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Degradation of dioxane by combination of ultrasound and ozone microbubbles

超音波とオゾンマイクロバブルを併用したジオキサンの分解

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1. Introduction

Application of ultrasound in degradation of refractory materials, i.e., sonochemistry has been extensively studied. Sonochemical effects include pyrolysis of chemical species inside the cavitation bubbles and radical reactions (oxidation and reduction) inside and adjacent to the bubbles. These effects have been used for the degradation of aqueous pollutants and for synthesizing nano-materials. However, the sonochemical reaction performance is still not high enough for practical usage. In order to enhance sonochemical reaction performance, ozone millimeter-sized bubbles (millibubbles) has been used in sonochemical reaction to decompose pollutants in water[1].

In the present study, degradation of dioxane has been investigated by utilizing ultrasound and ozone micro-sized bubbles (microbubbles), respectively and simultaneously. The mechanism has been discussed.

2. Experimental

The experimental apparatus is shown as **Fig. 1**. The reaction vessel was made of transparent acrylic resin. The dimensions of the vessel were 120 mm in length, 160 mm in width and 600 mm in height. Five transducers with 50 mm in diameter, operated at 495 kHz, were stuck on the side wall of rectangular vessel. A signal generator was used and the output was connected to power amplifier so that the signal was amplified to drive transducers. The reflector plate was made of stainless steel. The distance between transducers and reflector plate was 40 mm.

The ozone concentration and gas flow rate was 101.5 mg/L and 30 mL/min, respectively. The ozone was sparged by microbubbles or millibubbles generator.

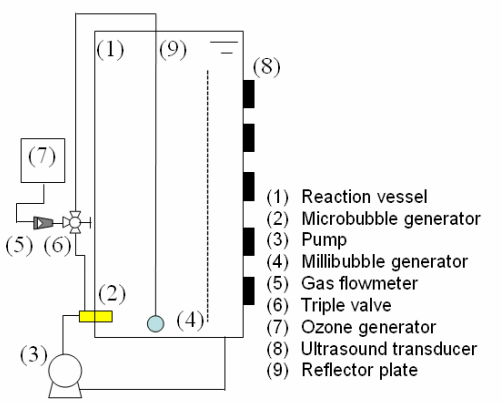

Fig. 1. Experiment apparatus.

Dioxane solution at concentration of 10 mg/L and volume of 10.25 L was used. The dioxane concentration after experiment was measured by gas chromatography.

3. Result and discussion

The effect of ozone bubble size has been investigated. **Fig. 2** shows the change of dioxane concentration with time for ozone milli or microbubbles. The ordinate indicates $\ln(C/C_0)$, where C_0 and C represent the concentration of dioxane before and after experiment, respectively. The reactions obey first-order reaction kinetics. For the ozone millibubbles, the reaction kinetic constant is higher than that for millibubbles. These results infer that microbubbles have high reaction performance compared with millibubbles in degradation of dioxane. It is considered that the microbubbles have large gas-liquid interfacial area compared with millibubbles, which leads the ozone rapidly dissolves into dioxane solution.

Fig. 3 shows the change of dioxane concentration with time for ozone microbubbles, ultrasound and combination of ultrasound and ozone microbubbles (US/O_3(μB)). The total input electrical

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power of transducers was 150 W. For ultrasound irradiation and combined ultrasound with ozone microbubbles, the reactions obey first-order reaction kinetics. The reaction kinetic constants for ultrasound and combination are 0.0024 s^{-1} and 0.0063 s^{-1}, respectively. However, the sum of reaction kinetic constants for ultrasound and ozone microbubbles (US+O_3(μB)) is 0.0049 s^{-1}. It indicates the synergistic effect exists in combination of ultrasound and ozone microbubbles.

Fig. 4 shows the influence of input electrical power of transducers on reaction kinetic constant for ultrasound and combination of ultrasound and ozone microbubbles. The reaction kinetic constants increase with input electrical power of transducers. The reaction kinetic constants for combination of ultrasound and ozone microbubbles are higher than those for the sum of ultrasound and ozone microbubbles. The difference of reaction kinetic constant between combination and sum increases with input electrical power of transducers.

