A FUDAMENTAL STUDY ON DEGRADATION OF ORGANIC COMPOUNDS WITH HIGE PRESSURE WATERJETS

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1. INTRODUCTION

Soil has ability for environmental preservations such as clarifying and reserving water, and has been considered as one of the most important systems of nature. However, soil and groundwater have been contaminated by industrial activities. In 1970s, large-scale contaminations of the soil and groundwater were revealed in Love Canal, USA. After this incident, the contaminations of soil and groundwater have attracted much attention. In Japan, the contamination of soil and groundwater have been reported since 1990s, and against the contaminations, "Contaminated Soil Countermeasure Law" was enforced in 2003.

To remediate the contaminations, many techniques have been developed. However, these techniques have several problems such as long processing time, energy inefficiency and costliness. Moreover, these techniques cannot deal with the contaminations at more than 20 m in depth. Accordingly, to remediate the contaminations at great depth, a new technique is required to be developed.

To remediate the contaminations, watejets techniques have been utilized for cleaning soils. This technique also has been utilized for degrading organic compounds in water with iron powder. When water is jetted in water, a large number of cavitation bubbles are induced. The cavitation bubbles may induce radicals when they collapse. In sonochemical fields, the radicals induced by the collapses of the cavitation bubbles are known to have a capability to degrade organic compounds. However, cavitation generators used in this field are an ultrasonic bath and an ultrasonic prove, and these may not easily induce a large number of cavitaton bubbles under a high ambient pressure. Furthermore, there have been no results about the degradation of the organic compounds with cavitation bubbles induced by waterjets.

In this suty, to clarify the capability of the cavitation induced by waterjets to degrade organic compounds, degradation tests for an organic compound with waterjets were conducted under high ambient pressures of up to 3 MPa. Main purposes in this study are summarized by the following three points:

1) Design and development of a new experimental system with waterjets.
2) Investigation of effects of driving pressure (p), ambient pressure (p_a), horn angle (2θ) and volume of sample (V) on degradation of an organic compound.
3) Comparison of degradation efficiency obtained by waterjets with that obtained by an ultrasonic generator.

2. Experimental system and method

2.1 Experimental system

In this study, to degrade an organic compound with waterjets under high ambient pressure, a new experimental system was developed. Fig. 1 shows a schematic diagram of the experimental system with waterjets. The experimental system consists of a water tank, a high pressure water pump, a pressure vessel, an ambient pressure control valve, sampling ports, a cooling system and a measurement system.

The water tank 1 has a capacity of 200 l and is made of polyethylene resin. The high pressure pump 2 is manufactured by Sugino Machine Limited. Its maximum pressure and flow are 98.1 MPa and 40 l/min, respectively. The pressure vessel 3 has a bearing capacity of 3.0 MPa. A wagterjets nozzle is attached at the bottom of the pressure vessel. Fig. 2 shows the cross-section of the waterjets nozzle used in this study. The diameter (d) is 1.4 mm. The nozzle has a horn angle (2θ) at the nozzle exit to enhance cavitation. The ambient pressure control valve 4 adjusts the ambient pressure (p_a) in the pressure vessel. The sampling ports are installed to take samples during the experiments. Those parts are connected with high pressure hoses, and the solution in this system is circulated continuously.

2.2 Experimental method

Table 1 shows the experimental conditions used in this study. A solution of oxalic acid with an initial concentration of 100 mg/l was prepared, and was poured into the water tank. The ambient pressure in the pressure vessel was adjusted by the ambient pressure control valve. After the ambient pressure was increased to a designated value, waterjetting started. Since the

temperature in the water tank increased with the impinging time, the high pressure water pump was stopped when temperature in the water tank reached 55 ºC, and when the solution in the water tank was cooled down to 20 ºC with a cooling system, waterjetting started again until the impinging time reached the designated value.

2.3 Analytical method

A high-pressure liquid chromatography (HPLC) was used for analyzing the samples. Samples ware analyzed twice, and a mean value was used as the concentration of the sample (C).

