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Kinetics Analysis for Development of a Rate Constant Estimation Model for Ultrasonic Degradation Reaction in the Presence of Particles

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Degradation of hazardous organic compounds using ultrasound is an attractive advanced oxidation technology for wastewater treatment, and it is well known that the ultrasonic degradation reaction is enhanced by particle addition. In this study, the effects of ultrasonic irradiation conditions and particle addition on the degradation rate constant were investigated using pseudo-first-order chemical reaction model. Moreover, the application of this model to degradation of other organic compounds in the presence of particles by other research groups has been investigated. The degradation reaction was enhanced by particle addition, and the apparent degradation rate constant is proportional to the increase in amount of particle. In addition, the constant of proportionality is not influenced by degraded material and ultrasonic frequency. However, particle type influences the constant of proportionality.

1. Introduction

Recently, ultrasound is used in various applications such as medical imaging, non-destructive testing of materials, welding of thermoplastics, and chemical reactions. Frequency between 20 kHz and 2 MHz is mainly used in chemical reaction process such as synthesis of polymer particles and nano materials. Ultrasound is also considered to be an attractive advanced oxidation technology for the degradation of hazardous organic compounds in water (Adewuyi, 2001). The efficiency and rate of reaction in an ultrasonic field are influenced by frequency. In general, the maximum sonochemical effect caused by a cavitation has been observed around 300 kHz, and sonochemical efficiency value (SE_{KI}) has been proposed (Koda *et al*., 2005). SE_{KI} is often useful for evaluating the effect of frequency on sonochemical reaction rate quantitatively. On the other hand, degradation of phenol and some of its derivatives such as chlorophenol and nitrophenol using ultrasound has been investigated by many researchers (Kidak *et al.*, 2006, Kobayashi *et al.*, 2011). The ultrasonic degradation of dyes has also been investigated (Okitsu *et al*., 2005, Merouani *et al*., 2010). In these studies, the effects of ultrasonic frequency, power, dissolved gas and solution pH on degradation have been investigated. In addition, the ultrasonic degradation reaction is enhanced by particle addition. Especially, the combination of photocatalysis and ultrasound is considered to enhance the degradation rate. The degradation of phenol by ultrasonic irradiation in the presence of TiO_2 particles has been investigated in complete darkness (Kubo *et al.*, 2005). Sekiguchi and Saita (2001) have been investigated the effect of Al_2O_3 particles on the degradation of chlorobenzene in an ultrasonic field.
In our previous study, the ultrasonic degradation of methylene blue at frequencies of 22.8, 127, 490, 940, and 1640 kHz has been performed at various ultrasonic power levels, and the rate of ultrasonic degradation of methylene blue is of the pseudo first order with respect to ultrasonic frequency, and degradation readily progresses at frequencies of 127, 490, and 940 kHz. In addition, the maximum degradation rate has been observed at 490 kHz, and that sonochemical efficiency and the apparent degradation rate constant per unit power have a linear relationship (Kobayashi *et al.*, 2012).

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The kinetics of ultrasonic degradation has been investigated, and the model for estimating the apparent degradation rate constant of methylene blue as model hazardous organic compounds using ultrasonic power, sonochemical efficiency value, initial concentration of degraded compound, and sample solution volume is proposed (Kobayashi *et al*., 2014). Moreover, the effects of particle addition on ultrasonic degradation of methylene blue were investigated (Kobayashi *et al.*, 2013). The ultrasonic degradation in the absence and presence of TiO_2 or Al_2O_3 particles for various frequencies was carried out. The enhancement of degradation rate by particle addition was influenced by both ultrasonic frequency and type or diameter of particles. However, the effects of degraded materials on enhancement of reaction rate were not investigated quantitatively.
In this study, the ultrasonic degradation of methylene blue was carried out, and the effects of ultrasonic irradiation condition on the degradation rate constant were investigated. The effects of degraded materials and particle type on enhancement of degradation were also investigated by comparing previous study.

2. Experimental methods

Figure 1 shows the experimental apparatus. A stainless steel vibration plate attached with PZT transducer (Honda Electronics Co., Ltd.) was installed in the center of the water bath at the bottom. The ultrasonic frequency was operated at 490 kHz. The diameters of the vibration plate, and the 490 kHz transducer were 100 mm, 50 mm, and 50 mm, respectively. The transducers were driven by a power amplifier (1040L, E&I), which in turn was driven by a continuous sinusoidal wave produced using a signal generator (WF1974, NF Corp.). The effective electric power input to the transducer was calculated from the voltage at both ends of the transducer, the current measured using an oscilloscope (TDS3012C, Tektronix Inc.), and a current probe (TCP202, Tektronix Inc.). The diameter and the approximate volume of the glass reactor were 85 mm and 1 L, respectively. The temperature of the water bath was kept constant by a thermostat.

