# THE APPLICATION OF MICRO/NANO BUBBLES WITH UV IRRADIATION FOR THE DECOMPOSITION OF METYHL ORANGE USING SHIRASU-POROUS-GLASS (SPG) MEMBRNANE

Tasaki T<sup>1</sup>, Fujimoto K<sup>1</sup>, Wada T<sup>1</sup>, Kai S<sup>2</sup>, Ohe K<sup>2</sup>, Oshima T<sup>2</sup>, Baba Y<sup>2</sup>, Kukizaki M<sup>3</sup>

<sup>1</sup>JST Innovation Satellite Miyazaki, 1-1 Gakuen Kibanadai Nishi, Miyazaki, 889-2192, Japan; <sup>2</sup>Department of Applied Chemistry, Faculty of Engineering, University of Miyazaki, 1-1,Gakuen Kibanadai Nishi, Miyazaki, 889-2192, Japan; <sup>3</sup>Department of Material Development, Miyazaki Prefecture Industrial Technology Center, 16500-2 Higashi Kaminaka, Sadowara, Miyazaki, 880-0303, Japan

### **Abstract**

The photodegradation of organic compounds such as methyl orange using micro/nano bubbles with UV irradiation was studied. Photodegradation experiments were conducted with a BLB black light blue lamp (365 nm), a UV-C germicidal lamp (254 nm) and an Ozone lamp (185 nm + 254 nm) with oxygen micro/nano bubbling and without bubbling. The oxygen micro/nano bubbling under 185 nm + 254 nm irradiation shows high oxidation and mineralization rates of methyl orange. The photodedradation under 254 nm and 365 nm irradiation either with or without oxygen micro/nano bubbling were unaffected on the degradation of methyl orange. The findings of this study reveal that the micro/nano bubbles with short-wavelength light (185nm) irradiation play a crucial role in enhancing the oxidation and mineralization rates of methyl orange in aqueous solution.

#### Introduction

The removal of organic pollutants is very important because organic pollutants persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment<sup>1</sup>. Advanced oxidation processes (AOPs) such as photo-assisted Fenton, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, UV/solid catalyst, UV/TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>/UV have been widely investigated for the degradation of organic pollutants<sup>2,3</sup>. In general, however, AOP is of low efficiency and takes a relatively long time to purify water or air, resulting in high costs and limited competitiveness. In order to cope with the treatment of municipal and industrial wastewaters, a novel type of wastewater process is the subject of further investigation to overcome the drawbacks of AOP technology. Micro/nano bubbles have received great interests since they offer the unique characteristics such as their efficient gaseous solubility, large gas/liquid interfacial area and hydrodynamic effects<sup>4,5</sup>. We previously described a novel method for generating monodispersed micro/nano bubbles using Shirasu-porous-glass (SPG) membranes as the gas-liquid dispersion medium.<sup>6</sup> In this method, the gaseous phase is pressed through the SPG membrane into a flowing continuous liquid phase.

In this study, we examined the possibility of micro/nano bubbles for the degradation of organic compounds such as methyl orange as a model compound in aqueous solution under the short-wavelength UV irradiation. The factors such as UV wavelength, initial dissolved oxygen concentration and type of bubbling gases, and their effects on the oxidation and mineralization of methyl orange were investigated.

# **Materials and Methods**

Methyl orange ( $C_{14}H_{14}N_3SO_3Na$ , molecular weight = 327 g mol<sup>-1</sup>) was purchased from Wako Pure Chemical. Ind. Ltd. Sodium dodecyl sulfate (SDS, Wako Pure Chemical. Ind. Ltd., purity = 95.0 %) was used as a water soluble emulsifier to form monodispersed micro-bubbles. The SPG membranes (40 mm length  $\times$  10 mm outer diameter  $\times$  1.0 mm wall thickness) with mean pore diameter of 1.0  $\mu$ m were purchased from SPG Technology Co., Ltd., Japan. Our previous bubble formation studies revealed that the bubble diameter appeared to be 8.6 times larger than the pore diameter of SPG membranes<sup>6</sup>. In this study, micro bubbles with a mean pore diameter of 8.6 (8.6  $\times$  1.0)  $\mu$ m can be generated from SPG membrane with mean pore diameter of 1.0  $\mu$ m.

