Effect of Dissolved Gas on Sonochemical Oxidation

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1. Introduction

The cavitation phenomena is occurred by applying 20 kHz to 1Mhz ultrasound in the liquid.[1)] In the liquid phase, the bubbles are growth and collapse by ultrasonic pressure. When the bubbles are collapsed the energy is transferred to the water molecules, consequently highly reactive readicals, such as hydroxyl radical, are generated that called sonochemical effects.

There are a lot of researchers are conducted to enhance sonochemical effects by changing operating parameters and liquid conditions.[2-4)] Dissolved gas with novel gases (Ar, He, and Kr) is one of the effective options to increase sonochemical effect, more than five folds higher than the normal condition.[5-6)] Recently, the study has been conducted to find relationships between dissolved oxygen concentration and ultrasound to find the characteristics of gas saturated liquid in ultrasound system.[7)]

In this study, we measured dissolved oxygen concentration under the gas saturated conditions with four types of gas(Air, O_2, N_2, and Ar) during 20kHz ultrasound irradiation. Moreover, the concentration of radicals was measured to find the relationships between dissolved oxygen concentration and sonochemical effects.

2. Materials and Methods

The schematic of gas saturation process and ultrasonic irradiation process is shown in **Fig. 1**. The gases are provided with a gas diffuser by controlling flowrate (2LPM) for 20min to make gas saturation conditions before ultrasonic irradiation. The horn-type 20kHz ultrasound was applied in the ultrasonic irradiation process, and the power was 50% displayed on the ultrasonic transducer controller. The temperature was kept at 22.0±1.0℃ during sonication process. The diameter of a tip on the ultrasonic probe is 13 mm. The probe was located at a distance of 1 cm above the bottom of beaker to maximize the sonochemical effect.[4)] The dissolved oxygen concentration was measured at initial concentration in which the gas was sufficiently saturated in the liquid, and at 30-second intervals for 3 min ultrasonic irradiation using a DO meter (ProODO; YSI Inc., USA).

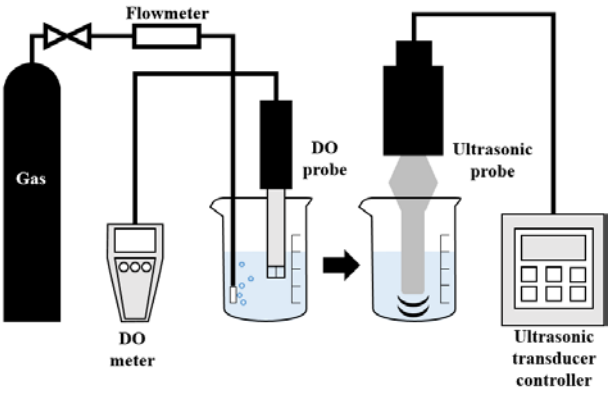

Fig. 1 Schematic of gas saturation and ultrasound irradiation process.

KI dosimetry was used to measure produced highly reactive radicals concentration.[8)] The iodide (I^-) reacts with radicals and form iodine (I_2) in the solution. Thereafter the excess amount of iodide and iodine react to form triiodide ions (I_3^-) that concentration was measured by analyzing its absorbance (350 nm) through UV-Vis spectrometer (Vibra S60, Biochrom Ltd., UK). The experimental sets were carried out three to six times, the data is marked with an error bar at each point on the graphs.

To analyze ultrasonic degassing and gassing of oxygen, the volumetric mass transfer coefficient and 1st order reaction constant was calculated to compare with the sonochemical effects in the gas-saturated ultrasonication system.

3. Results and Discussions

The dissolved oxygen concentrations with and without ultrasound irradiation were shown in **Fig. 2**. The concentrations were decreased (degassing of oxygen) with each of Air and O_2 saturated conditions, however, the concentration was increased (gassing of oxygen) with each of N_2 and Ar saturated conditions as shown in **Fig.2(A)**. The concentrations have little enhancement without ultrasound in all gas-saturated conditions (**Fig.2(B)**).

To analyze degassing of oxygen molecules in the liquid by ultrasound application, the 1st order kinetic constants were calculated. The dissolved oxygen concentrations were increased by 1±0.01 ppm and 11.04±0.26 ppm, for 3 minutes of sonication under air and O_2 saturated conditions,

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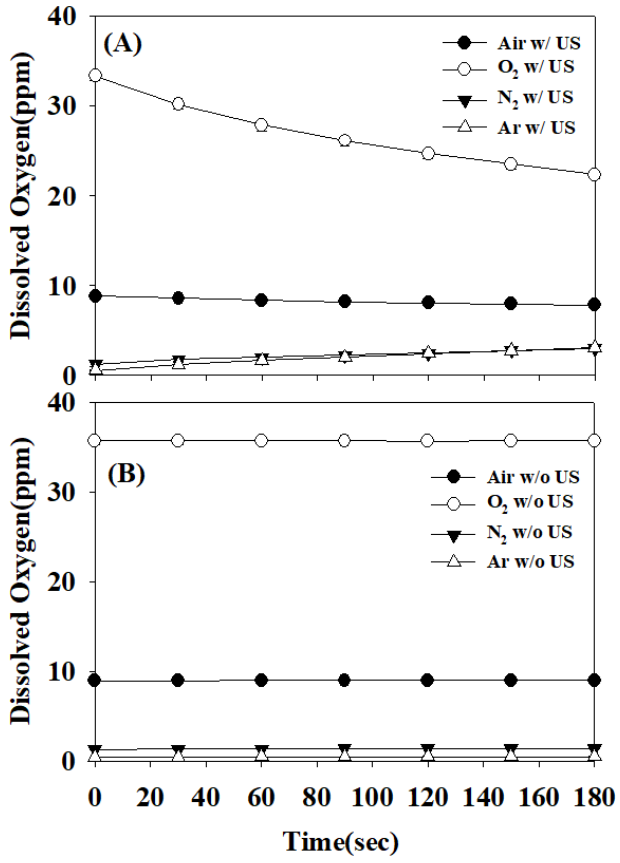