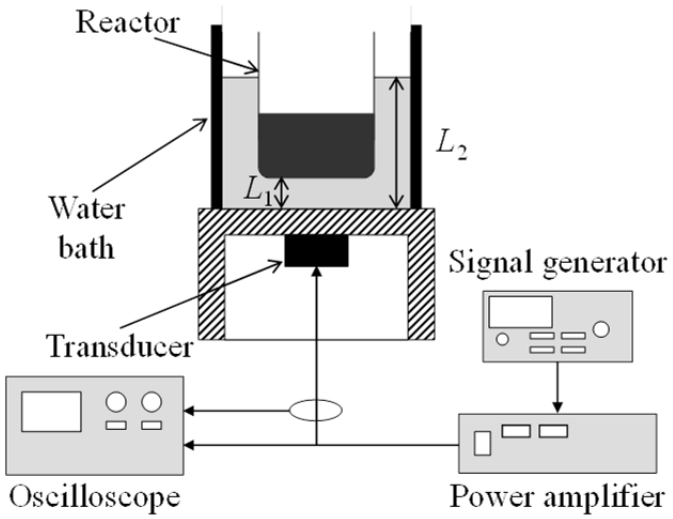

Figure 1: Experimental apparatus

Table 1 shows the experimental conditions for methylene blue degradation. Process variables were defined as follows: irradiation time and amount of particles (TiO_2 or Al_2O_3) addition (w). The ultrasonic frequency (f), ultrasonic output power calculated by calorimetry (P) (Contamine *et al.*, 1999), distance between the ultrasonic transducer and the bottom of the reactor (L_1), distance between the ultrasonic transducer and the level of the water bath (L_2), volume of the sample solution (V), temperature of the water bath (T), and initial concentration of methylene blue (C_0) were kept constant. The diameters of additive particles of TiO_2 and Al_2O_3 using this study were 300 nm and 50 μm, respectively.

Table 1: Experimental conditions of ultrasonic degradation of methylene blue

f [kHz]	P [W]	L_1 [mm]	L_2 [mm]	T [K]	C_0 [mM]	t [min]	V [mL]	w [g]
490	8	10	60	298	0.0105	0 - 30	100	0 - 2

Before ultrasonic irradiation, the sample solution and the remaining space in the reactor were deoxygenated with a nitrogen gas flow for 20 min.
After deoxygenation, the sample was irradiated with ultrasound under a continuous flow of nitrogen gas (0.1 L min^{-1}). After ultrasonic irradiation, the suspension was centrifuged to remove particles, and the concentration of methylene blue (*C*) was determined by measuring the absorbance of the sample at a wavelength of 665 nm using UV-vis spectrometer (Agilent 8453, Agilent Technologies). The determined absorbance was converted to a concentration through the standard curve of methylene blue.

3. Results and discussion

3.1 Degradation of methylene blue

Figure 2 shows the effects of amount of TiO_2 particle addition on the time dependence of methylene blue concentration at a frequency of 490 kHz and an ultrasonic power of 8 W.
The ultrasonic degradation rate of methylene blue is increased by TiO_2 particle addition. Therefore, the ultrasonic degradation is enhanced by TiO_2 particle addition. It is also found that the degradation of methylene blue in the presence of particles was also a pseudo-first-order reaction

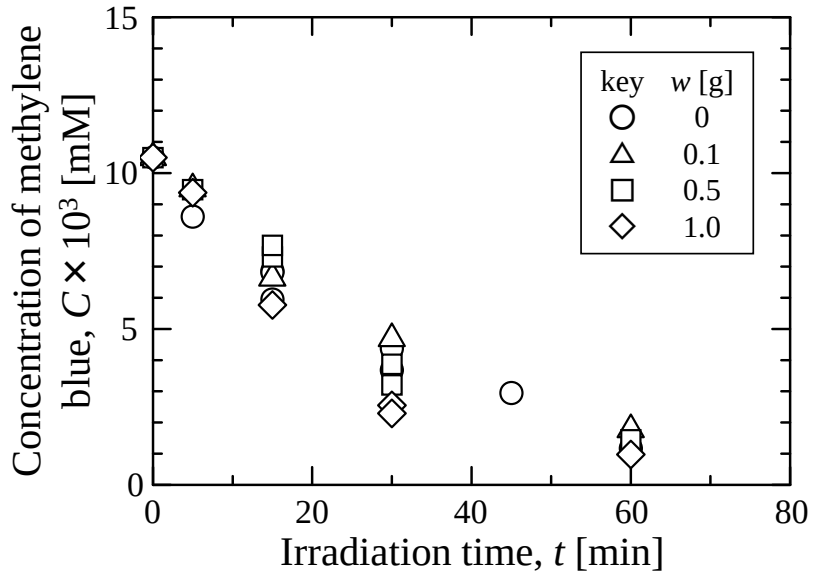

Figure 2: Effects of amount of TiO_2 particle addition on the time dependence of methylene blue concentration (f = 490 kHz, P = 8 W)

