Effect of pH on Decomposition of Organic Compounds Using Ozone Microbubble Water

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Microbubbles are tiny bubbles with a particle size of 1 - 100 μm . Microbubbles have been reported that the gas dissolving ability is excellent and hydroxyl radical generates when microbubbles collapse in water. On the other hand, ozone is a gas with high oxidation power and eventually decomposes into oxygen. So, ozone is environmentally friendly. Therefore, we thought that ozone microbubbles water, in which ozone is dissolved in microbubbles water, could be used to efficiently decompose persistent organic compounds while being environmentally friendly. In this study, we evaluated the decomposition of phenol, an object subject to wastewater regulation, by ozone water and ozone microbubbles water. At a constant dissolved ozone concentration, we could not confirm the effect of microbubbles in decomposing phenol. Also, under the same conditions, when the pH was changed, the effect of microbubbles could not be confirmed. However, under basic conditions, phenol was decomposed the most because of self-decomposition reaction of ozone. Therefore, the effect of microbubbles could not be confirmed in the phenol degradation by ozone microbubbles in this experiment.

Keywords: Microbubble, Ozone, Resist removal, Environmentally friendly Cleaning technique

1. Introduction

Microbubbles are tiny bubbles with a diameter of 1-100 μm and possess remarkable properties differing from those of normal bubbles. Firstly, rising speed of microbubbles in the water is slow, which follow scheme (1).

$$u_B = \frac{d_B^2 (\rho_L - \rho_G) g}{18 \mu_L} \quad (1)$$

Rising speed of microbubbles is given as (1), where u_B is the rising speed and d_B is the diameter. In addition, ρ_L and ρ_G are liquid and gas density, μ_L is liquid viscosity coefficient and g is gravitational acceleration. Due to the large diameter of normal bubbles, they float quickly in water, reach the gas-liquid interface, and disappear after a few seconds.

On the other hand, since the microbubbles have a small diameter, the rising speed is small, and the bubble collapses while shrinking. And, microbubbles can efficiently dissolve internal gas with surrounding liquid because internal gas pressure is increased by surface tension at the gas-liquid interface [1,2]. The size of bubble affects the pressure difference between the inside and outside of the bubble. The equation (Young-Laplace equation, (2)) is shown below.

$$\Delta p = \frac{4\sigma}{d_B} \quad (2)$$

Interfacial tension between gas phase and liquid phase is given as (2), where Δp is pressure difference between inside and outside, σ is the surface tension between water and air and d_B is the

diameter of the bubble. From this equation, the smaller the diameter, the larger the pressure difference. Since microbubbles shrink over time, the pressure difference becomes larger. This effect is called the self-pressurization effect. The most interesting property of microbubbles is their ability to generate hydroxyl radicals. Due to the self-pressurization effect, microbubbles shrink and release very strong energy upon collapsing, which reacts with some of the surrounding water to produce hydroxyl radicals (Figure 1). The standard redox potential of hydroxyl radicals is much higher than that of oxidants such as ozone and hydrogen peroxide. The hydroxyl radicals non-selectively decompose organic compounds. Therefore, it is thought that microbubbles are useful for decomposing persistent organic compounds [3,4].

Fig. 1. Mechanism of hydroxyl radical generated from microbubbles.

On the other hand, ozone is applied to environmentally friendly cleaning techniques for water and semiconductor manufacturing [5-13]. Ozone water degrades compounds with C=C bond to ketone and carboxylic acid [14,15]. Additionally, ozone generates reactive oxygen species through self-decomposition in water. Reactive oxygen species can degrade organic compounds because of its extremely strong oxidation power.

Therefore, we thought that ozone microbubbles water, in which ozone is dissolved in microbubbles water, could be used to efficiently decompose persistent organic compounds while being environmentally friendly [16-18].

In this study, we confirmed the effect of microbubbles by decomposing phenol, an object of wastewater regulation, by ozone microbubbles [19]. In order to focus on the behavior of the electric double layer of microbubbles, we changed the pH in the aqueous solution and decomposed phenol.

2. Experimental

2.1. Ozone microbubbles generation systems

Figure 2 shows a schematic diagram of the ozone microbubbles generator. Microbubbles were generated using pressurized dissolution method. Ozone gas was dissolved by pressurizing with 0.5 MPa using a bellows pump ($\Sigma P - 15 D - V$, Sigma Technology Co.). An ozone aqueous solution in a supersaturated state was generated and opened to the atmosphere through a dispersion nozzle (Resource Development Co., Ltd.) to generate microbubbles. The presence or absence of microbubbles was switched depending on this nozzle. Dissolved ozone concentration was measured using the ozone monitor (Ebara Kogyo Co., Ltd.). A low-pressure mercury lamp with an emission wavelength of 253.7 nm was used as the light source. Ozone water was supplied to the detection part, and the dissolved ozone concentration was measured by measuring the ultraviolet absorption amount.

