



Degradation of methyl orange using short-wavelength UV irradiation with oxygen microbubbles

Tsutomu Tasaki^a, Tsubasa Wada^a, Kanji Fujimoto^a, Shinji Kai^b, Kaoru Ohe^b,
Tatsuya Oshima^b, Yoshinari Baba^b, Masato Kukizaki^{c,*}

^a JST Innovation Satellite Miyazaki, 1-1 Gakuen Kibanadai Nishi, Miyazaki 889-2192, Japan

^b Department of Applied Chemistry, Faculty of Engineering, University of Miyazaki, 1-1 Gakuen Kibanadai Nishi, Miyazaki 889-2192, Japan

^c Department of Material Development, Miyazaki Prefecture Industrial Technology Center, 16500-2 Higashi Kaminaka, Sadowara, Miyazaki 880-0303, Japan

ARTICLE INFO

Article history:

Received 10 September 2007

Received in revised form 16 April 2008

Accepted 30 May 2008

Available online 13 June 2008

Keywords:

Photodegradation

Vacuum ultraviolet light (VUV)

Microbubble

Methyl orange

ABSTRACT

A novel wastewater treatment technique using 8W low-pressure mercury lamps in the presence of uniform-sized microbubbles (diameter = 5.79 μm) was investigated for the decomposition of methyl orange as a model compound in aqueous solution. 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) both with and without oxygen microbubbles. The results show that the oxygen microbubbles accelerated the decolorization rate of methyl orange under 185 + 254 nm irradiation. In contrast, the microbubbles under 365 and 254 nm irradiation were unaffected on the decolorization of methyl orange. It was found that the pseudo-zero order decolorization reaction constant in microbubble system is 2.1 times higher than that in conventional large bubble system. Total organic carbon (TOC) reduction rate of methyl orange was greatly enhanced by oxygen microbubble under 185 + 254 nm irradiation, however, TOC reduction rate by nitrogen microbubble was much slower than that with 185 + 254 nm irradiation only. Possible reaction mechanisms for the decolorization and mineralization of methyl orange both with oxygen and nitrogen microbubbles were proposed in this study.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The removal of organic pollutants from surface and groundwater is a demanding task 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. Several methods have been developed such as photo-assisted Fenton, $\text{O}_3/\text{H}_2\text{O}_2$, UV/solid catalyst, UV/ TiO_2 and $\text{H}_2\text{O}_2/\text{UV}$ reactions that provide high formation rates of hydroxyl radicals (OH^\bullet) for the degradation of organic pollutants [1–3]. These methods are generally referred to as advanced oxidation processes (AOP) and are well-established techniques to remove pollutants in various water treatment applications [4–8].

Among AOP, the photolysis of water using vacuum ultraviolet light (VUV, wavelength <200 nm), which represents a powerful method of OH^\bullet radical production, has been investigated recently [9,10]. Under irradiation with VUV light, water itself is homolyzed

into a hydrogen atom and hydroxyl radicals, and other oxidative species such as hydrogen peroxide could be formed simultaneously. This process has been paid much attention as it has resulted in a more rapid rate of mineralization and faster formation of biodegradable compounds than afforded by conventional UV treatments without addition of any chemical additives, e.g. hydrogen peroxide, Fenton or ozone [11]. Nevertheless, Heit and Braun [12] reported that the rate of total organic carbon (TOC) reduction under VUV irradiation is limited by a deficit in oxygen in small VUV-irradiated reaction sites, because carbon-centered radical is immediately scavenged by the dissolved molecular oxygen through the formation of peroxy radical. Oppenländer et al. [13] studied the efficiency of oxygen gas injection from ceramic air stone on the degradation rate of organic compounds using a xenon excimer source (Xe_2^* lamp, 172 nm). Their results show that the oxygen gas input enhanced the transfer of dissolved molecular oxygen into the VUV-irradiated reaction site leading to an increased rate of mineralization of organic model compounds such as 1-heptanol and benzoic acid. A similar study conducted by Han et al. [14] demonstrated that injecting oxygen gas from sintered porous glass plate increased efficiently the mineralization rate of *p*-chlorobenzoic acid under TiO_2/VUV (185 + 254 nm) irradiation.

* Corresponding author. Tel.: +81 985 74 4311; fax: +81 985 74 4488.
E-mail address: kukizaki@iri.pref.miyazaki.jp (M. Kukizaki).

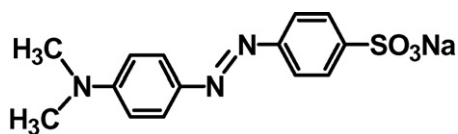


Fig. 1. Chemical structure of methyl orange.

Recently, Takahashi et al. has investigated the decomposition of phenol in aqueous solution with air microbubbles in the absence of a dynamic stimulus (e.g. UV irradiation and incident ultrasonic wave) [15]. Their study shows that air microbubbles are performed to remove small amount of organic compounds due to the free-radical generation from the collapse of microbubbles. Microbubbles are defined as bubbles with diameter of less than several tens of microns. Compared to conventional bubbles with diameters of several mm, microbubbles exhibit excellent gas-dissolution abilities such as a very large gas/liquid interfacial area, long stagnation, and pressurized interior gas due to surface tension [16]. It can be expected that the formation of microbubbles increases the efficiency of gas–liquid contact devices, for example, bubble columns, chemical reactors, gas absorbents and fermentors. Thus, microbubbles have potential to apply a broad range of advanced applications, in particular water and wastewater treatment technologies. Recently, a novel method for generating uniform-sized microbubbles using Shirasu porous glass (SPG) membranes as the gas–liquid dispersion medium was recently developed in our laboratory [17]. The advantage of this technique is that the resultant bubble size can be controlled by varying the pore size of the membrane, indicating that bubble size can be optimized for a large-scale application. It was thus of interest in the present work to investigate the degradation of organic compound in aqueous solution by microbubbles and UV irradiations as a novel wastewater treatment technique.

The objective of this study is to determine the feasibility of using microbubbles and short-wavelength wavelength UV irradiation

technique for the photodegradation of organic compound. Methyl orange, with reflectively high toxic, complex structure and non-biodegradability, is chosen as the model compound because it can be classified as both acid and azo dyestuffs, which are widely used in the textile industry. In this article, we examined the different experimental conditions such as UV wavelength, initial dissolved oxygen concentration, gas flow rate, initial pH and type of bubbling gases, and their effects on the decolorization and mineralization of methyl orange.

