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Ozonolysis of Organic Compounds in Water with Hollow Fiber Membrane Contactor

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Abstract
Decomposition of nitrobenzene or phenol in water was conducted in a hollow fiber membrane module by contacting a perfluorocarbon (PFC) containing ozone and an aqueous feed. Under most of experimental conditions, the mass-transfer of ozone in the PFC controls the decomposition rate. To introduce ozone bubbles with PFC to the fiber lumen is quite effective for enhancing the solute decomposition. This fact is interpreted as the mass-transfer enhancement in the micropore due to the disturbance of PFC.

Introduction
Ozone bubbling is carried out to decompose organic contaminants existing at low concentration in water. The problem of such a direct bubbling is that most of ozone introduced is unused and discharged because of its low solubility to water. For the effective use of O_3, the O_3 supply from O_3-loaded perfluorocarbon to water has been suggested [1,2]. Perfluorocarbon has a large O_3 solubility, chemical stability and very low vapor pressure. Guha et al.[1], have applied this organic solution as a liquid membrane to the contained liquid membrane contactor. Because of a large membrane thickness in this type of contactor, the mass-transfer in the membrane liquid controls the decomposition rate. In the present study, we suggested to use simpler hollow fiber contactor for ozonolysis of organic compounds in water. Decomposition behaviors of phenol and nitrobenzene were examined. In order to enhance the mass-transfer in PFC inside the pore, O_3 bubbles are introduced to the lumen side of hollow fiber with PFC. This effect of bubble flow on the decomposition rate was discussed

Experimental
An aqueous solution of nitrobenzene or phenol was used as a feed. The concentration was set to 0.5 mol/m^3. Perfluorocarbon used was FC70 (Sumitomo 3M). The membrane was mircroporous PTFE hollow fiber made by Goretex, whose I.D. of 0.2 cm, O.D. of 0.28 cm and maximum pore diameter of 2.0 μm. Two kinds of membrane module were used. The one has a single hollow fiber of 14 cm in length and a shell tube of 0.8 cm in I.D. The other has three fibers of 13.5

cm in length and the shell tube has 1.25 cm in I.D. A scheme of experimental set-up is shown in Fig. 1. Pure oxygen was supplied to the ozonator to produce ozone. The gas left from ozonator is introduced to PFC reservoir. The PFC is sent from the reservoir to the lumen side of hollow fiber to be contacted with the aqueous solution. In the membrane module, the feed solution flows in counter direction to the PFC flow. The aqueous solution left from the module was sent back to the reservoir. A given amount of the solution in the reservoir was sampled and analyzed with FID gas chromatograph.

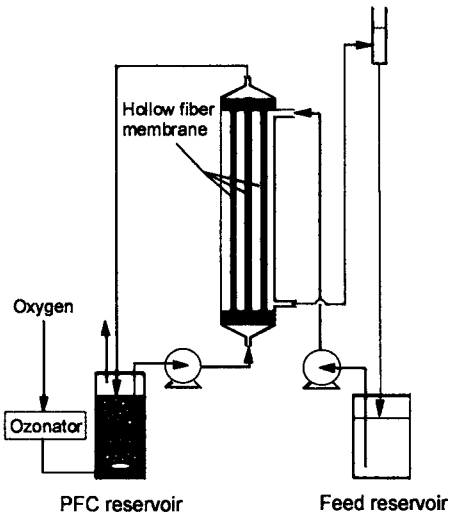

Fig.1 Experimental apparatus

Results and Discussion

In order to examine the extractability of PFC for the solutes, distribution ratios of nitrobenzene and phenol between PFC and water were measured. The ratio of nitrobenzene is 1.6 and that of phenol is 0.03.

