Removal of Microcystis in the Outer Moat of the Tokyo Imperial Palace Using Ozone Microbubbles

Daisuke Kobayashi[1], Mizuki Mitsuhashi[2], Tomoki Takahashi[1], Katsuto Otake[1], Atsushi Shono[*1]

[1]Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, Tokyo, Japan
[2]Department of Industrial Chemistry, Graduate School of Engineering, Tokyo University of Science, Tokyo, Japan

[*]ashono@ci.kagu.tus.ac.jp

***Abstract*-Increasing the quantities of nutrient salts from the inflow of wastewater in enclosed waters generate the phytoplankton microcystis, which causes an offensive odor. Thus, establishing a microcystis treatment method is required to improve such aqueous environments. In this study, a new technique that combines microbubbles and ozone was applied to a wastewater treatment process. The effects of microcystis removal on the water samples taken from the outer moat of the Tokyo Imperial Palace were investigated. In addition, a mechanism for a microcystis degradation process using ozone microbubbles is proposed.**

Keywords- Microbubbles; Ozone; Microcystis; Waste Water Treatment; Gas Flow Rate

I. INTRODUCTION

Recently, abnormal proliferation of the phytoplankton microcystis due to water pollution, particularly the increase of nutrient salts from the inflow of wastewaters, has become a serious environmental issue for enclosed water systems. The abnormal proliferation of microcystis causes an offensive odor, reduces oxygen levels, and increases fish mortality. Thus, establishing a method for microcystis treatment is required to improve aqueous environments.

Treatment methods for microcystis include flocculation, filtration, and oxidation. Oxidation methods are especially efficient for microcystis treatment and include chemical and biological treatments. The development of biological oxidation processes for microcystis treatment is considered economically feasible and widely applicable. However, it is difficult for such biological processes to remove toxic compounds. Hence, advanced oxidation processes such as those using ozone and hydrogen peroxide are required for microcystis treatment. Recently, ozone has been receiving considerable attention in the field of wastewater treatment [1]. Miao and Tao investigated the effects of ozonation on the removal and growth inhibition of algae [2]. Brooke *et al*. also reported that ozonation is effective for removing hepatotoxicity of microcystis [3]. Koch *et al*. reported the effects of ozonation on intermediates and products in the degradation process of azo dye [4]. Additionally, to intensify ozonation, it was combined with other oxidation methods [5, 6]. However, ozone has relatively low solubility and stability in water, and the application of ozonation may not be economically feasible.

A novel technology using microbubbles, typically having a diameter less than 50 μm, was established for application in aquaculture, wastewater treatment, and medicine [7-11]. Compared to conventional bubbles with diameter of several mm, a microbubble has a large interfacial area and bubble density, limited rise velocity in liquid, and high inner pressure. Mitani *et al*. reported that the overall mass transfer coefficient of ozone increases with decreasing bubble size because of the increase in overall surface area of the bubbles [12]. Li and Tsuge also reported that high ozone transfer efficiency was obtained by a new gas-induced contactor with microbubbles [13]. Shin *et al*. reported that the rate of phenol oxidation increases by increasing the rate of mass transfer of ozone into a solution using microbubbles produced by an electrostatic spraying method [14]. Chu *et al*. reported that ozonation of dyestuff wastewater is enhanced by microbubbles [15]. Ikeura *et al*. reported the removal of residual pesticides in vegetables using ozone microbubbles [7, 8]. Tsuge *et al*. also reported utilization of ozone microbubbles in the bactericidal process [16].

The outer moat of the Tokyo Imperial Palace is a typical enclosed water area, where accelerated microcystis growth occurs every summer. In this study, a new technique to combine microbubbles and ozonation was applied to wastewater from the outer moat. First, the effects of operating conditions on the diameter of ozone bubbles were investigated. Second, the effects of ozonation on the removal of microcystis were investigated by analysis of the treated water. The chemical oxygen demand (COD) and the concentrations of phosphate phosphorus (PO_4-P) and saccharides were measured. The purpose of this study is to investigate the effectiveness of ozone microbubble treatment on microcystis in suspended solution. This mechanism for microcystis degradation using ozone microbubbles is proposed.