2. Experimental

2.1. Reagents and materials

Methyl orange ($C_{14}H_{14}N_3SO_3Na$, molecular weight = 327 g mol^{-1} , maximum absorption wavelength = 465 nm) was purchased from Wako Pure Chemical. Ind. Ltd., chosen as the target compound and its chemical structure is shown in Fig. 1. Sodium dodecyl sulfate (Wako Pure Chemical. Ind. Ltd., purity = 95.0%) was used as a water soluble surfactant to form uniform-sized microbubbles [18]. De-ionized water supplied by a purification unit (SW AC-520, Shimadzu Co., Ltd., Japan) was used for the preparation and dilution of solutions. The SPG membranes (125.0 mm length \times 5.0 mm outer diameter \times 0.5 mm wall thickness) with mean pore diameter of $0.5 \mu\text{m}$ were purchased from SPG Technology Co., Ltd., Japan. The membrane was prepared by leaching of phase-separated glass in the Na_2O – CaO – MgO – Al_2O_3 – B_2O_3 – SiO_2 (Shirasu) system. The details for preparation procedures of the membrane were described elsewhere [18,19].

2.2. Experimental set-up

The reactor system used in this study is represented in Fig. 2 [20]. The system consists of a UV lamp, SPG module and photoreactor. Photodegradation experiments were carried out with the following

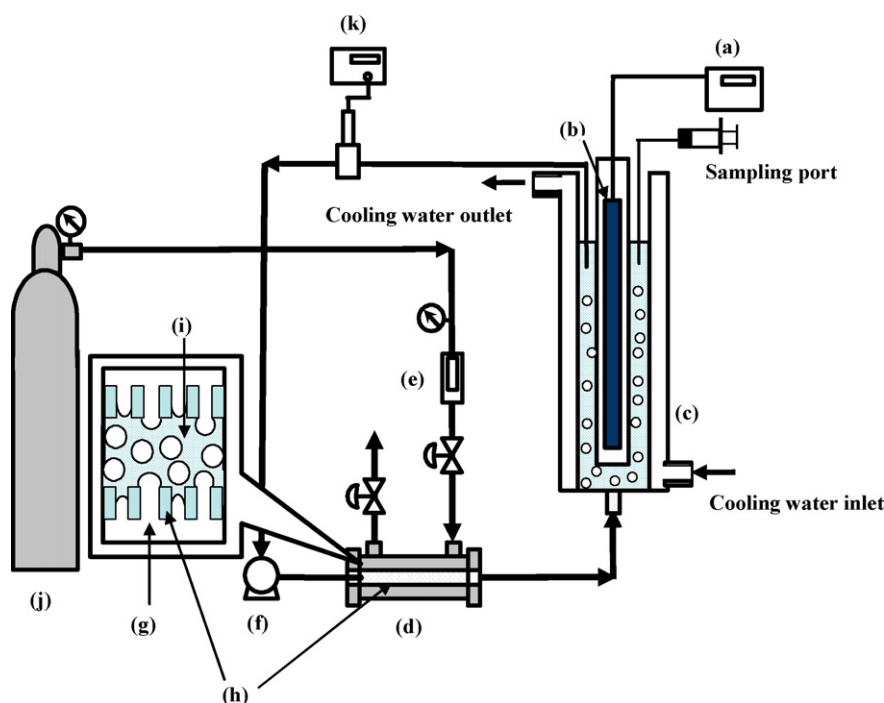


Fig. 2. Schematic diagram of the experimental apparatus. (a) UV power, (b) 8 W low-pressure mercury lamp, (c) photoreactor, (d) SPG membrane module, (e) flow meter, (f) circulation pump, (g) gaseous phase, (h) SPG membrane, (i) water phase, (j) gas cylinder, (k) pH meter and DO meter.

low-pressure mercury UV lamps: a BLB black light blue lamp with a maximum light intensity output at 365 nm (model FL8BLB, Sankyo Denki Co., Ltd., Japan), a UV-C germicidal lamp with a maximum at 254 nm (model GL8, Sankyo Denki Co., Ltd., Japan), and ozone lamp with a maximum at 254 nm and a smaller (<5%) emission at 185 nm (model GL8ZH, Sankyo Denki Co., Ltd., Japan). The electronic power consumption of all UV lamps was identical (8.0 W). The lamp was placed in the center of the photoreactor with quartz tube protection (external diameter 15 mm); the distance from the inner wall of the photoreactor to the external wall of the quartz tube was 17 mm. 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. The photodegradation experiments were conducted in a semi-batch mode. Industrial grade oxygen and nitrogen gases were pressed through the SPG membrane into a flowing continuous aqueous solution at a transmembrane/capillary pressure ratio of 1.1. The generated microbubbles were bubbled into the photoreactor through a SPG membrane module at a gas flow rate of 0–20 mL/min. The aqueous solution of 350 mL was circulated with a circulation pump (MDG-H2KA100A, Iwaki Co., Ltd., Japan) at a flow rate of 500 mL/min. The aqueous solution was thermostated at 293 ± 0.1 K (Advantec Co., Ltd., Japan). The concentration of dissolved oxygen and ozone in aqueous solution were constantly measured with a DO meter (DO-24P, DKK-TOA Co., Ltd., Japan) and Ozone meter (OZ-20, DKK-TOA Co., Ltd., Japan), respectively. A pH meter (HM-30R, DKK-TOA Co., Ltd., Japan) was used for the pH measurements. To determine the time course of methyl orange concentration, 5.0 mL of sample was taken at preselected time intervals. The concentration of methyl orange was determined with a UV–vis spectrometer (V-560, JASCO Co., Ltd., Japan). The concentration of methyl orange was calculated from the absorbance at the wavelength of 465 nm by using a calibration curve. Total organic carbon was measured with a TOC analyzer (TOC-V_{CPH}, Shimadzu Co., Ltd., Japan). TOC was calculated from the differences between the total carbon (TC) and inorganic carbon (IC).

2.3. Bubble size measurement

Diameter distribution of the generated bubbles was measured according to our previous study [17]. Bubble size measurement was carried out similarly to the degradation experiment outlined above. The only difference is that the aqueous solution in the former was prepared without methyl orange. The generated bubbles were measured by a laser diffraction particle size analyzer (SALD2100, Shimadzu Co. Ltd., Kyoto, Japan). The diameter distribution of the bubbles generated from the SPG membrane with a mean pore diameter of 0.5 μm is depicted in Fig. 3. The uniform-sized microbubbles with a mean diameter of 5.79 μm were generated from the SPG membrane.

