Effect of gas saturation and sparging on sonochemical oxidation activity in 300 kHz sonoreactors : A comparison of zero-order and first-order kinetics

Seongeun Lee[1,2†], Iseul Na[1,2], Younggyu Son[1,2]
([1]Department of Environmental Engineering, Kumoh National Institute of Technology
[2]Department of Energy Engineering Convergence, Kumoh National Institute of Technology)

1. Introduction

The ultrasound technology of advanced oxidation processes (AOPs) has captured the attention of researchers because it can achieve high sonochemical oxidation reactions without the use of chemicals. Although 300kHz has high production of oxidizing radicals, it is difficult for it to have a sufficient effect on a large scale due to the characteristics of the frequency.

Cavitational oxidation activity can be enhanced by various methods, and studies on dissolved gas injection, fine solid particle injection, and liquid mixing have been reported to improve the degree of cavitation. Buckett and Hua reported that the mixture of Ar/O_2(75:25) resulted in the highest sonochemical oxidation activity.[1] Gas sparging is expected to enhance cavitation activity by mixing the inside of the reactor liquid.

In previous high-frequency studies, researchers performed experiments without considering the water volume/height conditions to wavelength. Asakura et al. reported that liquid volume/height affects ultrasonic sonochemical oxidation reactions under various frequency conditions.[2] In this study, sonochemical oxidation reactions at 300kHz were analyzed based on various liquid volume/ height and gas saturation/sparging conditions. The gases dissolved were Ar/O_2(75:25) and N_2/O_2(75:25), and the liquid volume/height ranged from 25 mm (5λ) to 250 mm (50λ).

2. Materials and Methods

Fig. 1 shows a circular type sonoreactor equipped that was used in this study; it has an ultrasonic transducer module (Mirae Ultrasonic Tech., Bucheon, KOR) at the bottom. The mixing and flow rate of dissolved gas was controlled using a mass flow controller (HFC-D-302B, Teledyne Hastings Instruments), a static mixer (Gasline, Seongnam), and a mass flow meter (HFM-D-300B). The air flow rate was determined at a flow rate of 3L/min in a position that was 1cm away from the transducer module, as reported in a previous study.[3] Various liquid height/volume conditions were

bs9457@kumoh.ac.kr, yson@kumoh.ac.kr

calculated based on the frequency and wavelength, that ranged from 5λ(0.47L) to 50λ(4.30L).
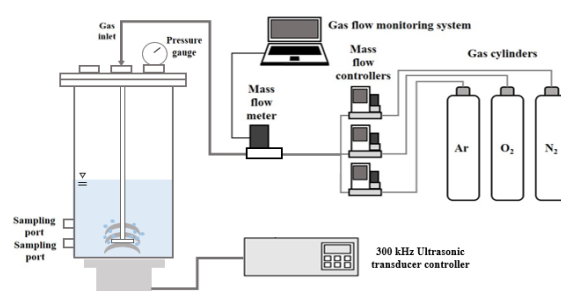

Fig. 1   A schematic of 300 kHz ultrasonic system and gas supply system used in this study.

The sonochemical reactions were confirmed using KI dosimetry, which is a zero-order reaction, as initial concentration of the KI solution was an excessive. However, because the pollutants decomposition has a relatively low initial concentration, it is interpreted at a first order reaction. To confirm the zero/first order reaction in the cavitation activity, the decomposition degree of Bisphenol-A (BPA) was quantified using HPLC (1260 Infinity II LC, Agilent).
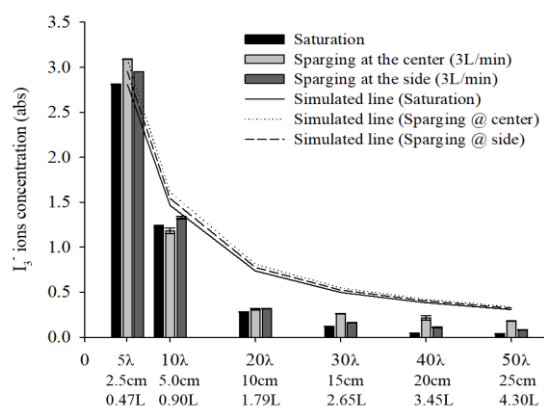
3. Results and Discussions

