Size Distribution and Filtering Characteristics of Pressure Dissolved Oxygen Ultrafine Bubbles

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Abstract - To understand the properties of oxygen ultrafine bubbles (O_2-UFB), we examined the evolution of the size distribution and the number density of O_2-UFB water at various O_2-UFB generation times. Results show that the UFB concentration increased with increasing generation time and the O_2-UFB size distribution was shifted to smaller sizes after longer generation times. In addition, the results suggested that O_2-UFBs need time to stabilize and achieve smaller sizes. UFBs remained in the water after storage for 7 days, but the water became contaminated by bacteria. Furthermore, a hydrophilic filter is recommended for medical applications because it blocks the particles but allows the passage of fine bubbles. It was found that the choice of the hydrophilic filter material affects the O_2-UFB transport rate and concentration.

Keywords – ultra fine bubbles, dissolved oxygen, concentration, filtering, size distribution

I. Introduction

Ultrafine bubbles (UFB) or nanobubbles are tiny bubbles with diameters on the order of nanometers. These bubbles have interesting and unusual properties, such as long lifetime, high surface area per volume, high stability, and rapid attachment to hydrophobic surfaces. These properties give rise to a wide range of potential applications of UFB in various areas, such as medicine [1-3], surface coating and cleaning [4-5], pollutant removal [6-7], microorganism disinfection [8] and agriculture and aquaculture [9-11].

However, there remain many unresolved questions about UFBs, motivating research efforts in a variety of research directions. The basic properties of UFBs and the correlation between electric conductivity and bubble concentration were studied and explained in terms of the bubbles' zeta potential [12]. It was reported that the zeta potential of UFB water is negative [13-15]. In addition, both the zeta potential and mean diameter of UFB depend on pH (at least at pH 3-8) [16]. A previous study reported that with increasing pH, the UFB become smaller and the zeta potential becomes more negative [17]. Presumably, the developed double layer provides a repulsive force that prevents inter-bubble aggregation and coalescence of the bubbles [15,18]. Many studies have reported evidence for the stability of nanobubbles for days or even months [10,15,19-20].

In 2017, our group (RMUTL, Thailand) started a research collaboration with Kyoto university to study the evolution of UFB distribution. In our preliminary study, bubbles and particles were investigated by using the resonant mass measurement technique (Archimedes, Malvern Panalytical, Ltd., UK). We found that 50% of the sample is present in the particle form, and the UFB-particle ratio did not vary with time. Then, we further investigated the size distribution of UFB in comparison to nanoparticles using the Horiba LA-960A (Horiba Ltd., Japan) and Malvern NanoSight LM10 instruments (Malvern Panalytical, Ltd., UK) [21]. The size distribution of air UFB changes rapidly and is wider than the nanoparticles' distribution. Therefore, this technique can distinguish bubbles from particles. Moreover, it was found that after the generation of nanobubbles water for a few days, the bubble size decreased from the micrometer to the nanometer scale and the UFB concentration also increased. However, the evolution of the characteristics of the O_2-UFBs with time has not been studied.

In medical applications, the nanobubble water must be bacteria- and particle-free. While the sterilization of the entire UFB generator is possible, it is complicated and time-consuming. Therefore, filtering through a filter of pore size 200–220 nm is commonly used in biological treatments because this procedure is very user-friendly and can remove micro-structured particles and bacteria in the solution. However, this raises a question of what kind of filter is suitable for filtering of O_2-UFB water for biological treatment. Furthermore, the difference in the filtering effect between the hydrophobic and hydrophilic filters has not been intensively investigated.

In this study, the evolution of the bubble size distribution with the UFB generator operation time and the factors that affect this distribution were studied by nanoparticle tracking analysis. In addition, the stabilities of O_2-UFB and dissolved oxygen levels over 7 days were investigated. Furthermore, the characteristics of the transport of O_2-UFBs in both hydrophilic and hydrophobic filters were examined.