3. Results and discussion

3.1. Effects of the UV light wavelength on the decolorization of methyl orange both with and without oxygen microbubbles

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 + 254 nm) with and without oxygen microbubbles is demonstrated in Fig. 4(a). The results suggest that there was no decolorization of methyl orange under 365 nm and 254 nm irradiation either with or without oxygen microbubbles. Oxygen microbubbles without UV irradiation had little effect on the decolorization of methyl orange as shown in Fig. 4(a). However, it can be clearly seen that the concentration of methyl orange decreased

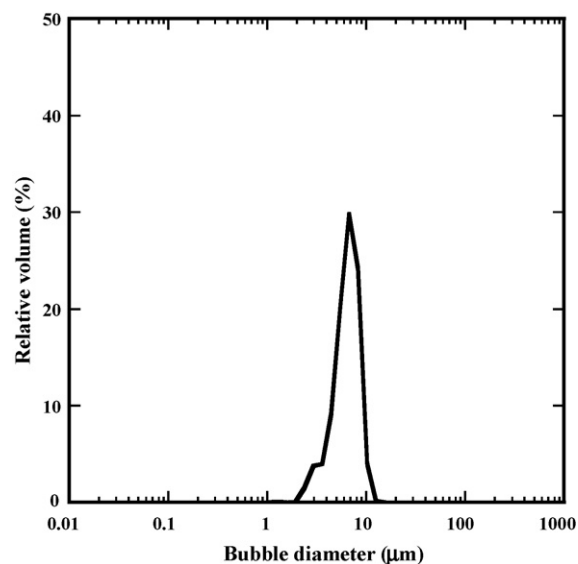


Fig. 3. Diameter distribution of microbubbles generated from the SPG membrane with a mean pore diameter of 0.5 μm .

with irradiation time using an ozone lamp which emits both 185 and 254 nm light. These findings indicate that 185 nm VUV light irradiation plays a major role in the decolorization of methyl orange in aqueous solution. It is also interesting to note that the oxygen microbubbles under 185 + 254 nm irradiation further accelerated the decolorization rate of methyl orange. There was a 94.1% decolorization efficiency with oxygen microbubble after 20 min VUV irradiation, whereas there was 90.8% decolorization efficiency without oxygen microbubble after 40 min VUV irradiation. The plots of the concentration of methyl orange versus irradiation time in Fig. 4(a) afford a straight line, indicating that the decolorization reaction of methyl orange under 185 + 254 nm irradiation is a pseudo-zero order reaction. The pseudo-zero order decolorization rate constants, k_0 (non-bubbling) = 0.256 mg/L min and k_1 (oxygen microbubbling) = 0.515 mg/L min were obtained from the experimental results, respectively. It was found that value of zero-order decolorization rate constant for oxygen microbubbles under 185 + 254 nm irradiation was about two or three times higher than those previously reported in the degradation study of methyl orange on the UV/photocatalysts process [21]. Fig. 4(b) shows the comparison between microbubble and large bubble systems for the decolorization of methyl orange under 185 + 254 nm irradiation. Photodegradation experiment in conventional large bubble system was carried out using porous air stone to provide polydispersed large bubbles. Size of polydispersed bubbles was measured by optical microscopy with a calibrated lens and polydispersed bubbles with a mean diameter of 562 μm were generated in conventional large bubble system. The result obtained in Fig. 4(b) indicates that the rate of decolorization of methyl orange in microbubble system is much faster than that in conventional large bubble system, suggesting that the size of bubbles would largely affect the rate of decolorization of methyl orange. It was also observed that the pseudo-zero order decolorization rate constant by oxygen microbubbles is 2.1 times higher than that by polydispersed large oxygen bubbles.

3.2. UV–vis spectrometry of photodegraded methyl orange

It is well known that the color of azo dyes such as methyl orange is characterized by the azo bonds ($-\text{N}=\text{N}-$) and their associated chromophores and auxochromes [22]. Fig. 5 shows that the UV–vis

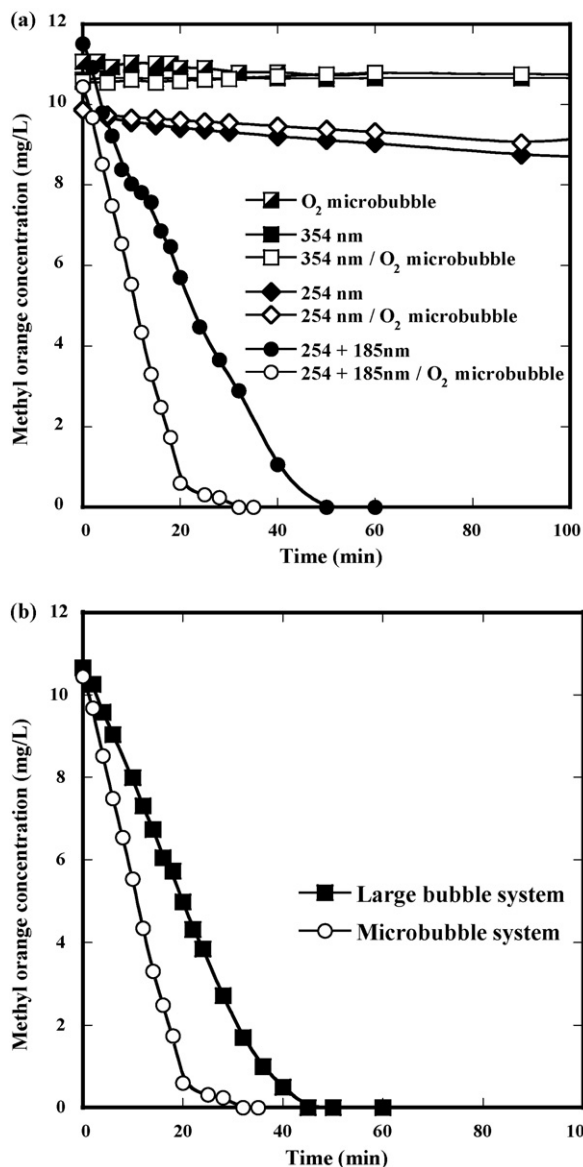


Fig. 4. (a) Time course of methyl orange concentration using the BLB black light blue lamp (365 nm), UV-C germicidal lamp (254 nm) and ozone lamp (185 nm + 254 nm) with and without oxygen microbubble. (b) Comparison between microbubble and large bubble systems for the decolorization of methyl orange under 185 + 254 nm irradiation. pH 7.0, gas flow rate = 10 mL/min.

spectra of methyl orange at different irradiation times vary with oxygen microbubbles. The absorptions of the visible bands at 270 and 465 nm decreased with 185 + 254 nm irradiation time. This result indicated that the aromatic rings at 270 nm and azo bonds at 465 nm of methyl orange degraded under 185 + 254 nm irradiation.

