

# Improvement of Phenol Degradation by UV Irradiation on Ultrasonic Atomized Droplets

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Photocatalysis such as TiO<sub>2</sub> particles are expected to be applied to the degradation of hazardous organic materials as an advanced oxidation processes (AOPs). However, UV light is shielded by the catalyst particles, so the area of catalytic activity is limited spatially. On the other hand, ultrasonic atomization has been reported to produce very fine droplets from bulk solutions, and to disperse particles in liquids into droplets. Therefore, it is expected that the combination of ultrasonic atomization and photocatalysis enables a higher concentration of photocatalytic particles in the atomized droplets. In this study, droplets containing TiO<sub>2</sub> were generated using an ultrasonic atomizer, and phenol degradation was carried out by UV light irradiation to the droplets. Kinetic analysis was performed by assuming the reaction to be a pseudo-first-order reaction, and the effects of particle concentration and particle size on the degradation rate constants were investigated.

The degradation rate constant increased with increasing TiO<sub>2</sub> particle addition. Phenol degradation by photocatalytic particles and UV irradiation was also investigated. The results were compared with those obtained with a device that uses a combination of ultrasonic atomization and UV irradiation. At the same TiO<sub>2</sub> particle concentration, the degradation rate of the device that combined ultrasonic atomization and UV irradiation was higher than that of the device that used UV irradiation. It is assumed that the equipment using a combination of ultrasonic atomization and UV irradiation increased the degradation rate because TiO<sub>2</sub> particles were concentrated and incorporated into the droplets, resulting in a higher particle concentration. It is estimated that TiO<sub>2</sub> particle concentration inside the droplet is twice as concentrated as evaluated from the results of degradation rate constant.

## 1. Introduction

Photocatalysis such as TiO<sub>2</sub> particles are expected to be applied to the degradation of hazardous organic materials as an advanced oxidation processes (AOPs). Catalytic activity, such as radical formation, is exhibited by energy sources such as UV light irradiation (Kormann et al., 1991). However, light is shielded by the added particles. A method that combines ultrasound and photocatalytic particles, which are not affected by the shielding effect of the particles, is investigated (Kubo et al., 2005, Park et al., 2011). Sekiguchi and Saita (2001) have also investigated the effect of alumina particle addition on ultrasonic degradation of organic materials. Degradation using ultrasound is strongly depend on the frequency. Kobayashi et al. (2012, 2014) have investigated the effects of ultrasonic frequency on degradation of methylene blue, and proposed a model for estimating rate constants using sonochemical efficiency. Honma et al. (2013) and Kobayashi et al. (2019) have reported that the enhancement of degradation rate by particle addition was influenced by both ultrasonic frequency and type or diameter of particles.

Combination of ultrasonic atomization and UV is also investigated for degradation of hazardous organic materials. Itoh et al. (2019) have reported that KI oxidation by simultaneous treatment of US/UV was higher than the sum of respective rate constants obtained by US treatment alone and UV treatment alone. It was suggested that oxidation reactions are promoted by catalytic reactions not only in solution but also in the fine mist generated by ultrasonic atomization. Kato et al. (2021) also proposed a wastewater treatment system using mist and photocatalyst, and the presence of mist in the reactor has been revealed to increase the removal rate of pollutants (Kato et al., 2022). Kato et al. (2023) have reported that US irradiation generates mist and UV

irradiation and  $\text{TiO}_2$  promote photocatalytic removal of phenol in the mist. However, the reasons for the synergistic effect of organic degradation by the combined use of atomized mist and UV have not been sufficiently clarified.

On the other hand, ultrasonic atomization has been reported to produce very fine droplets from bulk solutions, and to disperse particles in liquids into droplets (Suzuki et al., 2012, Nii et al., 2014). It has been reported that irradiating a sample suspension with 2.4 MHz ultrasound is able to separate particles of 90-320 nm, regardless of the type of material. Therefore, ultrasonic atomization has potential for use in particle classification as shown in Figure 1. Using ultrasonic atomization to capture particles in mist, the combined use of UV irradiation and ultrasonic atomization is to be expected to improve the efficiency of the organic material degradation process. In this study, droplets containing  $\text{TiO}_2$  were generated using an ultrasonic atomizer, and phenol degradation was carried out by UV light irradiation to the droplets. A higher concentration of photocatalytic particles in the atomized droplets is expected. For comparison, phenol degradation with  $\text{TiO}_2$  and UV light is also performed to estimate particle concentration in the mist. The purpose of this study is to investigate the effect of particle concentration and particle size on the degradation rate of phenol.

