論 文 の 内 容 の 要 旨

生物・環境工学　専　攻
平成 19 年度博士課程　入学
氏　　名　フェルナンダ　ユミ　ウシクボ
指導教員名　大下誠一

Fundamental Studies on the State of Water with the Generation of Micro and Nano-bubbles

（マイクロ・ナノバブル生成に伴うバブル含有水の状態に関する基礎研究）

1. Introducion

The use of micro and nano-bubbles (MNB) in water was reported to be effective for the acceleration of metabolism in shellfishes and vegetables [1, 2], accelerating the growth and increasing the yield of the products. This effectiveness, however, cannot be explained only by the increase of the dissolved oxygen (DO) concentration. Park and Kurata [2], using MNB in the solution for the hydroponic cultivation of lettuce, observed acceleration in growth in comparison with lettuce grown in solution containing similar DO concentration but without MNB. Therefore, the MNB should play an important role in the physiological activity of living organisms.

There are still many questions concerning the nano-bubbles that are not clear. Some of them are the stability and size of nano-bubbles after the introduction of MNB in water.

The present study aimed to investigate the state of water during and after the MNB generation and, more specifically, to study the existence and stability of bubbles in nano-scale in water after the introduction of MNB.

2. Micro and Nano-bubble Generation

Micro and nano-bubbles were produced in 2 liters of ultrapure water, obtained by a water purification system (Direct-Q, Nihon Millipore Ltd., Japan). The gas used to produce micro and nano-bubbles was pure oxygen.

A Micro-bubble Generator (OM4-GP-040, Aura Tec Co. Ltd., Japan) was used for the production of micro and nano-bubbles. The water and the oxygen were introduced in the inlet part of a magnetic gear pump (MDG-R2RVA100, Iwaki Co. Ltd., Japan) and subjected to a high pressure (0.25 to 0.27 MPa) in a pressurized tank. Flowing through the ejector nozzle in the outlet, the gas-supersaturated water was depressurized, leading to the nucleation of the bubbles, which were dispersed in the water. The water was circulated in this system for 40 minutes at 20°C. In this study, the water obtained after this procedure is referred to as “MNB water”.

3. ζ-Potential

3.1. Materials and Methods

ζ-potential measurements of the oxygen MNB water was performed using a Zeta Potential Analyzer (Zeecom, Microtech Co. Ltd., Japan). This system detects the electrophoretic mobility of particles in the range of 20 nm to 100 μm. The ζ-potential was calculated using the Smoluchowski equation.

3.2. Results

The ζ-potential for the oxygen MNB water just after the bubble generation was in the range from -44 to -40 mV. With time, the values decreased in absolute value (-38 ~ -33 mV). The pH was practically constant at pH 6.2~6.4. This result was similar to the data obtained by Takahashi [3], which were around -35 mV in distilled water with air micro-bubbles at pH 5.8.

The negative value of ζ-potential indicates the polarization of water molecules in the water, as no ions were added in this system. The high values of ζ-potential indicate the stability of particles in the liquid phase, as they will repel each other. This could be a hint to understand the possible stability of nano-bubbles.

4. Particle Size Distribution

4.1. Materials and Methods

Zetasizer Nano ZS particle size analyzer (ZEN3500, Sysmex Co., Japan), green badge (532 nm laser), was used to detect particles in MNB water after the bubble generation. This analyzer detects Brownian motion of particles from 0.6 nm to 6 μm through Dynamic Light Scattering method. The measurements were performed at 20°C and 5 to 10 replications were done.

4.2. Results

The particle size distribution of the oxygen MNB water just after the bubble generation showed a geometric mean diameter of 137 nm and a coefficient of variation of 61.2% (Fig 1(a)). The stability of the particle size distribution was shown by the regular shape of a mono-modal lognormal curve and good repeatability of the measurements. After three days of observation, larger particles with geometric mean diameter of 380 nm were detected and the dispersion of the distribution size was higher, with a coefficient of variation of 107.4%.