II. EXPERIMENTAL

A. *Preparation of Microcystis*

Water containing microcystis was gathered from the outer moat of the Tokyo Imperial Palace. As the water contains various organisms, it is difficult to observe the results for microcystis only. Hence, the water was first sieved using a sieve mesh of size 45 μm (No. 325). The obtained organisms were then dried and manually separated from the mixture of organisms.

Then, 9.1 g of the microcystis was suspended in 10 L of ion-exchanged water to obtain the sample solution.

B. Experimental Setup

Fig. 1 shows the experimental setup. The rectangular bubble column made of transparent acrylic plate had a cross section and height of 168 cm^2 and 76 cm, respectively. A microbubble generation nozzle (OMI-C200, Auratec) was set at the bottom of the bubble column. Ozone gas was generated from air by an ozone generator (ED-CG-R6, Eco Design) by the silent discharge method. Ozone gas and the sample solution were sent to the nozzle, and ozone microbubbles were generated. Gas flow rate was changed from 50 to 300 mL/min, and the concentration of ozone gas was set at 3.4 g/m^3. Gas flow rate was determined using a gas flow meter (FD-A10, Keyence) set between the ozone reservoir and valve. Gas flow rate was measured under zero-ozone conditions because the gas flow meter used in this study did not have ozone tolerance.

The flow rate for the sample solution was set at 16 L/min. The pH of the sample solution was maintained between 6.5 and 8.5 by adding NaOH.

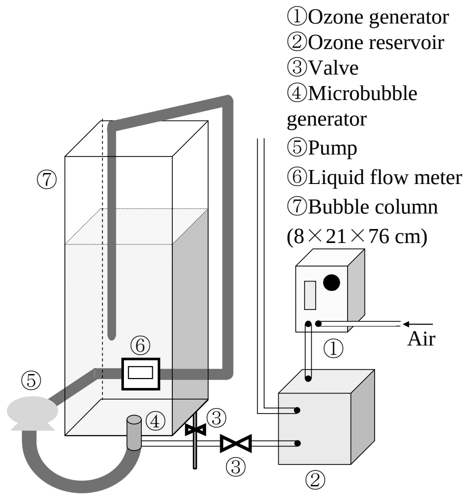


Fig. 1 Experimental setup

C. Analysis

The size distribution of small bubbles (d < 100 μm) was obtained using an AccuSizer 780 (Particle Sizing Systems), and the size distribution of large bubbles (d > 100 μm) was measured by visual observation using a high-speed camera (EX-FH20, Casio). The dissolved ozone concentration was determined by the indigo method.

The quantification of the microcystis degradation by ozone microbubbles was estimated from the COD [17] and concentrations of the PO_4-P and saccharide.

Fig. 2 shows a schematic image of the water analysis system. First, COD of the sample solution (COD_T) was measured by oxidation with potassium permanganate in acidity. Second, the sample solution was filtered with a cellulose acetate membrane filter (C045A047A, Advantec MFS Inc.). COD of the filtrate (COD_F) was similarly measured. The COD of the residue (COD_R) was estimated using Eq. (1). The concentration of PO_4-P in the filtrate was measured using a digital water analyzer (DPM-MT, Kyoritsu Chemical-Check Lab.) with a pack test for PO_4-P (WAK-PO4, Kyoritsu Chemical-Check Lab.). The concentration of the saccharide in the filtrate was measured by a phenol–sulfuric-acid method [18].