II. Methodology

A. *Characteristics and stability of O_2-UFB water*

Deionized water (G-10D, Organo Co., Ltd. Japan) was used to produce micro- and nanobubble water. Oxygen ultrafine bubble water (1 L) was produced using a desktop UFB generator (KVM-01-J, RMUTL, Thailand) based on the pressurized dissolution method. In this apparatus,

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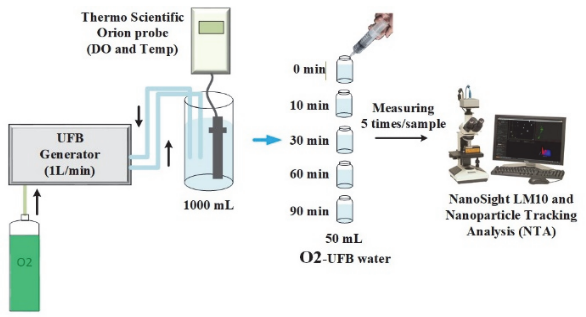

Fig. 1. Schematic of the experimental setup.

oxygen gas was supplied at a pressure of 0.05 MPa and the water pressure was approximately 0.8 MPa as shown in Fig. 1.

Dissolved oxygen (DO) concentration and the water temperature were measured during the generation of O_2-UFB water using a Thermo Scientific Orion probe (Thermo Fisher Scientific, USA) every 0, 10, 30, 60 and 90 minutes, respectively. O_2-UFB water (50 mL) was removed from a 1-L sample of nanobubble water every 0, 10, 30, 60 and 90 minutes, respectively (the UFB generator was operating for the entire 90 minutes' duration of the experiment), and the sample was transferred to a closed 50-mL glass container and kept for 30 minutes at room temperature (24 °C).

Then, the size distribution and concentration of the nanobubbles were analyzed using a nanoparticle tracking analysis instrument (NTA, Malvern NanoSight LM^{10}, UK) that detects the Brownian motion of the nanobubbles. Five replications were performed for each sample. All the samples were kept closed in a 50-mL glass bottle and were placed in the refrigerator (4 °C). Each sample was measured again after 5 hours, 1 day and 7 days, respectively.

B. *Filtering effect*

The experimental procedure of the filtering is shown in Fig. 2. Fresh O_2-UFB water (1 L) was produced by the KVM-01-VJ generator (RMUTL, Thailand) with the flow rate 1 L/min for 60 minutes. The UFB water pressure and oxygen gas pressure were set to 0.8 MPa and 0.1 L/min, respectively. The DO concentration in water was 38 mg/L. The size and concentration of the oxygen ultrafine bubble were investigated 5 times as the control using a NanoSight LM^{10} instrument.

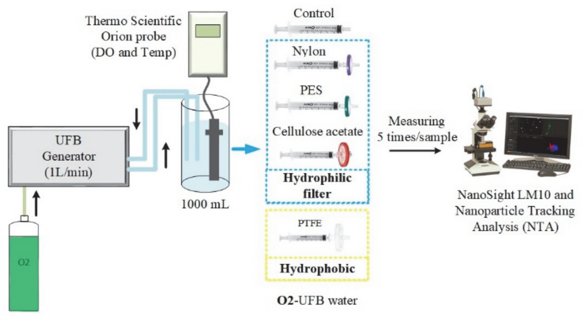

Fig. 2. Schematic of the experimental procedure for filtering.

Then, the sample was filtered using the different filters described in Table I and shown in Fig. 3. The distribution and concentration of O_2-UFB obtained after filtering were investigated by nanoparticle tracking analysis. The filtering process and the distribution measurement were carried out for a total of five times for each filter type using a new filter for each replication.

TABLE I
FILTER CHARACTERISTICS.

Number	Name	Type	Size (nm)
1	No filtering (Control)	N/A	N/A
2	Nylon	Hydrophilic	200
3	Polyethersulfone (PES)	Hydrophilic	220
4	Sterile cellulose acetate	Hydrophilic	200
5	Polytetrafluoroethylene (PTFE)	Hydrophobic	200

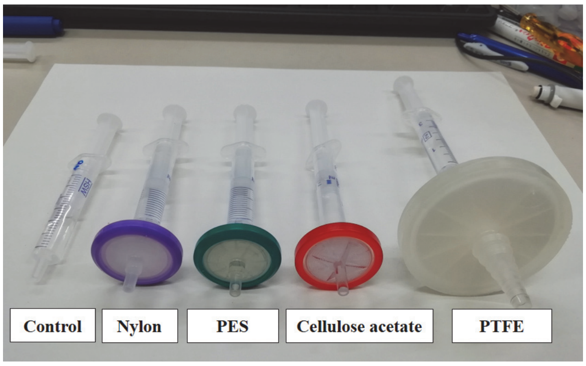

Fig. 3. Photographs of hydrophilic and hydrophobic filters.