3.3. Concentration of dissolved ozone and dissolved oxygen in aqueous solution under 185 + 254 nm irradiation

Fig. 6(a) shows the time course of dissolved ozone (DO₂) in methyl orange solution with 185 + 254 nm irradiation time under oxygen microbubbling and non-bubbling conditions. Dissolved ozone was undetected both in oxygen microbubbling and non-bubbling conditions under 185 + 254 nm irradiation. These results suggested that ozone generated from 185 nm light was immediately decomposed under irradiation with 254 nm light to form hydroxyl radicals and then, generated hydroxyl radicals oxidize

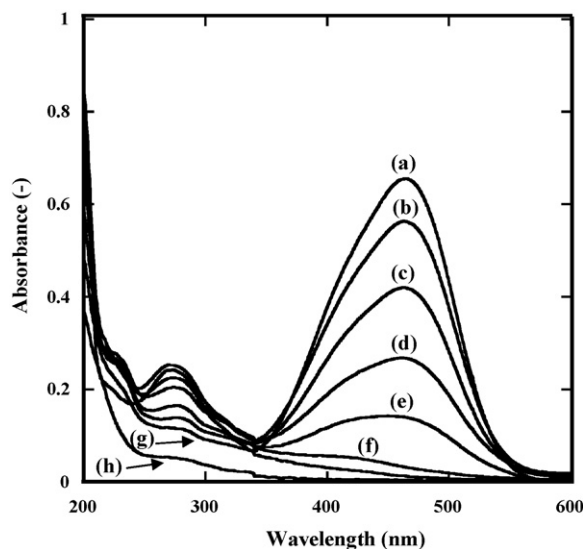


Fig. 5. The UV-vis spectra of methyl orange at different time course under 185 + 254 nm irradiation under oxygen microbubbling condition: (a) 0 min; (b) 4 min; (c) 8 min; (d) 12 min; (e) 15 min; (f) 20 min; (g) 30 min; (h) 60 min.

azo molecule. The hydroxyl radicals are more powerful ($E^0 = 2.85$ V) than ozone ($E^0 = 2.07$ V), indicating that the VUV process oxidizes organic compounds more efficiently than the conventional ozone method [23,24]. Moreover, the VUV process is cost effective because there is no treatment, such as the removal of the residual ozone or hydrogen peroxide, and minimization of the toxic ozone gas release

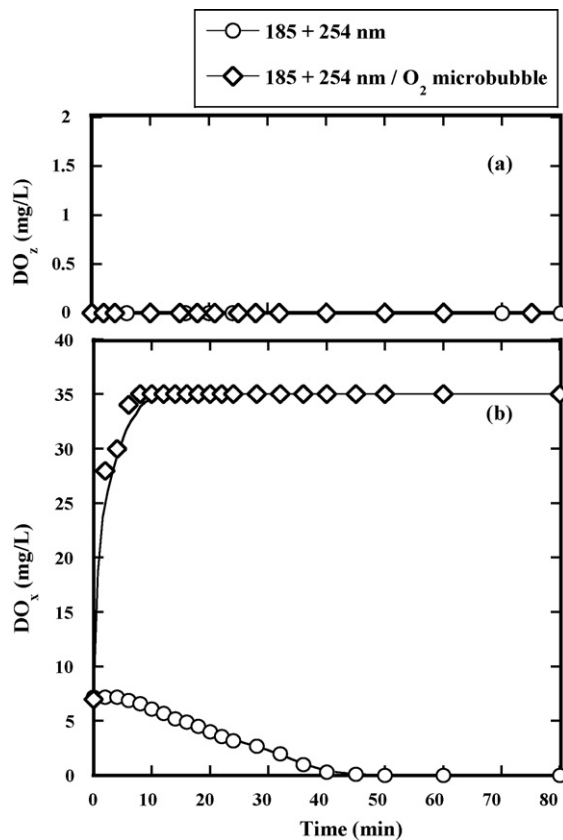


Fig. 6. Time course of ozone (a) and dissolved oxygen (b) concentration in 10 mg/L methyl orange solution under 185 + 254 nm irradiation with and without oxygen microbubbling.

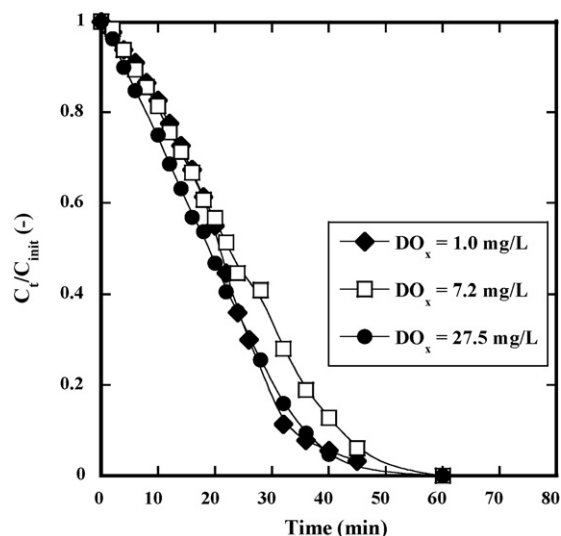


Fig. 7. Effect of initial concentration of dissolved oxygen on the decolorization rate of methyl orange without bubbling under 185 + 254 nm irradiation.

into the atmosphere. Yang et al. [25] observed that the operating costs of the VUV process for degradation of gaseous formaldehyde was 10 times smaller than that of the UV/TiO₂ process. The time course of dissolved oxygen (DO_x) with 185 + 254 nm irradiation time in oxygen microbubbling and non-bubbling conditions is depicted in Fig. 6(b). The concentration of DO_x under the non-bubbling condition decreased with 185 + 254 nm irradiation time. This is because dissolved oxygen in aqueous solution was consumed by the production of ozone at 185 nm light, as previously reported [26]. However, DO_x under oxygen microbubbles condition remained constant due to the constant supply of oxygen gas from the SPG membrane into the VUV irradiated reaction site.

3.4. Effect of the initial DO_x on the decolorization rate of methyl orange without bubbling condition

In order to examine the effect of oxygen microbubbles on the decolorization rate of methyl orange under 185 + 254 nm irradiation, photodegradation experiments were carried out with methyl orange solution at different initial DO_x (1.0, 7.2 and 27.5 mg/L) without bubbling. The different initial DO_x in 10 mg/L methyl orange solution were prepared by nitrogen and oxygen gas bubbling prior to 185 + 254 nm irradiation. Fig. 7 shows the effect of the initial DO_x on the decolorization rate of methyl orange under 185 + 254 nm irradiation without bubbling. It was found that the decolorization rate of methyl orange was independent of the initial DO_x in methyl orange solution under 185 + 254 nm irradiation. This finding indicates that the role of oxygen microbubbling for the supply of dissolved oxygen had little effect on the enhancement of the decolorization rate of methyl orange. In a previous study, Shirayama et al. [27] reported that photodegradation in the presence of dissolved oxygen resulted in the formation of O₃ and hydroxyl radicals. The 185 nm wavelength is a well-known source of ozone, and dissolved oxygen is converted into ozone under Hg emission at 185 nm produced by low-pressure mercury arcs as follows [28,29]



The ozone provides a high absorption cross-section at 254 nm. As a result, a two-step process has been proposed involving the light-induced homolysis of O₃ and the subsequent production of hydroxyl radicals (OH•) by the reaction of O(¹D) with water as

follows [30]:



Alternatively, photodegradation in the absence of dissolved oxygen resulted in the formation of hydroxyl radicals generated by the VUV photolysis of water (H₂O-VUV). Then, hydroxyl radicals oxidize methyl orange to convert to the intermediate products such as carbon dye radicals (Dye•) according to Eqs. (4) and (5) [31]



These reactions suggest that the VUV processes are much more efficient than UV (i.e. 254 and 354 nm) processes. As seen in Fig. 7, the initial DO_x in aqueous solution was unaffected by the decolorization rate of methyl orange, probably because highly reactive hydroxyl radicals can be produced by different ways according to Eqs. (1)–(5) in the presence and absence of dissolved oxygen in aqueous solution.