3. Results and discussion
3.1 Effect of driving and ambient pressures

Figs. 4 and 5 show the effects of the driving (p) and ambient (p_a) pressures on the degradation of oxalic acid. As the impinging time increases, the concentration ratio of oxalic acid decreases. As the driving pressure increases or as the ambient pressure decreases, the degradation rate increases. This is because the amount of cavitation bubbles induced by the waterjets increases as the driving pressure increases or as the ambient pressure decreases. Fig. 6 shows the relation between the driving pressure (p) and the first-order reaction rate (k). The first-order reaction rates obtained at driving pressures of greater than 60 MPa are much greater than those obtained at driving pressures of smaller than 60 MPa.

3.2 Effect of horn angle (2θ)

Fig. 7 shows the effect of the horn angle (2θ) on the degradation of oxalic acid. The horn angle remarkably affects the degradation rate. In particular, a horn angle (2θ) of 60 º gives the best performance in this study.

3.3 Effect of sample volume (V)

Fig. 8 shows the effect of the volume of the solution on the degradation of oxalic acid. The degradation rate decreases with the volume of the solution. The flow rate of waterjets (q_w) is determined by the pressure difference between the driving and ambient pressures ($\Delta p = p - p_a$) as given by

$$q_w = 0.93A\sqrt{\Delta p / \rho}, \tag{1}$$

where ρ is the density of the water. Since the ratio of the flow rate to the volume of the solution (q_w/V), which is a volume of the solution exposed to cavitation bubbles per unit time, decreases with the volume of the solution, the degradation rate increases with the volume of the solution.
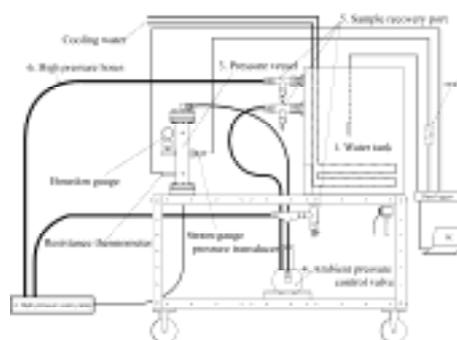
Fig. 1 Schematic diagram of the experimental system with waterjets.
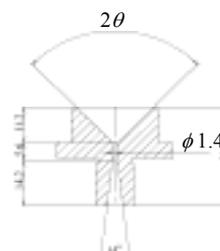
Fig. 2 Cross-section of waterjets nozzle used in this study.

Table 1 Experimental conditions used in this study.