III. Results and Discussions

A. *Characteristics of O_2-UFB water at various operation times*

As shown in Fig. 4, oxygen concentration in the original deionized water was 9.84 mg/L and then increased to 34.08 mg/L immediately after running the generator with 1,000 mL of water for 30 minutes. It was also observed that the concentration of UFBs increased with increasing generation time (Fig. 5). It is possible that the amount of the generated UFBs increases with increasing recirculation time. The O_2-UFB concentration reached 1.05×10^8 particles/mL after operation for 90 minutes. Furthermore, the water temperature increased from 17.3 °C to 30.6 °C within 90 minutes due to machine heating, which may affect the dissolved oxygen level in the O_2-UFB water because oxygen solubility decreases with increasing temperature [22]. Moreover, the increased temperature may cause the water to become contaminated

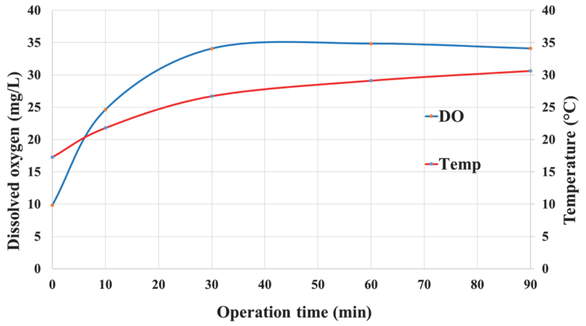

Fig. 4. Evolution of the DO concentration and temperature in O_2-UFB water.

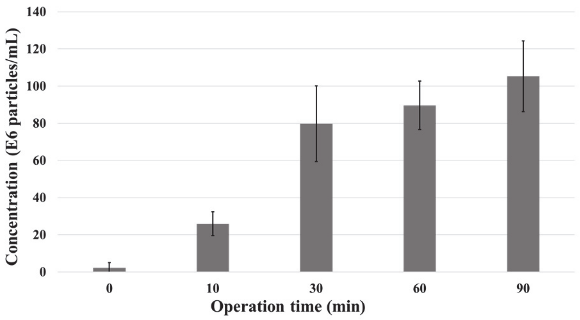

Fig. 5. Concentration of the O_2-UFBs for various operation times.

by the particles inside the generator. It is possible that the heating may cause some breakage of the generator, generating particles. Such particle contamination was also reported in a previous study [10]. Therefore, temperature control will be considered in future studies and filtering of O_2-UFB water is required for eliminate particle contamination.

Table II shows the average size and the concentration of UFBs at various operation times. In the beginning of operation (yellow line) as shown in Fig. 6, four peaks were observed in the UFB size distribution. Then, after operation for 30 minutes (red line), two peaks were observed in the UFB size distribution at 180 nm and 250 nm, respectively. Then, after operation for 60 minutes (green line), the concentration of UFBs increased and the two peaks shifted to the left (around 150-250 nm size), representing the decrease in the bubble size. It is possible that longer operation leads to the microbubble shrinkage because of gas dissolution and formation of UFBs [17].

At the operation time of 90 min (violet line), peaks at 280 nm peak and 440 nm are observed (Fig. 6). It is possible that the water temperature increase during the bubble generation by the pressurized dissolution method will cause the bubbles to grow either due to the non-uniform surface conditions or to the water contamination by particles. Moreover, higher temperature can decrease the solubility of the dissolved oxygen in the water.

B. *Stability of O_2-UFBs over 7 days*

Table III represents the average size and concentration of the fresh O_2-UFB and after storage for 5 hours and 1 day, respectively. In addition, the evolution of the fresh O_2-UFB distribution (black color) compared with the distributions of the O_2-UFB water after storage for 5 hours (red color) and 1 day (green color), respectively as shown in Fig. 7. While the dissolved oxygen level of fresh O_2-UFB decreased from 34.85 mg/L to 22.08 mg/L and 13.88 mg/L after leaving the sample for 5 hours and 1 day, respectively (data not shown).