$$COD_R = COD_T - COD_F \tag{1}$$

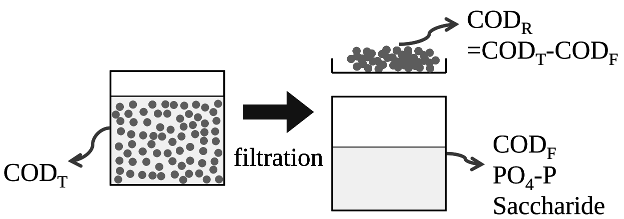


Fig. 2 Schematic of water analysis system

III. RESULTS AND DISCUSSIONS

A. Effects of Operating Conditions on the Size of Microbubbles

The diameter of the microbubble depends on operating conditions. Table 1 shows the effect of gas flow rate on the bubble diameter. The bubble diameter increased with increasing gas flow rate. Miyahara and Nagatani also reported that microbubbles were generated with decreasing gas flow rate [19]. Fig. 3 shows the effect of the gas flow rate on the ozone concentration in the solution at pH = 8.0. The concentration of ozone increased with increasing gas flow rate. This phenomenon is well agreed with previous research [20].

When gas is aerated in a bubble column of equal volume, the ozonation efficiency is typically expected to improve with decreasing gas flow rate because the specific interfacial area is high due to decreasing bubble diameter. However, the efficiency of ozonation increased with increasing gas flow rate. Both the gas–liquid contact area, as well as the gas holdup and flow pattern in the column, was influenced by the dissolution of ozone gas. Additionally, the concentration of ozone in the dispersed gas was low. Most of the dispersed gas was nitrogen. The solution was found to be degassed by nitrogen microbubbles at a low gas flow rate. Therefore, there is an optimum operating condition for microcystis treatment.

TABLE 1 EFFECT OF GAS FLOW RATE ON DISTRIBUTION OF PROPORTION OF BUBBLE DIAMETER

		Gas flow rate [mL/min]		
		50	**150**	**300**
Bubble diameter [μm]	20 − 60	71.5%	21.1%	18.3%
	60 − 400	14.4%	3.7%	0.1%
	400 − 1000	12.5%	61.2%	31.1%
	1000 − 3000	1.6%	14.0%	50.5%

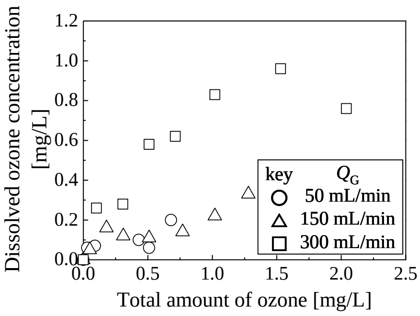
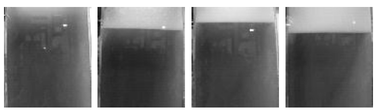


Fig. 3 Effect of gas flow rate on ozone concentration in solution

B. Effect of Ozonation on Microcystis Solution

Fig. 4 shows the photographs of the sample solution during the ozone microbubble treatment. The gas flow rate was 150 mL/min and the pH of the solution was 7.0. It was observed that the green microcystis solution became transparent and colorless with ozonation. The ozone microbubble treatment was effective for bleaching the green microcystis solution.



Time, *t* [min]	0	40	80	120
Total amount of ozone [mg/L]	0	2.06	4.13	6.19

Time, *t* [min]	180	240	300	360
Total amount of ozone [mg/L]	9.29	12.4	15.5	18.6

Fig. 4 Photographs of sample solution during ozone microbubble treatment at Q_G = 150 mL/min and pH = 7.0

Fig. 5 shows the time dependence of COD. Again, the gas flow rate was 150 mL/min and the pH of the solution was 7.0. The total COD of the sample solution decreased and COD_R decreased drastically. The sample solution became transparent with decreasing COD_R, whereas COD_F increased. At this point, we have postulated that the microcystis cell wall was destroyed and that the intercellular material was eluted.

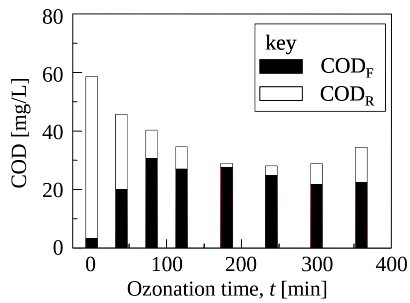


Fig. 5 Time dependence of COD at Q_G = 150 mL/min and pH = 7.0

Fig. 6 shows the effect of gas flow rate on the variation ratio of COD (COD/COD_0). The pH of the solution was 8.5. When the gas flow rate was 300 mL/min, COD did not change with ozonation. On the other hand, when the gas flow rates were 50 and 150 mL/min, COD decreased at the initial stage of ozonation. From the results of the distribution of proportion of bubble diameter, microbubbles were considered to be effective for decreasing COD in microcystis solution in comparison with conventional bubbles.