Organic compound	Oxalic acid								
Initial concentration C_0 [mg/l]	100								
Horn angle, 2θ [°]	30					60		90	
Driving pressure p [MPa]	88.3		58.9	68.5	78.5	88.3			
Ambient pressure p_a [MPa]	0.3							1.0	3.0
Volume of waer V [l]	40	60	80						
Impinging time t [min]	25	30	25	30	60	45	120	25	25	25
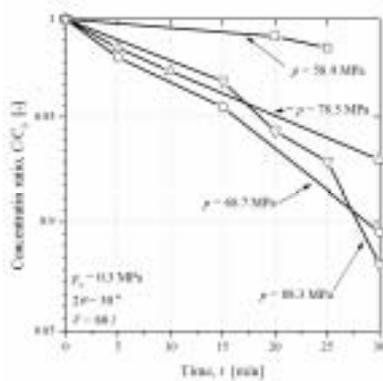
Fig. 4 Effect of driving pressure (p) on degradation of oxalic acid.
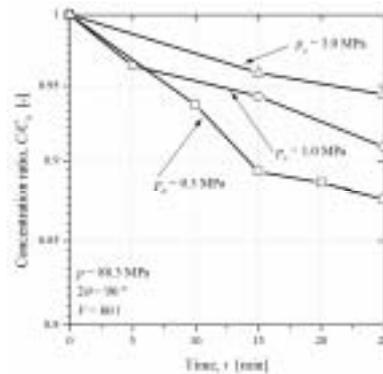
Fig. 5 Effect of ambient pressure (p_a) on degradation of oxalic acid.
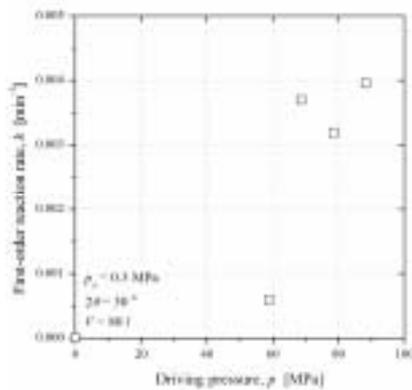
Fig. 6 Relation between driving pressure (p) and first-order reaction rate (k).
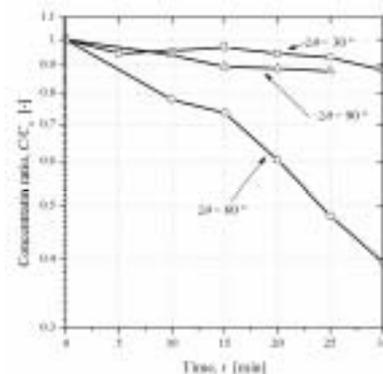
Fig. 7 Effect of horn angle (2θ) on degradation of oxalic acid.
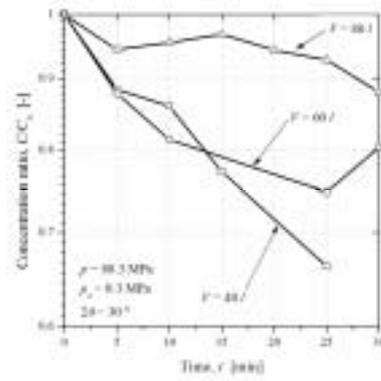
Fig. 8 Effect of sample volume (V) on degradation of oxalic acid.

3.5 Degradation by ultrasonic generator

An ultrasonic bath manufactured by BRANSON was used as an ultrasonic generator. The frequency and power of the ultrasonic generator are 44 kHz and 180 W, respectively. Fig. 9 shows a schematic diagram of the experimental system with the ultrasonic generator. Table 2 shows the experimental conditions used for the tests with the ultrasonic generator. Fig. 10 shows variation in the concentration ratio with time when the ultrasonic generator was used. Oxalic acid was only a little degraded by the ultrasonic generator.
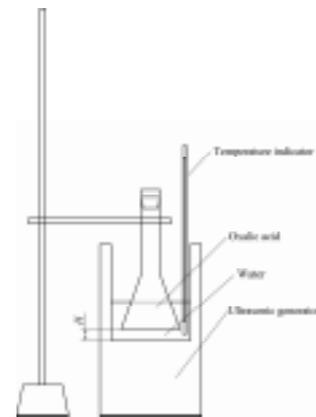
Fig. 9 Schematic diagram of the experimental system with ultrasonic generator.

Table 2 Experimental conditions used for test with ultrasonic generator.

Organic compound	Oxalic acid
Initial concentration C_0 [mg/l]	100
Volume of solution V [ml]	200
Distance between ultrasonic generator and bottom of flask H [cm]	4.3, 8.7
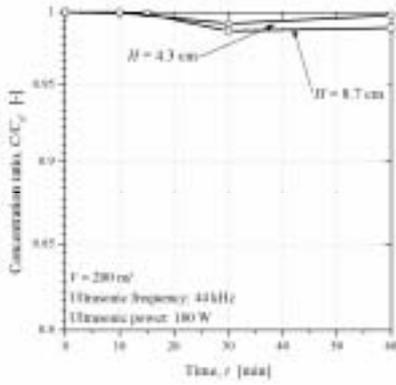
Fig. 10 Variation in concentration ratio with time.