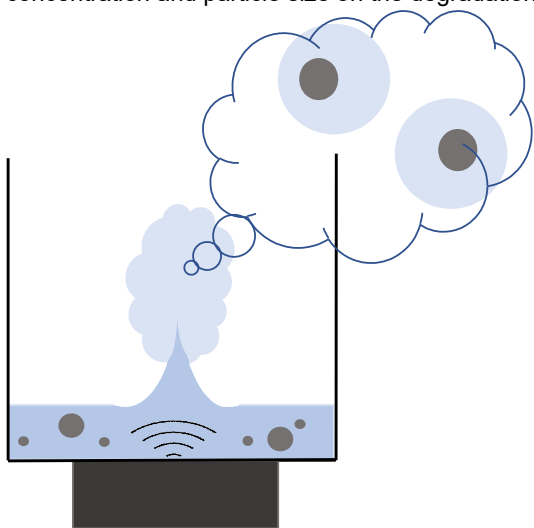


Figure 1: Concept of particle classification by ultrasonic atomization

## 2. Experimental

### 2.1 Materials

Phenol (99.0 %, Kanto Chemical Co., Inc.) was used as a model material for hazardous organic compounds, and  $\text{TiO}_2$  of Anatase form (98.5 %, Kanto Chemical Co., Inc.) was selected as the photocatalysis. Acetonitrile (99.9 %, Kanto Chemical Co., Inc.) was used for HPLC analysis.

### 2.2 Apparatus

The experimental apparatus with a combination of ultrasonic atomization and UV is shown in Figure 2. Phenol aqueous solution of  $50 \times 10^{-3} \text{ dm}^3$  with the concentration of  $1 \text{ mmol dm}^{-3}$  was added to a reactor. Outer dimensions of the acrylic reactor were 70 mm in length, 70 mm in width, and 200 mm in height. An ultrasonic transducer with a frequency of 1.6 MHz was attached to the bottom of the reactor.  $\text{TiO}_2$  particles were suspended in the solution. The UV lamp (16 W, LUV-16, AS ONE Corporation) has a main wavelength of 365 nm. The atomized mist was irradiated with UV light from the side of the reactor. The distance between the reactor wall and the UV light was approximately 100 mm. Light irradiation was performed at this position because UV irradiation makes the wall of the reactor hot.

The experimental setup for UV alone is shown in Figure 3. Phenol aqueous solution of  $50 \times 10^{-3} \text{ dm}^3$  with the concentration of  $1 \text{ mmol dm}^{-3}$  was added to a glass reactor. A stirrer was placed in the reactor and stirred at 350 rpm with a magnetic stirrer. UV light was irradiated from the top of the reactor. The distance between the sample liquid surface and the UV light was approximately 50 mm.

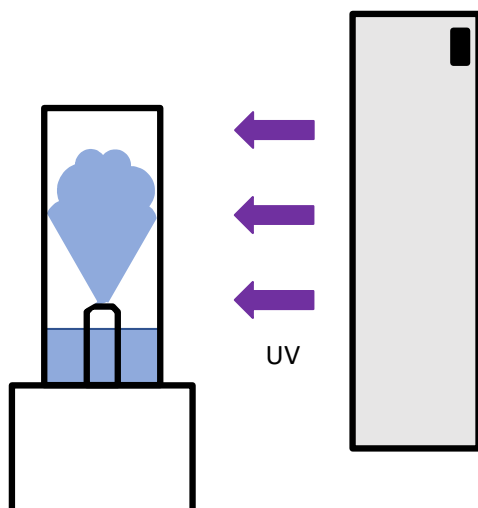


Figure 2: Experimental apparatus with a combination of ultrasonic atomization and UV

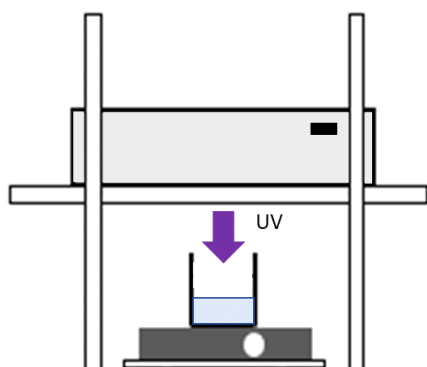


Figure 3: Experimental apparatus for UV alone

### 2.3 Experimental conditions

Initial concentration of phenol ( $C_0$ ) was fixed at  $1 \text{ mmol dm}^{-3}$ . Reaction time ( $t$ ), concentration of  $\text{TiO}_2$  particles ( $C_P$ ), and diameter of  $\text{TiO}_2$  particles were changed. Table 1 shows the operating conditions.