3.5. Effect of type of microbubbles and flow rate of oxygen microbubbles on the decolorization rate of methyl orange

The effect of the type of microbubbles on the decolorization rate of methyl orange under 185 + 254 nm irradiation is shown in Fig. 8. The result indicates that the decolorization rate of methyl orange with nitrogen microbubbles was the same as that with oxygen microbubbles. This is due to the fact that the decolorization rate of methyl orange was unaffected with the concentration of dissolved oxygen in aqueous solution as discussed above. The effect of flow rate of oxygen microbubbles on the decolorization of methyl orange is depicted in Fig. 9. The results shows that the decolorization rate of methyl orange increases with an increase of flow rate of oxygen microbubbles. It was reported that microbubbles have unique characteristics compared with large bubbles: a very large gas/liquid interfacial area; high gas-dissolution rate; and bubble-stability [32–34]. Furthermore, Khinast et al. [35] suggested recently that microbubbles caused hydrodynamic effects in the

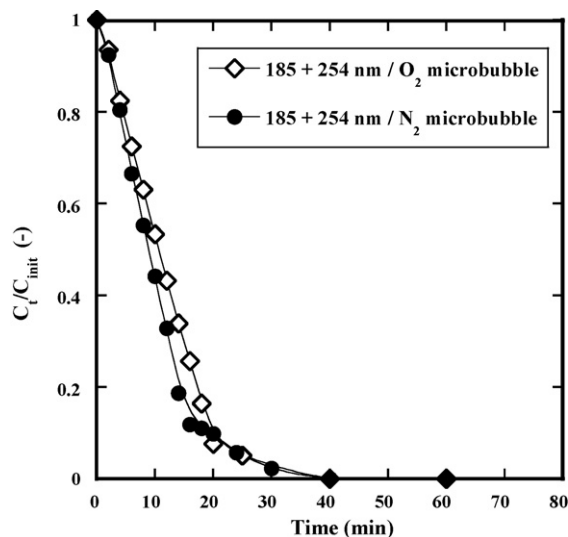


Fig. 8. Effect of type of microbubbling gases on the decolorization rate of methyl orange under 185 + 254 nm irradiation. Dye concentration = 10 mg/L, pH 7.0, gas flow rate = 10 mL/min.

bubble column reactor during the degradation studies of cyclohexane. Taking account of the results obtained in Figs. 8 and 9, the hydrodynamic effect caused by microbubbles enhanced the mass transfer rate of substrate from bulk solution in and out of the VUV-irradiated reaction site, leading to a significantly high rate of decolorization of methyl orange in aqueous solution. In addition, it is possible that the enhancement of the decolorization rate of methyl orange could be attributed to the scattering of the VUV light by microbubble particles [36]. The incident path of the 185 nm light penetrating into water is very short due to its high absorption coefficients (1.8 cm^{-1} at 298 K) [14,37]. The intensity of 185 nm VUV light would be decreased to nearly 90% in 5 mm thickness of water [14]. Thus, the substrate could be better irradiated by 185 nm light due to the scattering effect caused by microbubble particles.

3.6. Effect of initial pH on the mineralization rate of methyl orange with oxygen microbubbles under 185 + 254 nm irradiation

The total organic carbon concentration is very important because it is one of the best observations to conclude the exact point in time when methyl orange has been entirely degraded and the complete mineralization has been achieved. The mineralization experiments were carried out with 10 mg/L methyl orange solution without a surfactant from the practical point of view. The amount of hydroxyl radicals produced by UV irradiation is greatly affected by the pH and as a result effective dye decomposition is highly dependant on the pH of the solution. The time course of pH with oxygen microbubbles at different initial pHs and the effect of initial pH on the mineralization rate of methyl orange with oxygen microbubbles under 185 + 254 nm irradiation are shown in Fig. 10(a) and (b), respectively. The initial pHs at higher than 4.0 decreases with irradiation time, while pHs in the solution remained almost constants at initial pH 2.9 and 4.0 as indicated in Fig. 10(a). This result indicates that methyl orange could be converted to organic acids such as formic acid and oxalic acid [38], thereby reducing the neutral and alkaline solution pH. As demonstrated in Fig. 10(b), the mineralization rate of methyl orange sharply increased with increasing pH from 2.9 to 6.9. This is largely attributed to hydroxyl radicals that are formed from ozone decomposition at high pH, whereas molecular ozone remains the dominant oxidant at low pH [23]. However, slower mineralization rate was noted when the initial pH increase

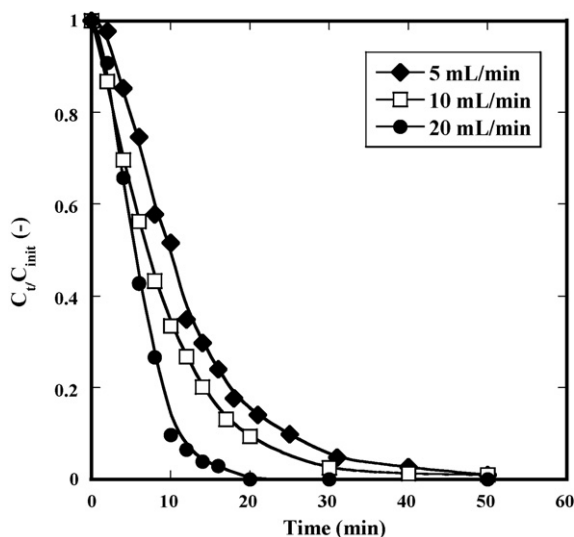


Fig. 9. Effect of flow rate of oxygen microbubbles on the decolorization rate of methyl orange under 185 + 254 nm irradiation. Dye concentration = 10 mg/L, pH 7.0.