Fig. 2   Comparison of ultrasonic oxidation activity under gas saturation and sparging conditions of Ar/O2(75:25).
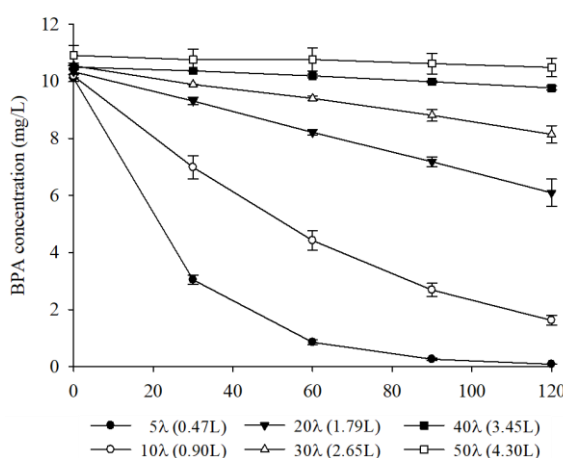
Fig. 3 Sonochemical degradation of BPA at a liquid height of 5λ to 50λ under the gas saturation condition of Ar/O2 (75:25).

Sonochemical oxidation reaction was analyzed by applying gas saturation/sparging at various liquid volume/height. As shown in **Fig. 2**, if the liquid volume/height increases, the concentration of I_3^- ions decreases under low sonochemical oxidation activity. In a typical chemical reaction, if the liquid volume/height increases under the same conditions, the concentration will be inversely proportional. This is shown by the simulation line in Fig. 2, and the I_3^- concentration decreased as the volume increased under the condition of 5λ. However, in this study, the experimental results were lower than the results shown by the simulated line at a liquid volume/height above 10λ. It is judged that the inverse proportion is caused by the increase in liquid volume/height, and the cavitation activity additionally decreased according to the liquid volume/height.

In the first order reaction, the BPA sonochemical degradation (initial concentration of 10 mg/L) was performed by applying the same liquid volume/height and dissolved gas conditions as in the 0th reaction experiment. The BPA sonochemical degradation at the gas saturation conditions are showed in **Fig. 3**. In the case of gas saturation, the low liquid volume/height (5-10λ) increased BPA sonochemical degradation (97.4%, 80.0%), whereas the high liquid volume/height (20~50λ) significantly decreased BPA sonochemical degradation (28.2%, 3.6%). Table. 1 shows the reaction time to obtain various treatment efficiencies using the calculated first order reaction rate constant to compare and analyze the BPA sonochemical degradation under different liquid volume/height.

Table. 1 First order reaction kinetics constants of the sonochemical degradation of BPA under the gas saturation condition and calculated reaction times for various BPA removal efficiencies.

Liquid height/volume	Reaction kinetics Constants (min^{-1})	Reaction time of Removal efficiency		
		50%	90%	99%
5λ (0.47L)	40.0×10^{-3} (R^2: 0.9985)	21.2	70.4	140.8
10λ (0.90L)	15.5×10^{-3} (R^2: 0.9962)	51.3	170.6	341.1
20λ (1.79L)	4.40×10^{-3} (R^2: 0.9903)	246.7	819.4	1,638.9
30λ (2.65L)	2.10×10^{-3} (R^2: 0.9891)	427.9	1,421.3	2,842.7
40λ (3.45L)	0.40×10^{-3} (R^2: 0.9675)	1,283.6	4,264.0	8,528.1
50λ (4.30L)	0.03×10^{-3} (R^2: 0.9200)	2,236.0	7,427.7	14,855.4

As shown in **Table. 1**, the removal efficiency has rapid time at 5λ compared to that at other liquid volume/height. For example, the time at a liquid volume/height of 50λ was 9.2 times larger than that at 5λ, but the reaction time was approximately 106 times larger. This means that the 99% BPA sonochemical degradation at 5λ was repeated 100 times at 50λ. Therefore, in designing a water treatment process using ultrasound technology, the optimal liquid volume/height according to the wavelength is important. If this is not considered, the efficiency of the entire process may be lowered.

References
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