Table 1: Operational conditions

frequency $f$ [kHz]	Initial concentration of phenol $C_0$ [mmol $\text{dm}^{-3}$ ]	Reaction time $t$ [min]	Concentration of $\text{TiO}_2$ $C_P$ [g $\text{dm}^{-3}$ ]	Diameter of $\text{TiO}_2$ [nm]
1.6	1.0	0 – 90	0 – 0.5	10 – 30 100 – 300

### 2.4 Analysis

Concentration of phenol ( $C$ ) was determined using high performance liquid chromatography (HPLC) system. After the reaction, particles were removed by centrifugation and analyzed by HPLC. Luna Omega Polar C18 was used as the column. The column temperature was set at  $30^\circ\text{C}$ , the mobile phase was acetonitrile and pure water (3:7), and the flow rate was  $0.8 \text{ mL/min}$ . In previous studies, phenol degradation by ultrasound or photocatalysis is often considered a pseudo-first-order reaction. In this study, we thought a simple model would be preferable to investigate the effect of operating conditions on the degradation rate. Therefore, phenol degradation was assumed to proceed in a pseudo-first-order reaction, and degradation rate constants ( $k_{\text{app}}$ ) were estimated using Eq(1) and the temporal change of phenol concentration.

$$C = C_0 \exp(-k_{\text{app}}t) \quad (1)$$

### 3. Results and Discussion

#### 3.1 Effects of TiO<sub>2</sub> concentration on degradation of phenol

The degradation rate was measured by ultrasonic irradiation without the addition of titanium dioxide particles in order to investigate the effect of degradation by ultrasound alone. As a result, the degradation rate constant was calculated to be 0.0003 min<sup>-1</sup>. It has been revealed that oxidative degradation by hydroxyl radicals is the dominant mechanism of degradation of phenol by ultrasound (Shimakage et al., 2016). It is expected that the contribution of phenol degradation by ultrasound is negligible because the sonochemical efficiency (Koda et al., 2003) is low at the frequency used in the present study.

Figure 4 shows the effects of TiO<sub>2</sub> concentration on the degradation rate constant in the experimental using a combination of ultrasonic atomization and UV light irradiation. When particle size is small, the degradation rate constant increases even at higher particle concentrations. However, as the particle concentration increases above 0.1 g/L, the rate constant approaches a constant value. On the other hand, when the particle size was large, the maximum degradation rate constant occurred at a particle concentration of 0.05 g dm<sup>-3</sup>. In addition, the degradation rate decreased with increasing particle concentration. When the particle size was large, the accumulation of particles on the transducer at the bottom of the reactor was observed. It is suggested that the degradation rate constant decreased due to the accumulation of particles on the transducer, which reduced the amount of atomized mist.

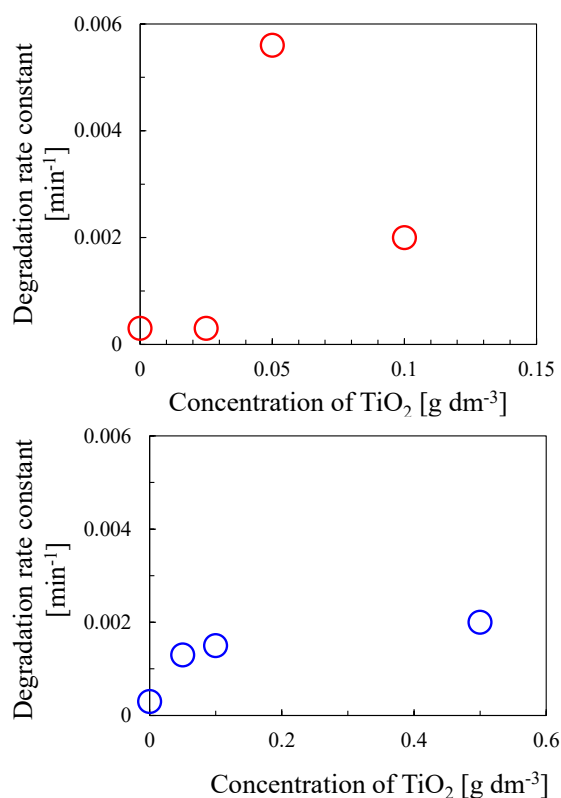


Figure 4: Effects of TiO<sub>2</sub> concentration on the degradation rate constant in the experimental using a combination of ultrasonic atomization and UV light irradiation (a) 100 – 300 nm, (b) 10 – 30 nm

#### 3.2 Effects of TiO<sub>2</sub> concentration on degradation of phenol

Figure 5 shows the effects of particle size on degradation rate constant in the experimental using a combination of ultrasonic atomization and UV light irradiation. TiO<sub>2</sub> particle concentration was 0.05 g dm<sup>-3</sup>. The degradation rate constant was about four times higher for the large particle size compared to the small particle size. In the present system, it is considered that particles between 100 and 300 nm were more easily incorporated into the atomized mist. Since the ultrasonic operating conditions, such as ultrasonic frequency, were not changed in this study, there is no way to know what factors affect particle incorporation into the atomized droplets. However, it

is necessary to investigate the relationship between the size of particles that are easily incorporated into droplets formed by ultrasonic atomization and the operating conditions.