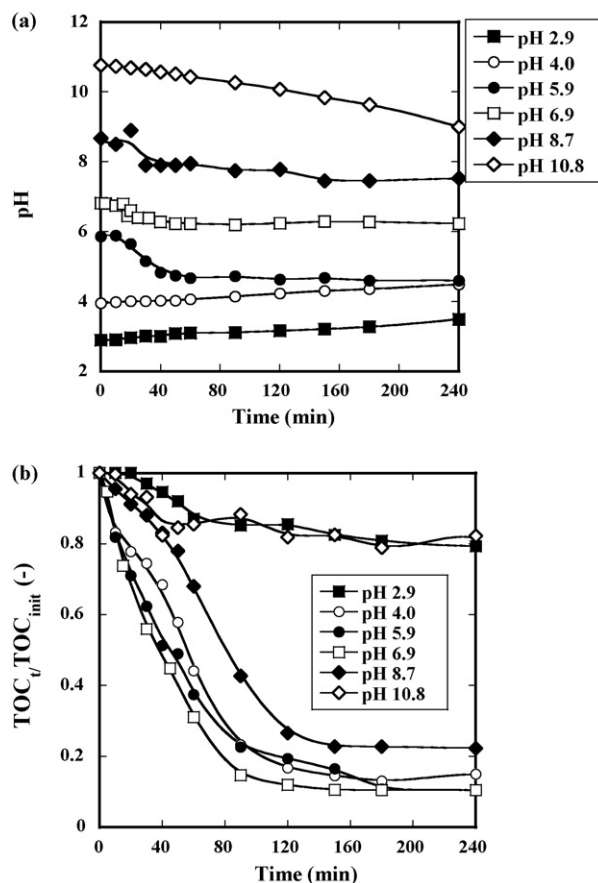


Fig. 10. (a) Time course of pH with oxygen microbubbles at different initial pHs under 185 + 254 nm irradiation. (b) Effect of initial pH on the mineralization rate of methyl orange with oxygen microbubbles under 185 + 254 nm irradiation. Dye concentration = 10 mg/L, gas flow rate = 10 mL/min.

from 6.9 to 10.8. Staehelin and Hoigné [39] proposed a mechanism of OH^\bullet hydroxyl radicals generation, in which the dissolved ozone reacts with OH^- to produce HO_2^\bullet and $\text{O}_2^{\bullet-}$ free radicals. According to this mechanism, OH^- ions can promote the production of $\text{O}_2^{\bullet-}$ free radicals and H^+ ions can accelerate the formation of HO_3^\bullet free radicals, both ions enhance for the complete generation of OH^\bullet free hydroxyl radicals. Shu and Huang [40] also remarked that dissolved ozone would tend to react with azo dyes rather than free radicals in UV enhanced ozonation process. Thus, optimal pH for the degradation could be required. To verify this point, further study would be needed to determine the degradation mechanism involving ozone and hydroxyl radicals in VUV and microbubble system in the future work.

3.7. Effect of initial DO_x on the mineralization rate of methyl orange under 185 + 254 nm irradiation without bubbling condition

Fig. 11 shows the effect of the initial DO_x on the mineralization rate of methyl orange under 185 + 254 nm irradiation without bubbling condition. Contrary to the result obtained in Fig. 7, it can be seen from Fig. 11 that the mineralization rate of methyl orange increases with an increase of DO_x in aqueous solution. It is considered that methyl orange can be degraded into final products such as H_2O and CO_2 by different ways in the presence and absence of dissolved oxygen in aqueous solution [41].

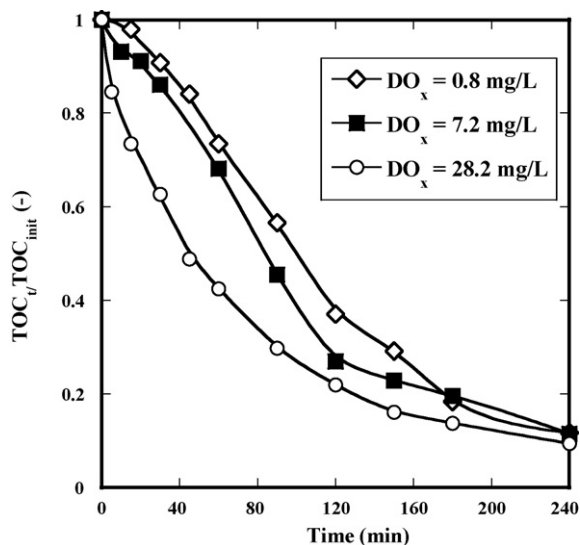


Fig. 11. Effect of concentration of dissolved oxygen on the mineralization rate of methyl orange without bubbling under 185 + 254 nm irradiation. Dye concentration = 10 mg/L, pH 7.0, gas flow rate = 10 mL/min.

3.8. The effect of kind of microbubbles on the mineralization rate of methyl orange under 185 + 254 nm irradiation

The time course of TOC concentration of methyl orange under oxygen, nitrogen microbubbling and non-bubbling condition is shown in Fig. 12. The result indicates that the mineralization rate of methyl orange by oxygen microbubbles is much faster than that by nitrogen microbubbles and UV irradiation directly. There was a 96.9% mineralization efficiency of methyl orange with oxygen microbubble after 240 min irradiation. This finding seems to reflect the different radical reaction mechanisms between predominantly peroxy radical chemistry for oxygen bubbling and carbon radical chemistry for nitrogen bubbling. In previous studies, Stefan et al. [42] and Zhang et al. [43] suggested that short-lived hydrogen and carbon radical were scavenged by dissolved molecular oxygen, resulting in the formation of longer-lived peroxy radicals. The peroxy radicals are key intermediate in the mineralization of methyl orange solution. The recombination of carbon-centered radicals is

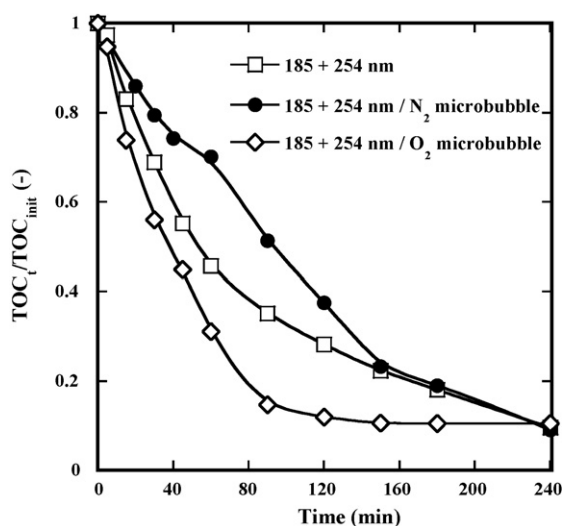
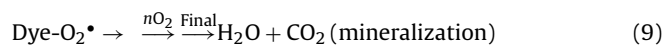
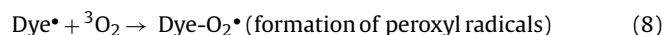
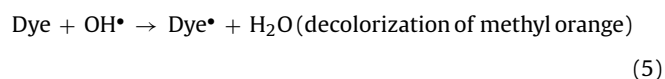
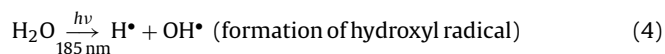
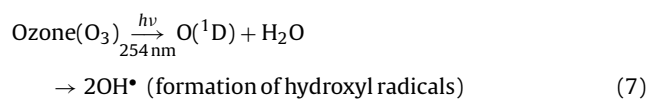
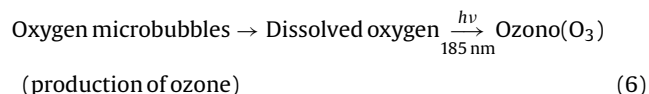