Fig. 2. Schematic illustration of ozone microbubbles generation system.

2.2. Decomposition treatment of phenol by ozone microbubbles

Ozone microbubbles were generated in 3 L of ion exchanged water. Dissolved ozone concentration was stabilized at 30 and 60 mg/L at $15 \pm 1^\circ \text{C}$ water temperature. 3mmol of phenol (Wako Pure Chemical Industries) was dissolved in ozone microbubbles and ozone water and stirred for 5-60 minutes. The decomposition rate and decomposition products of phenol were measured using HPLC. The total organic carbon (TOC) content of the treated samples was measured using the combustion catalytic oxidation method. The pH of the aqueous phenol solution was adjusted by using hydrochloric acid (Wako Pure Chemical Industries) and sodium hydroxide (Wako Pure Chemical Industries).

3. Results and Discussion

3.1. Relationship between supplied ozone gas concentration and dissolved ozone concentration with and without microbubbles

Fig. 3 shows relationship between supplied ozone gas concentration and dissolved ozone concentration with and without microbubbles. The dissolved ozone concentration increased in proportion to the ozone gas supply. When the ozone gas supply was kept constant, the dissolved ozone concentration of ozone microbubbles water was higher than that of ozone water. This result suggests that microbubbles have a large specific surface area and dissolved a lot of gas.

Fig. 3. Relationship between dissolved ozone concentration of ozone water with (●) or without (●) microbubbles and ozone gas supply.

3.2. Decomposition of phenol by using ozone microbubbles

Phenol was decomposed by circulating ozone microbubbles water and ozone water for 5 min, and the HPLC chromatogram of the aqueous solution is shown in Fig. 4. It was found that the phenol was decomposed by 70-90% by ozone water and ozone microbubbles water treatment for 5 min. Divalent phenol was also observed as a decomposition product [20,21]. When the concentration of the ozone gas supply was kept constant at 120 g/Nm³, the phenol was decomposed better by treatment with ozone microbubbles water than with ozone water. This could be attributed to the increase in dissolved ozone concentration by using microbubbles. On the

other hand, when the dissolved ozone concentration was kept constant at 30 mg/L, there was no dominant difference in phenol degradation between ozone microbubbles water and ozone water. From these results, the direct reaction by ozone was the main reaction for the decomposition of phenol, and the effect of OH radicals, which are thought to be generated from the collapsing of microbubbles, could not be confirmed. Therefore, hydrogen peroxide, one of the decomposition products, which is considered to be due to OH radicals generated by the self-decomposition of ozone.

Fig. 4. HPLC chromatogram of untreated (black) and treated phenol aqueous solution. In addition, these treated solutions were prepared by ozone water (blue) and ozone microbubbles (red, green) for 5 min, respectively.

3.3. Relationship between decomposition of phenol by treatment of ozone microbubbles and pH

The residual rate of phenol treated with ozone water and ozone microbubbles water for 5 min is shown in Fig. 5. In all conditions, phenol was found to be decomposed by 80-90%. Although the superiority of microbubbles could not be confirmed in all conditions, phenol was decomposed the most under basic conditions. This is thought to be due to the reaction of ozone and hydroxyl ions, which produced a large number of reactive oxygen species (scheme 3.).

Fig. 6 shows the time course of TOC of phenol solution treated by ozone microbubbles and ozone water. The 60-minute treatment resulted in a 40-60% reduction in TOC. The decrease in TOC was not observed under acidic conditions than under neutral or basic conditions. It is thought that this is because under acidic conditions, it is difficult for ozone to cause self-decomposition reaction and generate

reactive oxygen species. This suggests that changes in pH affect ozone, but not microbubbles.

Fig. 5. Decomposition rate of phenol before the treatment (a), after the treatment by ozone water in the ((b), (d) and (f)) presence or ((c), (e) and (g)) absence of microbubbles at various pH (—: pH = 6, —: pH = 2.2, —: pH = 10).

Scheme 3. Self-decomposition reactions of ozone.

4. Conclusion

At the same ozone gas supply, the dissolved ozone concentration was higher in the ozone microbubble water than in the ozone water. Therefore, phenol was treated at the same dissolved ozone concentration to investigate the degradation effect of microbubbles. As a result, no significant difference in decomposition of phenol could be confirmed in ozone water and ozone microbubble water treatment. The same experiment was also conducted by varying the pH. As a result, the effect of microbubbles could not be confirmed at any pH. At pH = 2.2, the mineralization of phenol did not progress as much as at pH = 6 or 10. This is thought to be due to the difficulty of self-decomposition of

ozone to progress. It is assumed that the decomposition of phenol is not caused by microbubbles, but caused by ozone.

Fig. 6. TOC of aqueous solution of phenol after the treatment by ozone water in the (closed symbol) presence or (open symbol) absence of microbubbles at various pH (—: pH = 6, —: pH = 2.2, —: pH = 10).

5. References

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