TABLE II
SIZE AND CONCENTRATION OF THE O2-UFB AT VARIOUS OPERATION TIME.

Operation time (min)	Average size (nm)	Concentration (E8 particles/mL)
0	49.00±67.12	0.02±0.03
10	265.60±68.70	0.26±0.07
30	238.60±77.71	0.80±0.23
60	176.60±32.19	0.90±0.15
90	240.20±69.22	1.06±0.21

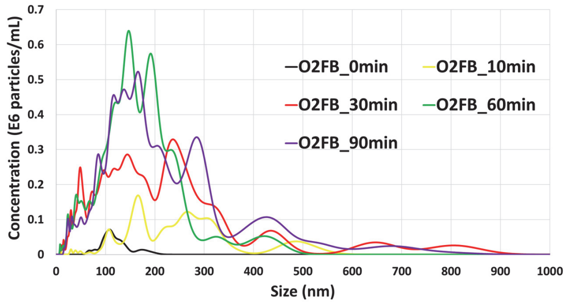

Fig. 6. O_2-UFB distributions at various operation times (average values, n=5).

TABLE III
SIZE AND CONCENTRATION OF THE FRESH O2-UFB AND AFTER STORAGE FOR 5 HOURS AND 1 DAY, RESPECTIVELY.

O2-UFB water	Average Size (nm)	Concentration (E8 particles/mL)
Fresh	176.60±32.19	0.90±0.15
After storage for 5 hrs	206.80±45.59	1.07±0.37
After storage for 1 day	230.20±64.83	0.92±0.39

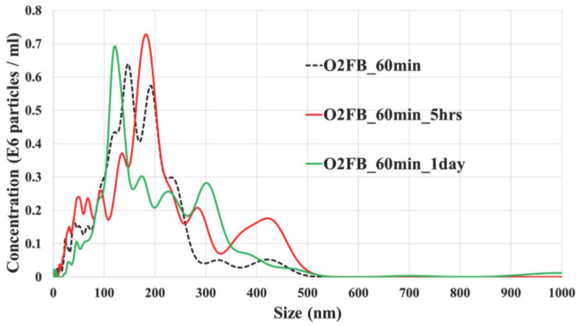

Fig. 7. Evolution of the fresh O_2-UFB distribution and the distributions after storage for 5 hours and 1 day, respectively. (average values, n=5).

These data suggest that after the UFB generator stops operating, the DO level of O_2-UFB tends to decrease even if the sample is kept in a closed container due to the shrinkage of the microbubbles and some bubbles burs to the water surface. In addition, the size of fine bubbles decreases and the bubbles become more stable after storage for 1 day as shown in Fig. 7. This data is in agreement with the results of a previous study [21] that found that the bubble size tends to change from the micrometer scale to the nanometer scale after the end of the UFB generation. However, other studies [15,23] using the dynamic light scattering (DLS) method reported that the diameter of the bubbles increases after storage for 1 or 2 days. However, DLS is more sensitive to large particles or bubbles than to smaller bubbles, which is a disadvantage for nanobubble size measurements. Therefore, it is possible that a relatively high concentration of micro bubbles (larger size) was detected in the DLS study.

The concentration of the dissolved oxygen of the O_2-UFB water decreased from 34.85 mg/L (original) to 11.34 mg/L after storage for 7 days (data not shown). Nevertheless, this DO concentration is still above the saturation level, similar to the result obtained in [15]. While a distribution of bubble sizes in UFB water was still found by the NanoSight LM[10] measurements after storage for 7 days, the O_2-UFB concentration was reduced (data not shown), in agreement with the results obtained in previous work [10,24]. These results suggest that a negative zeta potential of UFBs may create a repulsive force that contributes to the stabilization of the nanobubbles and prevents bubble coalescence. Furthermore, bacteria were found in the water after storage for 7 days. This suggest that oxygen rich –UFB generation may have the side effect of promoting bacterial contamination because aerobic bacteria can survive and grow in an oxygenated environment.

C. *Effects of hydrophobic and hydrophilic filters*

It was found that neither fine bubble water nor normal water can pass through the hydrophobic filter (data not shown). Presumably, the hydrophobic material of the filter repels water so that all liquid samples were blocked by this filter except for organic solvents or aqueous solutions. Therefore, a hydrophobic filter is not suitable for ultrafine bubble water filtration.