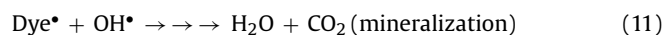
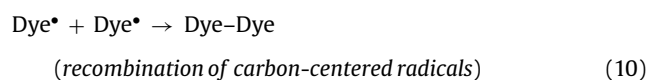
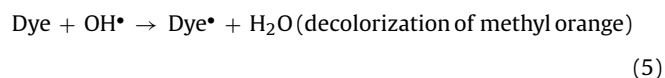
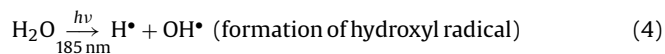
Fig. 12. Effect of type of microbubbling gases on the mineralization rate of methyl orange under 185 + 254 nm irradiation. Dye concentration = 10 mg/L, pH 7.0.

possible to form under the condition of oxygen deficiency [9,13]. This assumption agrees with the experimental results showing that the mineralization of methyl orange takes place slowly under nitrogen microbubbling and non-bubbling condition as shown in Fig. 12. It is likely that the oxygen deficit could be diminished by oxygen microbubbles, leading to the enhancement of TOC reduction due to the formation of peroxy radical. The possible decolorization and mineralization of methyl orange pathways in microbubbling and non-bubbling conditions were described by the following reactions [44]:

- Oxygen microbubbles under 185 + 254 nm irradiation:



- Nitrogen microbubbles and non-bubbling under 185 + 254 nm irradiation:



On the basis of results obtained in this study, it can be concluded that oxygen microbubbles with 185 nm VUV light was crucial for the enhancement of the decolorization and mineralization of methyl orange in aqueous solution.

4. Conclusions

Microbubbles with VUV irradiation (185 + 254 nm) were combined to enhance the decolorization rate of methyl orange in aqueous solution. However, microbubbles under 365 and 254 nm irradiation had little effect on the decolorization rate of methyl orange. The pseudo-zero order decolorization rate with oxygen microbubbles under 185 + 254 nm irradiation was about two times higher than that without bubbling. These findings suggest that the microbubbles with 185 nm VUV light play an important role in the enhancement of the decolorization rate of methyl orange.

The initial dissolved oxygen concentration and type of microbubbles were found not to significantly affect the decolorization rate of methyl orange. On the other hand, the mineralization rate of methyl orange under oxygen microbubbling condition was much faster than that for nitrogen microbubbling. In oxygen microbubbling condition, peroxy radical is generated from the carbon radical scavenged by dissolved molecular oxygen, leading to an increased rate of mineralization of methyl orange. It was demonstrated that microbubble system using 185 nm VUV light provide a potential wastewater treatment for the degradation of organic compounds in terms of not only the kinetic rate, but also the operation costs as well. For practical use, SPG membranes could guarantee optimum sizes of gas molecules and gas inputs at low-pressure losses. The results discussed above are encouraging and further studies regarding the degradation of various organic compounds in a wide range of sizes of gas molecules are currently in progress.

Acknowledgement

This work was supported by a Practical Application Research grant from the Japan Science and Technology Agency (J.S.T.).