Fig. 2 Changes of dissolved oxygen concentration according to dissolved gases with ultrasound (A), and without ultrasound (B).

and the kinetic constant of each process are 0.73×10^{-3} s^{-1} (R^2=0.95) and 2.4×10^{-3} s^{-1} (R^2=0.97), respectively.

The volumetric mass transfer coefficient (K_La) of each of N_2 and Ar saturated conditions under with/without ultrasound was calculated to analyze oxygen gassing by ultrasound. The values of N_2 w/US, N_2 w/o US, Ar w/ US, and Ar w/o US were 1.5×10^{-3} s^{-1} (R^2=0.98), 0.033×10^{-3} s^{-1} (R^2=0.93), 2.1×10^{-3} s^{-1} (R^2=0.99), and 0.039×10^{-3} s^{-1} (R^2=0.97), respectively. In the previous research, the 0.43×10^{-3} s^{-1} (US) and 0.02×10^{-3} s^{-1} (w/o US) under 28kHz plate type ultrasound applications.[7] It was confirmed that the kinetic constants and the mass transfer coefficients (K_La) of w/ ultrasound become larger than w/o ultrasound according to the difference between the oxygen saturation concentration (C_{sat}, 8.53 ppm at 22℃, 1 atm) and initial oxygen concentration (C_{ini}) of each gas saturated condition, the ultrasound seems to play a role in accelerating to the equilibrium state.

The concentrations of triiodide ions (I_3^-) for each process are shown in **Fig. 3**. The generation rate of I_3^- (μM/s) of Air, O_2, N_2, and Ar saturated conditions are 7.7×10^{-3} μM/s (R^2=0.97), 12.1×10^{-3} μM/s (R^2=0.99), 5.7×10^{-3} μM/s (R^2=0.92), and 28.8×10^{-3} s^{-1} (R^2=0.95), respectively. The R-squared

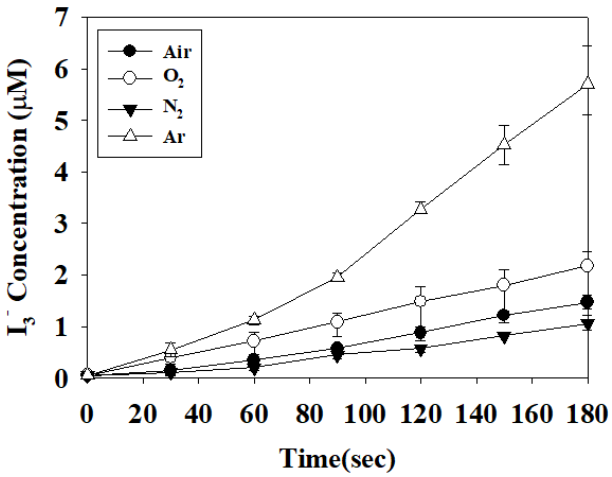

Fig. 3 I_3^- concentration according to the time under various dissolved gas-saturated conditions by applying 20 kHz ultrasound.

values in the degassing process (Air and O_2), are higher than those in the gassing process (N_2 and Ar), because of the change of dissolved oxygen makes unstable sonochemical reactions. The sonochemical effects is more increased in the presence of a mixture with O_2 and Ar than a condition in which a single Ar gas-saturated condition because O_2 can provide the source of highly reactive radicals, such as hydroxyl radical, and its optimum value around 25% of O_2 with Ar.[9]

Acknowledgment

This work was supported by National Research Foundation (NRF) of Korea (No. 2019R1I1A1A01059501) and by the Korea Ministry of Environment (MOE) as "SEM (Subsurface Environment Management)" Program (project No. 2021002470001).

References

1. M. Ashokkumar and T. Mason: *Sonochemistry* (2000) p. 1
2. K. Daisuke, H. Chiemi, M. Hideyuki, T. Tomoki, S. Yuichiro, K. Chiaki, O. Katsuto, and S. Atsushi, Jpn. J. Appl. Phys. **53**. (2014) 07KE03
3. H. Hisashi and O. Yuki, Jpn. J. Appl. Phys. **54** (2015) 07HE10
4. Y. No and Y. Son: Jpn. J. Appl. Phys. **58** (2019) SGGD02
5. I. Hua and M. Hoffmann: Environ. Sci. Technol. **31** (1997) 2237
6. J. Rooze, E. Rebrov, J. Schouten and J. Keurentjes: Ultrason. Sonochem. **18** (2011) 209
7. J. Choi, H. Lee and Y. Son: Ultrason. Sonochem. **70** (2021) 105334
8. S. Koda, T. Kimura, T. Kondo and H. Mitome: Ultrason. Sonochem. **10** (2003) 149
9. R. Pflieger, T. Chave, G.Vite, L. Jouve and S. Nikitenko: Ultrason. Sonochem. **26** (2015) 169