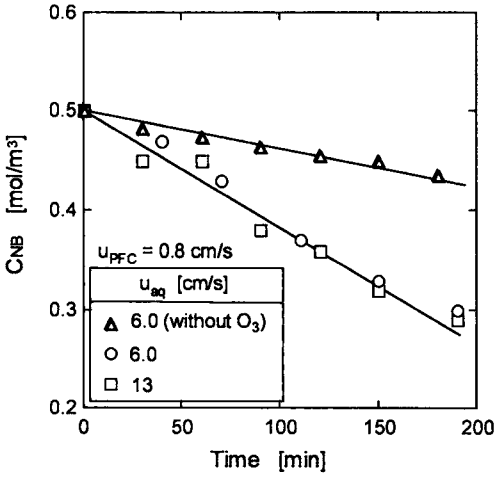

Fig.2 Time course of nitrobenzene concentration

Nitrobenzene decomposition: Figure 2 shows a typical plot of nitrobenzene concentration versus time. Concentration of nitrobenzene in feed decreased by contacting PFC without containing O_3 because of the extraction. When O_3 is dissolved in PFC, the reduction rate is significantly increased by the progress of decomposition. Very small effect of aqueous phase velocity was observed on the reduction rate.

To compare the solute reduction rate for different modules, the rate is expressed by moles of solute per unit outside surface area of hollow fiber per time. In Fig. 3, those values for nitrobenzene and phenol were plotted against PFC velocity. With the increase of PFC velocity, the decomposition rate of nitrobenzene increased largely. From the above results, the reduction rate of nitrobenzene is controlled by the mass transfer of O_3 in PFC. The nitrobenzene extracted in PFC at the interface will diffuse to the lumen side of hollow fiber and react with O_3 inside the micropore. Since the diffusion resistance of O_3 in the liquid film can be reduced by the rapid

flow of PFC, the transfer rate of O_3 in the micropore will determine the decomposition rate.

Phenol decomposition: Because little amount of phenol is extracted to PFC, the feed concentration was constant by supplying PFC without O_3. When the O_3 diffused to the interface, it will react with the phenol and the concentration started to decrease. The reduction rate was constant for aqueous feed velocity from 1.3 cm/s to 14 cm/s. While for the change of PFC velocity, the reduction rate increased as shown in Fig. 3. Thus the O_3 transfer in PFC controls the phenol decomposition rate.

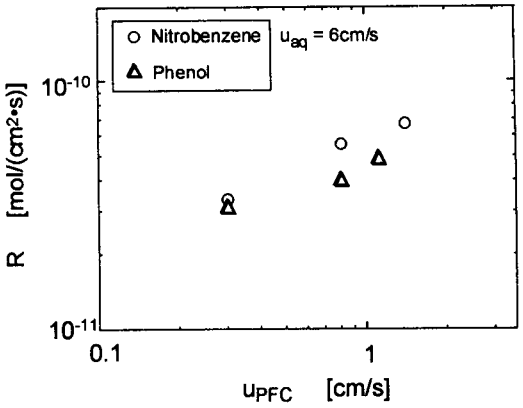

Fig.3 Decomposition rates of solutes

Table 1 Effect of ozone bubble flow rate on decomposition rate of nitrobenzene

u_{PFC} [cm/s]	Q_{O3} [cm³/s]	R [mol/(cm²•s)]
1.5	0	5.9×10^{-11}
0.69	0.2	8.7×10^{-11}
0.13	1.3	1.1×10^{-10}

u_{aq} = 13.6 cm/s

Effect of bubble flow inside hollow fiber: Since the mass transfer of O_3 in PFC controls the decomposition rate of nitrobenzene and phenol, to disturb the PFC inside the pore will enhance the decomposition rate. When O_3 bubbles were introduced to the fiber lumen, the bubble flow would fluctuate the PFC in the pore and also O_3 would be supplied. To examine the effect of bubbles on the decomposition rate, experiments were carried out with a membrane module having a single hollow fiber. **Table 1** shows decomposition rates of nitrobenzene with supplying O_3 bubbles. With increasing O_3 flow rate, the decomposition rate increased even though the PFC velocity decreased. In addition, the reduction rate for Q_{O3} =1.3 cm^3/s was much bigger than that for very high PFC velocity. As for phenol, the largest decomposition rate, 5.1×10^{-11} mol/(cm^2s), was observed with a supply of O_3 bubbles to the fiber lumen. These facts clearly demonstrate that the O_3 diffusion in the pore is effectively enhanced by the flow of O_3 bubbles.

References

[1] A. K. Guha, et al., *AIChE J.*, **41**, (1995)1998

[2] C. Y. Chang and J. N. Chen, *Wat. Sci. Tech.*, **29**(1994)343