References

- [1] M.I. Stefan, J.R. Bolton, Mechanism of the degradation of 1,4-dioxane in dilute aqueous solution using the UV/Hydrogen peroxide process, *Environ. Sci. Technol.* 32 (1998) 1588–1595.
- [2] H. Sudy, C.D. Traversay, Applications of advanced oxidation processes: present and future, *Water Sci. Technol.* 49 (2004) 227–233.
- [3] H.M. Coleman, V. Vimonses, G. Leslie, R. Amal, Degradation of 1,4-dioxane in water using TiO₂ based photocatalytic and H₂O₂/UV processes, *J. Hazard. Mater.* 146 (2007) 496–501.
- [4] I. Ilišz, A. Bokros, A. Dombi, TiO₂-based heterogeneous photocatalytic water treatment combined with ozonation, *Ozone Sci. Eng.* 26 (2004) 585–594.
- [5] D. Jiraraj, F. Unob, A. Hagège, Degradation of Pb–EDTA complex by a H₂O₂ UV process, *Water Res.* 40 (2006) 107–112.
- [6] B. Xu, N. Gao, X. Sun, S. Xia, M. Rui, M. Simonnot, C. Causserand, J. Zhao, Photochemical degradation of diethyl phthalate with UV/H₂O₂, *J. Hazard. Mater.* B139 (2007) 132–139.
- [7] T. Aarhi, G. Madras, Photocatalytic degradation of Rhodamine dyes with Nano-TiO₂, *Ind. Eng. Chem. Res.* 46 (2007) 7–14.
- [8] M.L. Satuf, R.J. Brandi, A.E. Cassano, O.M. Alfano, Quantum efficiencies of 4-chlorophenol photocatalytic degradation and mineralization in a well-mixed slurry reactor, *Ind. Eng. Chem. Res.* 46 (2007) 43–51.
- [9] T. Oppenländer, S. Gliese, Mineralization of organic micropollutants (homologous alcohols and phenol) in water by vacuum-UV-oxidation (H₂O–VUV) with an incoherent xenon–excimer lamp at 172 nm, *Chemosphere* 40 (2000) 15–21.
- [10] T. Alapi, A. Dombi, Direct VUV photolysis of chlorinated methanes and their mixtures in an oxygen stream using an ozone producing low-pressure mercury vapor lamp, *Chemosphere* 2007 67 (2007) 693–701.
- [11] A.M. Braun, I.G. Pintori, H.P. Popp, Technical development of UV-C and VUV-photochemically induced oxidative degradation process, *Water Sci. Technol.* 49 (2004) 235–240.
- [12] G. Heit, A.M. Braun, Spatial resolution of oxygen measurements during VUV-photolysis of aqueous systems, *J. Inf. Record* 22 (1996) 543–546.
- [13] T. Oppenländer, C. Walddörfer, J. Burgbacher, M. Kiermeier, K. Lachner, H. Weinschrott, Improved vacuum-UV (VUV)-initiated photomineralization of organic compounds in water with xenon excimer flow-through photoreactor (Xe₂^{*} lamp, 172 nm) containing an axially centered ceramic oxygenator, *Chemosphere* 60 (2005) 302–309.
- [14] W. Han, P. Zhang, W. Zhu, J. Yin, L. Li, Photocatalysis of *p*-chlorobenzoic acid in aqueous solution under irradiation of 254 nm and 185 nm UV light, *Water Res.* 38 (2004) 4197–4203.
- [15] M. Takahashi, K. Chiba, P. Li, Free-radical generation from collapsing microbubbles in the absence of a dynamic stimulus, *J. Phys. Chem. B* 111 (2007) 1343–1347.
- [16] D.M. Skyba, S. Kaul, Advances in microbubble technology, *Coronary Artery Dis.* 11 (2000) 211–219.
- [17] M. Kukizaki, M. Goto, Size control of nanobubbles generated from Shirasuporous-glass (SPG) membranes, *J. Membr. Sci.* 281 (2006) 386–396.
- [18] M. Kukizaki, M. Goto, Spontaneous formation behavior of uniform-sized microbubbles from Shirasu porous glass (SPG) membranes in the absence of water-phase flow, *Colloids Surf. A: Physicochem. Eng. Aspects* 296 (2007) 174–181.
- [19] M. Kukizaki, T. Nakashima, Acid leaching process in the preparation of porous glass membrane with surface modification, *Membrane* 29 (2004) 301–308.
- [20] T. Tasaki, K. Fujimoto, S. Kai, T. Oshima, K. Ohe, M. Kukizaki, Y. Baba, Photodegradation of organic compounds in UV irradiated micro/nano bubble prepared with Shirasu-Porous-Glass (SPG) membranes, in: Proceedings of 2006 Japan/Taiwan/Korea/ Chemical Engineering Conference, Kagoshima, Japan, 2006.
- [21] C. Wang, X. Wang, B. Xu, J. Zhao, B. Mai, P. Peng, G. Sheng, J. Fu, Enhanced photocatalytic performance of nanosized coupled ZnO/SnO₂ photocatalysts for methyl orange degradation, *J. Photochem. Photobiol. A: Chem.* 168 (2004) 47–52.
- [22] N. Guetta, A. Amar, Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension. Part I. Parametric study, *Desalination* 185 (2005) 427–437.
- [23] A. López-lópez, J.S. Pic, H. Debellfontaine, Ozonation of azo dye in a semi-bath reactor: a determination of the molecular and radical contributions, *Chemosphere* 66 (2006) 2120–2126.
- [24] S. Echigo, H. Yamada, S. Matsui, S. Kawanishi, K. Shishida, Comparison between O₃/VUV, O₃/H₂O₂, VUV and O₃ processes for the decomposition of organophosphoric acid triesters, *Water Sci. Technol.* 34 (1996) 81–88.
- [25] L. Yang, Z. Liu, J. Shi, Y. Zhang, H. Hu, W. Shanguan, Degradation of indoor gaseous formaldehyde by hybrid VUV and TiO₂/UV processes, *Sep. Purif. Technol.* 54 (2007) 204–211.
- [26] G. Heit, A.M. Braun, VUV-photolysis of aqueous systems: spatial differentiation between volumes of primary and secondary reactions, *Water Sci. Res.* 35 (1997) 25–30.
- [27] H. Shirayama, Y. Tohezo, S. Taguchi, Photodegradation of chlorinated hydrocarbons in the presence and absence of dissolved oxygen in water, *Water Res.* 35 (2001) 1941–1950.
- [28] J. Jeong, K. Sekiguchi, K. Sakamoto, Photochemical and photocatalytic degradation of gaseous toluene using short-wavelength UV irradiation with TiO₂ catalyst: comparison of three UV sources, *Chemosphere* 57 (2004) 663–671.
- [29] T. Alapi, A. Dombi, Comparative study of the UV and UV/VUV-induced photolysis of phenol in aqueous solution, *J. Photochem. Photobiol. A: Chem.* 188 (2007) 409–418.
- [30] R. Kamps, H. Müller, M. Schmitt, S. Sommer, Z. Wang, K. Kleiner, Photooxidation of exhaust pollutants. I. Degradation efficiencies, quantum yields and products of benzene photooxidation, *Chemosphere* 27 (1993) 2127–2142.
- [31] Z. László, A. Dombi, Oxidation of [Fe(CN)₆]⁴⁻ and reduction of [Fe(CN)₆]³⁻ in VUV-irradiated aqueous solutions, *Chemosphere* 46 (2002) 491–494.
- [32] S. Fujikawa, R. Zhang, S. Hayama, G. Peng, The control of micro-air-bubbles generation by a rotational porous plate, *Int. J. Multiphase Flow* 29 (2003) 1221–1236.
- [33] M. Takahashi, T. Kawamura, Y. Yamamoto, H. Ohnari, S. Himuro, H. Shakutsui, Effect of shrinking microbubbles on the gas hydrate formation, *J. Phys. Chem. B* 107 (2003) 2171–2173.
- [34] M. Sadatomi, A. Kawahara, K. Kano, A. Ohtomo, Performance of a new micro-bubble generator with a spherical body in a flowing water tube, *Exp. Ther. Fluid. Sci.* 29 (2005) 615–623.
- [35] J.G. Khinast, A.A. Koynov, T.M. Leib, Reactive mass transfer at gas–liquid interfaces: impact of micro-scale fluid dynamics on yield and selectivity of liquid-phase cyclohexane oxidation, *Chem. Eng. Sci.* 58 (2003) 3961–3971.
- [36] M.M. Aslan, C. Crofcheck, D. Tao, P. Meguc, Evaluation of micro-bubble size and gas hold-up in two-phase gas–liquid columns via scattered light measurement, *J. Quant. Spectrosc. Radiat. Transf.* 101 (2006) 527–539.
- [37] J. Weeks, G.M.A.C. Meaburn, S. Gordon, Absorption coefficients of liquid water and aqueous solution in the far ultraviolet, *Radiat. Res.* 19 (1963) 559–567.
- [38] F. Chen, Y. Xie, J. He, J. Zhao, Photo-Fenton degradation of dye in methanolic solution under both UV and visible irradiation, *J. Photochem. Photobiol. A: Chem.* 138 (2001) 139–146.
- [39] J. Staehelin, J. Holgné, Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reaction, *Environ. Sci. Technol.* 19 (1985) 1206–1213.
- [40] H. Shu, C. Huang, Degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation process, *Chemosphere* 31 (1995) 3813–3825.
- [41] C. Tang, V. Chen, Photocatalytic degradation of reactive black 5 using TiO₂/UV in an annular photoreactor, *Water Res.* 38 (2004) 2775–2781.
- [42] M.I. Stefan, J. Mack, J.R. Bolton, Degradation pathways during the treatment of methyl *tert*-butyl ether by the UV/H₂O₂ process, *Environ. Sci. Technol.* 34 (2000) 650–658.
- [43] Y. Zhang, M. Zhou, X. Hao, L. Lei, Degradation mechanisms of 4-chlorophenol in a novel gas–liquid hybrid discharge reactor by pulsed high voltage system with oxygen or nitrogen bubbling, *Chemosphere* 67 (2007) 702–711.
- [44] Y.S. Shen, B.H. Liao, Study on the treatment of Acid Red 4 wastewater by a laminar-falling-film-slurry-type VUV photolytic process, *Water Sci. Res.* 55 (2007) 13–18.