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Sterilization in the water by bubbling of atmospheric-pressure reactive plasma gases
大気圧反応性プラズマガスのバブリングによる水中殺菌

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A compact plasma-bubbler made up of a μplasma source and a porous ceramics has proposed to attain sterilization in the water. The μplasma is excited by a pulsed high voltage between a thin metal pipe electrode and a GND plate, so that pure O_2 μplasma can be generated. Plasma gas is ejected into the water through a porous ceramics. Chemical probe method using terephthalic acid revealed that OH radicals are produced by the O_2 plasma gas bubbling. The O_2 plasma gas bubbling showed strong inactivation for *Bacillus subtilis* and *Saccharomyces cerevisiae*, but weak inactivation for *E. coli*.

1. Introduction

Recently, Plasma production in and in contact with liquid has attracted much attention because of their applications to degradation of organic compounds, sterilization, water purification and synthesis of nanomaterials [1,2]. UV, electron, ion and radical flows originated from a plasma and also shock wave induce physical and chemical reaction in a liquid, for example oxidation-reduction, electrolysis and reactive species production. In particular, various active species (·OH, O_2^-, O_3, H_2O_2, etc) generated at the plasma-liquid interface play an important role in oxidation and degradation of organic pollutants and bacteria. We have proposed a mild water treatment by ejecting the atmospheric-pressure μplasma (APμP) gas into a water using a microbubble aerator or a porous ceramics bubbler [3,4]. This is similar to the concept of down flow plasma processing in LSI fabrication. In the previous work, the effect of O_2/N_2 ratio in the plasma gas on decolorization of a dye and inactivation of bacteria in an environmental foul water was examined. It revealed what kind of reactive species (ROS or RNS) play a dominant role in decomposition and sterilization [5].

In this study, a compact plasma-bubbler is presented. OH radical production by O_2 and air plasma gas bubbling is examined by means of chemical probe method. The O_2 plasma gas bubbling is applied to inactivation treatment of several bacteria.

2. Experimental setup

Figure 1 shows a photograph of a compact plasma-bubbler which consist of an APμP source and a porous ceramics. APμP of pure O_2 gas is generated between a metal pipe electrode with an inner/outer diameter of 0.7 mm/0.9 mm and a grounded metal plate. The pipe electrode is excited by a pulsed high voltage with the peak-to-peak voltage of 8-9 kV, pulse repetition frequency of 950 Hz. Power consumption of a discharge is 28 W. Light emitted from the APμP is measured by a multichannel spectroscope (Hamamatsu Photonics PMA-11). A dye solution dissolving Indigo Carmine in a deionized pure water of 1.0 L (a concentration of 20 mg/L) is used as a specimen to evaluate a decolorization activity. The absorbance of the dye at 610 nm, O_3 and H_2O_2 concentrations in a pure water treated by a plasma-bubbler are measured using a digital water analyzer (Kyoritsu λ-9000). Chemical dosimetry based on terephthalic acid (TA) is used to measure the OH radicals dissolved in the liquid [6]. Aqueous solution of TA (Kanto Chemical Co. Inc.) is prepared

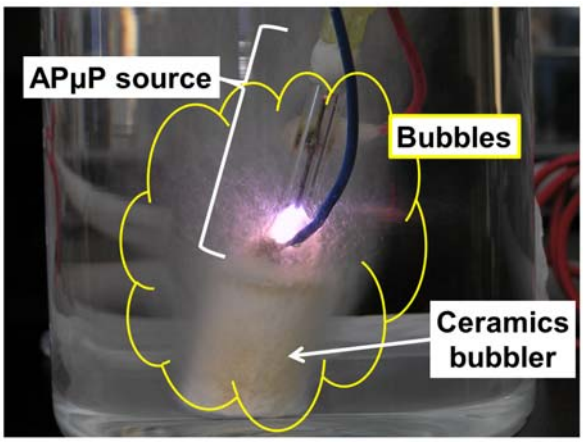

Fig.1 A compact plasma-bubbler in the water. The O_2 APμP is generated by a pipe-GND electrodes.