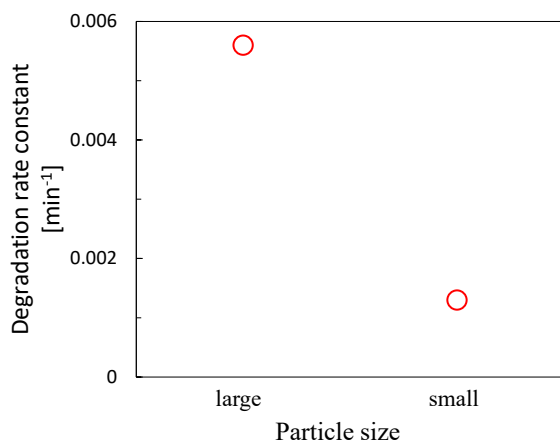


Figure 5: Effects of particle size on the degradation rate constant in the experimental using a combination of ultrasonic atomization and UV light irradiation

### 3.3 Effects of TiO<sub>2</sub> concentration on degradation of phenol

Figure 6 shows the effects of TiO<sub>2</sub> concentration on the degradation rate constant in the experimental using UV light alone system. TiO<sub>2</sub> particle size was 100 – 300 nm. At a particle concentration of 0.05 g dm<sup>-3</sup>, where the maximum degradation rate constant is obtained with the system using both ultrasound and UV light, the rate constant is 0.002 min<sup>-1</sup> with UV alone. However, the degradation rate constant in the combined system is about 0.005 min<sup>-1</sup>. It is revealed that the combined use of UV light and ultrasonic atomization has a synergistic effect and improves degradation, because ultrasound alone does not degrade most of the materials. The particle concentration in the mist formed by ultrasonic atomization is estimated around 0.12 g dm<sup>-3</sup> from the results of degradation rate constants. It was also suggested that TiO<sub>2</sub> were incorporated into the atomized droplets, and the concentration of particles in the droplets increased.

The combined use of ultrasonic atomization and UV light irradiation make the reaction more efficient, suggesting the possibility of process intensification. Ultrasonic atomization can also be applied to continuous operation by circulating bulk gas to capture the mist. Therefore, it can be applied to large-scale processing by continuous operation and is expected to achieve industrial application.

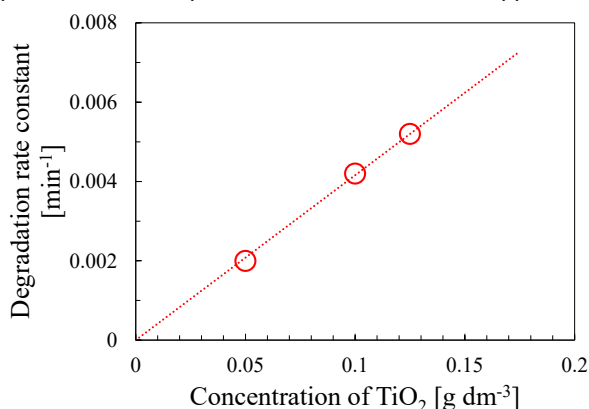


Figure 6: Effects of TiO<sub>2</sub> concentration on the degradation rate constant in the experimental using UV light alone system

## 4. Conclusions

Degradation of phenol was performed in an apparatus that used a combination of ultrasonic atomization and UV light irradiation, and the effects of operating conditions on the degradation rate constant, were examined.

It is assumed that the equipment using a combination of ultrasonic atomization and UV irradiation increased the degradation rate because TiO<sub>2</sub> particle was concentrated and incorporated into the atomized mist droplets, resulting in a higher particle concentration.

### Nomenclature

$C$  – concentration of phenol, mmol dm<sup>-3</sup>  
 $C_0$  – initial concentration of phenol, mmol dm<sup>-3</sup>  
 $C_P$  – concentration of TiO<sub>2</sub>, g dm<sup>-3</sup>  
 $f$  – ultrasonic frequency, kHz  
 $k_{app}$  – degradation rate constant, min<sup>-1</sup>  
 $t$  – reaction time, min

### Acknowledgments

This work was supported by JSPS KAKENHI Grant Number JP20K05212.

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