3.6 Comparison of degradation between waterjets and ultrasonic generator

To compare the results obtained by both the waterjets and the ultrasonic generator, the time ($T_{1/2}$) and the energy (E_h) required to degrade oxalic acid to half concentration as well as the degradation efficiency (e) were investigated. The first-order reaction rate in the water tank (k_T) was determined by calculating the concentration in the water tank ($C_T(t)$) (Eq. (2)), and $T_{1/2}$, E_h and e were determined by Eqs. (3) to (5). The power (W_0) of the high pressure pump is 110 kW. Tables 3 and 4 show the time ($T_{1/2}$) and the energy (E_h) required to degrade oxalic acid to half concentration and the degradation efficiency (e) for both the waterjets and the ultrasonic generator.

$$C_T(t) = C_0 \exp(-q_w t/V)\left\{1 + \frac{q_w}{q_w - Vk}\left(\exp\left(\frac{q_w - Vk}{V}\right)t - 1\right)\right\}, \qquad (2)$$

$$T_{1/2} = -\ln(1/2)/k_T, \qquad (3)$$

$$E_h = W_0 T_{1/2}, \qquad (4)$$

$$e = \frac{\frac{1}{2}C_0 V}{E_h}, \qquad (5)$$

The time required to degrade oxalic acid to half concentration ($T_{1/2}$) obtained by the waterjets is smaller than that obtained by the ultrasonic generator. On the other hand, the energy required to degrade oxalic acid to half concentration (E_h) obtained by the waterjets is greater than that obtained by the ultrasonic generator. This is because both the power of the high pressure pump and the volume of solution in the experimental system with the waterjets are greater than those with the ultrasonic generator. Accordingly, the degradation efficiency (e) obtained by the waterjets is much greater than that obtained by the ultrasonic generator. This means that the waterjets can degrade much more oxalic acid than the ultrasonic generator with the same energy consumption.

Table 3 Half time ($T_{1/2}$) and energy (E_h) required to degrade to half concentration and degradation efficiency (e) obtained by watejets (p = 88.3 MPa, p_a = 0.3 MPa, V = 80 l).

2θ [°]	k_T [min^{-1}]	$T_{1/2}$ [min]	E_h [GJ]	e [mg/MJ]
30	3.95 x 10^{-3}	175.4	1.16	3.46
60	2.87 x 10^{-2}	24.2	0.16	25.0
90	4.83 x 10^{-3}	143.4	9.46	4.23

Table 4 Half time ($T_{1/2}$) and energy (E_h) required to degrade to half concentration and degradation efficiency (e) obtained by ultrasonic generator.

H [cm]	k [min^{-1}]	$T_{1/2}$ [min]	E_h [MJ]	e [mg/MJ]
8.7	1.87 x 10^{-4}	3699.2	0.04	0.25

4. CONCLUSIONS

Main results obtained in this study can be summarized as follows:
1) The cavitation bubbles induced by the waterjets can degrade oxalic acid under high ambient pressures of up to 3 MPa.
2) The degradation rate of oxalic acid with waterjets increases with the driving pressure and decreases with the ambient pressure. When the driving pressure is greater than about 60 MPa, the degradation rate increases rapidly with the driving pressure.
3) The horn angle at the nozzle exit remarkably affects the degradation rate of oxalic acid. Especially, the horn angle (2θ) of 60 ° gives the best performance in this study.
4) The degradation efficiency with the waterjets is much greater than that with the ultrasonic generator.

REFERENCES

[1] Okumura *et al*, 2001, Cavitation Clouds induced by Submerged High-pressure waterjets under High Ambient and its Significance on the performance of Submerged waterjets. *Journal of Jet Flow Engineering*, 18 (3), 4-12.
[2] Sato *et al*, 2000, Development of Advanced Aquq-Environmental Protection Technology Using High-Speed Cavitating Water Jets. *Journal of Jet Flow Engineering*, **17** (1), 19-28.