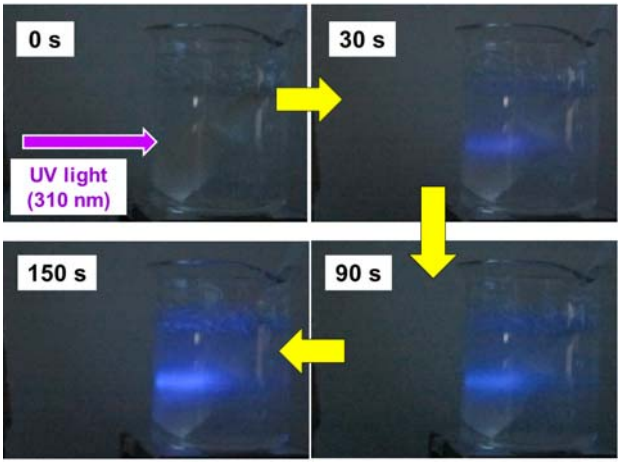

Fig.2 Photos of fluorescence from TA solution during the O_2 plasma gas bubbling.

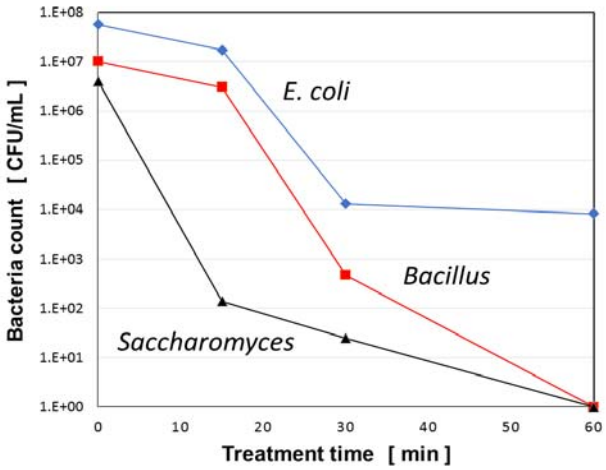

Fig.3 Survival curves of various bacteria by the O_2 plasma gas bubbling treatment.

by dissolving TA in the distilled water containing NaOH. The initial pH is adjusted to be 6.5-7.0. The solution volume in a quartz vessel is 100 mL. The LED (Revox, λ=313.5 nm, FWHM 10.4 nm) is used as a light source to excite 2-hydroxyterephthalic acid (HTA). Bacteria inactivation test is carried out for *Escherichia coli* (*E. coli*), *Bacillus subtilis* and *Saccharomyces cerevisiae*. The sample volume treated by a plasma-bubbler is 400 mL and an initial concentration of bacteria is set to be 10^6-10^7 CFU/mL.

3. Results and discussion

Optical emission spectrum of the O_2 APμP showed intense OI lines at the range from 615 to 845 nm. In addition, O_3 gas concentration increased from 20 to 400 ppm with increasing O_2 flow rate from 0.2 to 1.0 mL/min. Figure 2 shows time-dependent fluorescence images under the irradiation of the UV light (310 nm) when the O_2 plasma gas bubbling is carried out in the TA solution. From this result, it implies that OH radicals are formed from a water according to the following reaction;

$$O(^1D) + H_2O \rightarrow 2 \cdot OH \qquad (1)$$

On the other hand, no fluorescence was observed in the case of air plasma gas bubbling.

The pH, O_3, H_2O_2 and NO_2 concentrations in a water after the O_2 plasma-bubbling are 5.5-7, < 0.20 ppm, < 0.10 ppm and < 0.02 ppm, respectively.

The dependence of the decolorization time of an Indigo Carmine solution on a distance between APμP source and a porous bubbler was examined. It is found that O_3 is a dominant oxidizing agent when the distance is more than 1.5 m, on the other hand, the decolorization time decreased stepwise with decreasing the distance. It implies that reactive oxygen species such as ·OH as well as O_3 play an important role in decomposition of organic compounds.

Figure 3 shows the plasma gas bubbling time dependence of survival of several kind of bacteria. The O_2 plasma gas bubbling showed strong inactivation for *Bacillus subtilis* and *Saccharomyces cerevisiae*, but weak inactivation for *E. coli*. It is known that O_3 has a strong sterilization ability for *E. coli*. and *Saccharomyces cerevisiae*. In this case, reactive oxygen species other than O_3 may be a dominant oxidizing agent, since the dissolved O_3 concentration is less than 0.20 ppm.

4. Conclusions

A compact plasma-bubbler made up of a μplasma source and a porous ceramics has proposed to attain sterilization in the water. Chemical probe method using terephthalic acid revealed that OH radicals are produced by the O_2 plasma gas bubbling. The O_2 plasma gas bubbling showed strong inactivation for *Bacillus subtilis* and *Saccharomyces cerevisiae*, but weak inactivation for *E. coli*.

Acknowledgments

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