By contrast, hydrophilic filters were found to be suitable for filtering O_2-UFB and were able to eliminate the contamination by bacteria or particles with the diameters of more than 200 nm [24]. However, selection of appropriate materials for hydrophilic filters is crucial for efficient filtering in medical applications.

Figs. 8 and 9 show that UFBs disappeared after passing through a Nylon (200 nm) filter. This result is in agreement with the previous report [24] that after the application of this filter, the bubble density decreased by 90% compared to the control. This result suggest that Nylon filters are suitable for ultrafine bubble filtration and provide nano-bubble-free water as the control because of their high blocking capability.

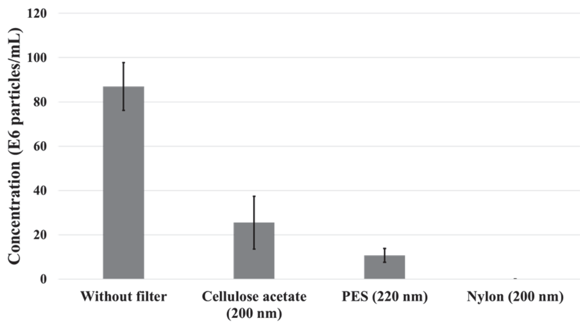

Fig. 8. Concentration of bubbles in O_2-UFB water after passing through various filters.

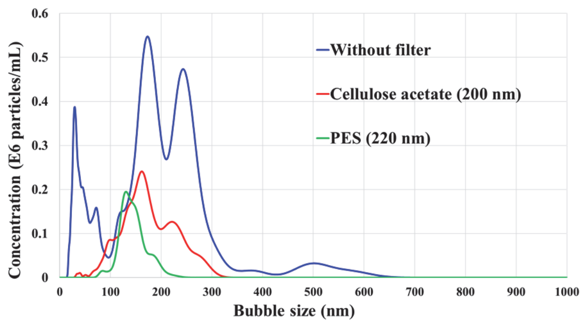

Fig. 9. O_2-UFB distribution after passing through various filters.

On the other hand, hydrophilic filters made of polyethersulfone (PES, 220 nm) and sterile cellulose acetate (200 nm) allow only 12% and 29%, respectively, of the original UFB water to pass through the filter as shown in Figs. 8 and 9. Therefore, both these hydrophilic filter materials were found to be suitable for use in medical applications due to their high filtering efficiency.

By contrast, bubbles with the sizes greater than 300 nm were still present after cellulose acetate filtering (red line in Fig. 9). Presumably, after fine bubbles pass through the cellulose acetate filter, they agglomerate into bubbles with larger size because of the non-uniform surface conditions or the change in the zeta potential. The mechanism of filtering of fine bubbles is different from the mechanism for particle filtering for which the filter can block almost all the particles that are larger than the size of the filter. Therefore, further work is necessary to understand the mechanism of the nanobubble filtering effect.

IV. Conclusion

In this study, we measured dissolved oxygen levels and the evolution of the amount of O_2-UFB with the UFB generator operation time by detecting the Brownian movement of UFB. In addition, effects of both hydrophobic and hydrophilic filters were investigated. The results show that

· UFBs concentration increased with increasing operation time and the size distribution of O_2-UFB shifted to smaller sizes for longer operation times.

· O_2-UFB water requires time for stabilization and formation of smaller bubbles. Then, the dissolved oxygen can be retained at the concentration of 11.34 mg/L for 7 days in a closed container. However, bacteria were found in the sample.

· Hydrophobic filters were found to be not suitable for UFB filtration because UFB cannot pass through the filter.

· Hydrophilic filters were found to be most favorable for selecting the size of UFB with a high filtering efficiency. However, the material of the hydrophilic filters is very important and this study suggests that

i. Nylon is suitable for UFB filtration due to its high blocking capacity

ii. Polyethersulfone is recommended for filtering in medical applications because it can block both bubbles and particles with the sizes greater than 220 nm

iii. Sterile cellulose acetate (200 nm) is also suitable for filtering but may give rise to microbubble formation.

Therefore, the filtering effect is currently unsatisfactory and requires further investigation in future work.

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