The reactor system used is represented in Fig.1. The system consists of a UV lamp, SPG module and photoreactor. Photodegradation experiments were carried out with the following UV lamps: a BLB black light blue lamp with a maximum light intensity output at 365 nm (Sankyo Denki Co., Ltd., Japan), a UV-C germicidal lamp with a maximum at 254 nm (Sankyo Denki Co., Ltd., Japan), and ozone lamp with a maximum at 254 nm and a smaller (< 5 %) emission at 185 nm (Sankyo Denki Co., Ltd., Japan). An aqueous solution was prepared by 10 mg/L concentration of methyl orange containing 0.05 wt. % SDS adjusted to pH 7.0 with HCl and NaOH.

Industrial grade oxygen gas was bubbled into the photoreactor through the SPG membrane module at a gas flow rate of 40 mL/min. The aqueous solution of 150 mL was circulated with a circulation pump at a water flow rate of 500 mL/min. The aqueous solution was thermostated at 293  $\pm$  0.1 K. To determine the time course of the methyl orange concentration, 1.0 mL of sample was taken at preselected time intervals. The concentration of methyl orange was determined with a UV-Visible spectrometer (V-560, JASCO Co., Ltd., Japan).

### **Results and Discussion**

The time course of concentration of methyl orange using the BLB black light blue lamp (365 nm), UV-C germicidal lamp (254 nm) and ozone lamp (185 nm + 254 nm) with and without oxygen micro-bubbling are shown in Fig.2. There was no oxidation of methyl orange under 365 nm and 254 nm irradiation either with or without oxygen micro-bubbling. However, using an ozone lamp which emits both 185 and 254 nm light, the concentration of methyl orange decreased with irradiation time. It should be noted that the oxygen micro-bubbles under 185 nm + 254 nm irradiation greatly enhanced the oxidation rate of methyl orange. Under this experimental condition, there was a 94.1 % oxidation efficiency of methyl orange after 20 min irradiation. Fig.3 shows UV-visible spectra of methyl orange at different 185 + 254 nm irradiation times vary with oxygen micro-bubbling. The absorptions of the visible bands at 270 nm and 480 nm decreased with 185 + 254 nm irradiation time. The finding of this study indicates that 185 nm VUV light irradiation plays a crucial role in the degradation of azo bonds and aromatic rings of methyl orange in aqueous solution. The enhancement of oxidation rate of methyl orange with micro bubbling would be attributed to the characteristics of micro bubbles such as mixing effect, high gas dissolution rate, large gas/liquid interfacial area and light scattering effect<sup>7</sup>.

This study demonstrates that micro bubbles irradiated with 185 nm VUV light provide an attractive alternative to conventional AOP technologies for the degradation of organic pollutant in wastewaters. The kinetic study and degradation mechanism of various organic compounds under 185 + 254 nm in a wide range of bubble size are currently in progress.

# Acknowledgements

This work was supported by a Practical Application Research grant from the Japan Science and Technology Agency.

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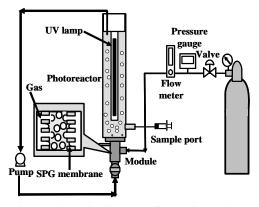


Fig.1 Schematic diagram of experimental setup.

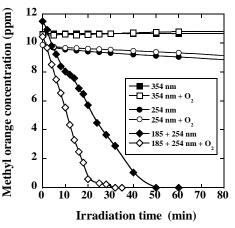


Fig.2 Time course of methyl orange concentration using various UV wavelength lamps with or without oxygen micro- bubbling.

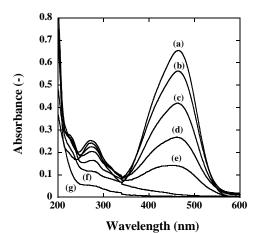


Fig.3 The UV-visible spectra of methyl orange at different time course under 185 + 254 nm irradiation with oxygen micro-bubbling: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, (f) 30 min, (g) 60 min.