conditions \cite{41}.

### 4. Conclusions

In this study, sonochemical and sonophysical activities were quantitatively analyzed to understand the relationship between the two activities in a heterogeneous system (solid and liquid) and whether sonophysical activity in a heterogeneous system could be enhanced under conditions where high sonochemical activity could be obtained in a homogeneous system (only liquid). KI dosimetry and the bead desorption test were applied for various probe position (T, M, and B) and bead size (0.2 mm, 1.0 mm, and 4.00 mm) conditions. The highest sonochemical oxidation was obtained at position B in both homogeneous and heterogeneous systems, although considerably lower activity was observed in the heterogeneous system due to significant attenuation and unstable reflection of ultrasound in the bead layer and suspension. The highest sonophysical activity (desorption) was also obtained for the 0.2 mm beads, which were not suspended because of their heavier weight. In addition, no significant desorption was observed in the attached bead condition. This indicates that sonophysical desorption primarily occurred in the suspended beads around the probe body. To understand the degree of sonophysical activity around the probe body, an aluminum foil erosion test was conducted using a cylindrical aluminum foil tube. Evidently, the SCL zone, related to sonochemical activity, largely overlapped the sonophysical active zone around the probe body. However, extremely low sonophysical activity was obtained in the region just below the emitting tip, although high sonochemical activity was observed in the bottom region. Consequently, the probe position B was suggested as the optimal position for both the sonochemical and sonophysical activities. It was expected that the results of this study could be useful for optimizing ultrasonic extraction and washing processes.

**CRediT authorship contribution statement**

**Jongbok Choi:** Methodology, Investigation, Validation, Writing – original draft. **Younggyu Son:** Conceptualization, Methodology, Writing – review & editing, Visualization, Supervision, Funding acquisition.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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