In order to clarify the synergy mechanism due to combination of ultrasound and ozone, the t-butanol has been added into dioxane solution as radical trap agent. **Table 1** shows the influence of t-butanol addition. The reaction kinetic constant for combination with t-butanol addition has minimum, though without t-butanol it has a maximum.

For combination usage of ultrasound and ozone system, ozone is decomposed thermolytically by sonolysis:

$$O_3\,(g)+)))\rightarrow O_2\,(g)+O(^3P)\,(g) \quad (1)$$

$$O(^3P)\,(g)+H_2O\,(g)\rightarrow 2\cdot OH\,(g) \quad (2)$$

$$\cdot OH+\cdot OH\rightarrow H_2O_2 \quad (3)$$

From these results, the synergistic effect can be ascribed to eq.(1), (2) and (3). The ozone does not only directly reacted with dioxane solution but also reacted with ultrasound and release ·OH radical. The ·OH radical reacts with solution and form H_2O_2 which further enhances the reaction performance. When increasing ultrasound input electrical power, the ·OH radical yields by eq.(1), (2) and the formation of H_2O_2 by eq.(3) increased which enhances the reaction performance.

Conclusion

Combination of ozone microbubbles and ultrasound enhances dioxane degradation.

Reference

1) H. Zhang et. al.: Ultrason. Sonochem., **14** (2007) 552.

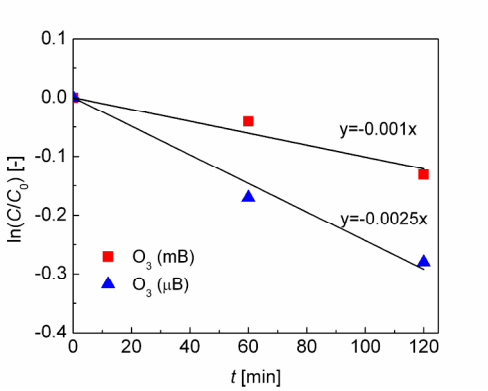

Fig. 2. Change of dioxane concentration with time for ozone milli or microbubbles.

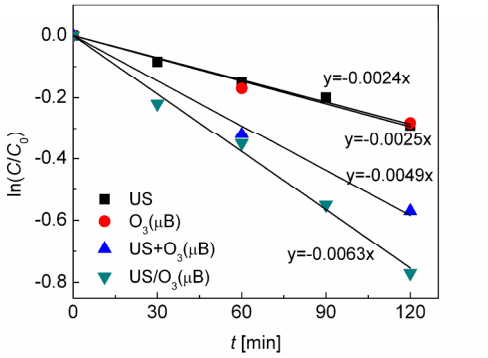

Fig. 3. Change of dioxane concentration with time for ozone microbubbles, ultrasound and combination of ultrasound and ozone microbubbles.

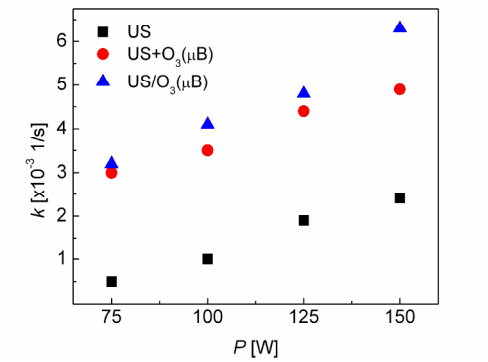

Fig. 4. Influence of input electrical power on reaction rate constant of dioxane for ultrasound and combination of ultrasound and ozone microbubbles.

Table I. Influence of t-BuOH in reaction.

	k [×10^{-3} 1/s]
O_3(μB)	2.5
O_3(μB)/t-BuOH	1.5
US/ O_3(μB)	6.3
US/ O_3(μB) /tBuOH	0.9