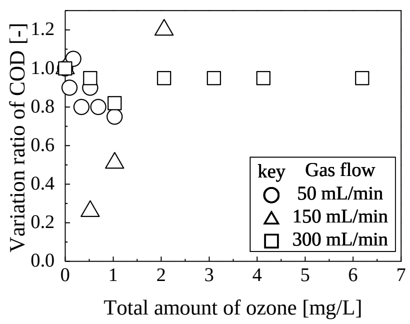


Fig. 6 Effect of gas flow rate on variation ratio of COD at pH = 8.5

Fig. 7 shows the time dependence of concentrations of PO_4-P and saccharide. The gas flow rate was 150 mL/min, and the pH of the solution was 7.0. The concentrations of PO_4-P and saccharide increased with increasing ozonation time.

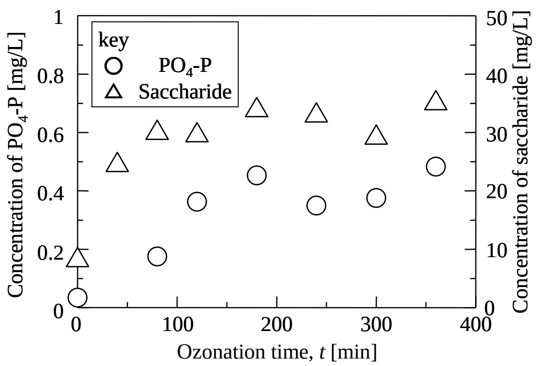


Fig. 7 Time dependence of concentrations of PO_4-P and saccharide at Q_G = 150 mL/min and pH = 7.0

C. Degradation Mechanism of Microcystis

From the experimental results, the degradation of microcystis is considered to progress in the following steps. At the initial stage of ozone injection, ozone decomposed the cell wall of microcystis, and the solution became transparent with decreasing COD_R. Therefore, the removal of solid microcystis by ozone treatment was effective for making a colorless and transparent solution. On the other hand, intercellular organic compounds such as phycocyanin were eluted gradually from the solution. Additionally, COD_F increased. At the second stage, the eluted phycocyanin was degraded by ozone, and the decomposition of the microcystis cell wall decreased. However, under the conditions of this study, the value of COD_F did not reach 0 mg/L. The reason for this low ability to remove COD was determined to be the low concentration of ozone. However, the detailed degradation mechanism will be investigated in the future.

D. Improvement of Water Treatment Process Using Ozone Microbubbles

Ozone treatment was found to clear the color of microcystis suspended in water effectively. However, ozone treatment was not sufficient to remove COD. Additionally, the concentrations of PO_4-P and saccharide were increased with the progressing degradation of the microcystis cell wall by ozone treatment. As the concentration of nutrient salts in water increases, it is likely to become an environment in which microcystis proliferates easily. The microcystis was cultivated using ozone treated water for one week, at the end of which it died out. Therefore, ozone treatment is considered effective for removal of microcystis; however, the reduction in the COD value is not satisfactory.

IV. CONCLUSIONS

The diameter of ozone gas microbubbles increased with increasing gas flow rate. The green microcystis sample solution became transparent and colorless after ozone microbubble treatment. The process for removal of microcystis by ozonation was considered to have two stages. In the first stage, the cell wall of microcystis is decomposed by ozone, and the intercellular material is eluted. In the second stage, the eluted intercellular materials such as phycocyanin are degraded. Additionally, the microcystis was cultivated using ozone treated water with sufficient nutrient salts and died out within one week. The process for removal of microcystis was improved by ozone microbubble treatment.

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