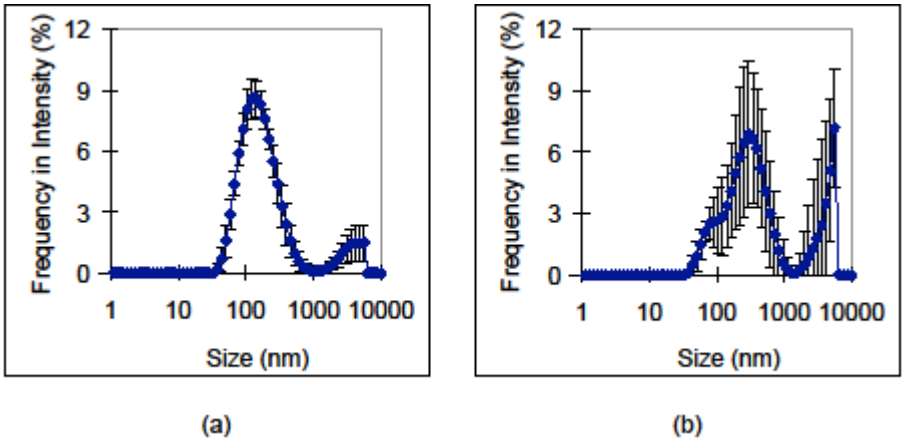

Fig 1 Average particle size distribution (n = 10) of the oxygen MNB water (a) just after stop the bubble production and (b) after 6 days. The vertical bars represent the standard deviation at each measurement point.

Finally, on the sixth day after the bubble generation, the particle size distribution curves were no longer mono-modal, with no repeatability and the dispersion of the distribution became very high (181.2%) as shown in Fig 1(b). This result indicated an insufficient concentration of particles to be detected by the instrument. The decrease in the particles concentration suggests the disappearance of nano-bubbles due to the dissolution of oxygen into the water.

5. Proton NMR Spin-lattice Relaxation Time

5.1. Materials and Methods

Five replications of each sample (control and MNB) were collected in tightly closed 10 mm diameter NMR tubes. Proton spin-lattice relaxation time (T_1) was measured in a pulsed spectrometer (JNM-MU25A, JEOL, Japan) at 25 MHz frequency and at constant temperature of 20°C, using the saturation recovery pulse sequence.

The experiment consisted in using manganese solution as control. Solutions of 3, 5, 10, 15, 40 mM of manganese (II) chloride tetrahydrate ($Mn_2Cl \cdot 4H_2O$, Kanto Chemical Co. Inc., Japan)

were prepared (control sample), then oxygen MNB were generated in this solution (O_2 MNB solution). A more detailed analysis was done at 10 mM manganese solution, diffusing oxygen through a gas diffuser, which did not contain MNB (O_2 without MNB solution).

5.2. Results

It was verified that T_1 increased ($p<0.05$) after the introduction of oxygen as MNB in all the manganese concentrations tested. The DO concentration increased from about 7.7~ 9.4 $mg \cdot L^{-1}$ in control sample to 35.8~39.6 $mg \cdot L^{-1}$ in oxygen MNB solution.

One important point is that the increase in T_1 was not caused by the increase in DO concentration. The O_2 without MNB solution at 10 mM Mn^{2+} concentration had similar DO concentration as the O_2 MNB solution: 37.1 $mg \cdot L^{-1}$ and 38.8 $mg \cdot L^{-1}$, respectively. However, the T_1 of the O_2 without MNB solution did not differ statistically from the control sample ($p<0.05$). Therefore, the generation of micro and nano-bubbles is the only reason for the T_1 increase observed in O_2 MNB solution.

The major reason for the relaxation time change in oxygen MNB solutions was the change in apparent concentration of manganese ions. As bubble surfaces are negatively charged, as indicated by the ζ-potential measurements, some amount of manganese ions should adsorb on the bubble surface, resulting in a lower apparent Mn^{2+} concentration in the solution. Since the paramagnetic material decreases T_1 only when in direct contact with the water molecule, the lower apparent concentration of Mn^{2+} of the solution induced a lower paramagnetic effect. As a consequence, a longer T_1 was observed in solutions containing MNB. This fact confirms the stability of nano-bubbles in the solution after the generation of oxygen MNB.

6. Conclusion

Using different approaches, the existence of stable nano-bubbles in water was strongly suggested. The particle size distribution indicated the presence of particles with a few hundreds nanometers in diameter during some days. Moreover, the change in T_1 of Mn^{2+} solution after the introduction of oxygen MNB suggested the presence of nano-bubbles by the adsorption of Mn^{2+} on the bubble surface. The stability of nano-sized bubbles could be explained by both the highly dissolved gas concentration in water and the electrically charged interface of the bubbles, supported by the ζ-potential measurements.

References

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