Figure 3 shows the effects of concentration of particles on the enhancement factor of degradation of methylene blue at a frequency of 490 kHz and an ultrasonic power of 8 W. Here, k_{app} and $k_{app,\,0}$ represents the apparent degradation rate constant in the presence of particles and the apparent degradation rate constant in the absence of particles, respectively. The enhancement factor of degradation increases with increasing amount of particle addition both TiO_2 and Al_2O_3.
The apparent degradation rate constant is proportional to the increase in amount of TiO_2 particle until amounts of particle is approximately 1.3 g, and concentration of TiO_2 particle is approximately 13 g/L. The optimal concentration of TiO_2 was 0.25 g/L in the photocatalytic irradiation system, because the UV light was hindered by the excess TiO_2 particles (Lee et al., 1999). However, such a phenomenon is not observed in this ultrasonic irradiation system. Thus, TiO_2 particles are used effectively in the sonocatalytic irradiation system.
On the other hand, ultrasonic degradation of methylene blue was also improved in the presence of Al_2O_3 particles, and the apparent rate constant is also proportional to the increase in amount of Al_2O_3 particle. Moreover, the enhancement of degradation rate constant by TiO_2 particle addition is more effective than that by Al_2O_3 particle addition. It is guessed that the presence of the reactive particles of TiO_2 enhances OH radical generation.

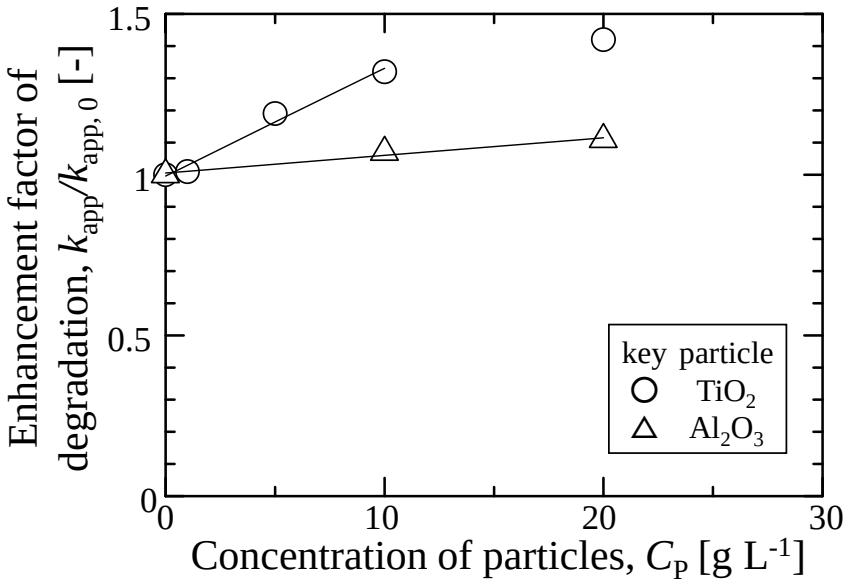

Figure 3: Effects of concentration of particles on the enhancement factor of degradation of methylene blue (f = 490 kHz, P = 8 W)

3.2 Degradation of phenol and chlorobenzene

Kubo *et al*. (2005) have been investigated the degradation of phenol in the presence of TiO_2 particles. The degradation reaction rate of phenol was enhanced by TiO_2 particle addition and degradation was a pseudo-first-order reaction. Figure 4 shows the effect of amount of TiO_2 particle addition on the apparent degradation rate constant of phenol. Here, ultrasonic frequency, ultrasonic power, initial concentration of phenol, volume of sample solution, and TiO_2 particle diameter were 20 kHz, 50 W, 1 mM, 25 mL, and 95 nm, respectively. The apparent degradation rate constant is proportional to the increase in amount of TiO_2 particle until amounts of particle is approximately 7 g, and concentration of TiO_2 particle is approximately 280 g/L.
Sekiguchi and Saita (2001) have been investigated the degradation of chlorobenzene in the presence of Al_2O_3 particles. The degradation reaction rate of chlorobenzene was also enhanced by Al_2O_3 particle addition and degradation was a pseudo-first-order reaction.

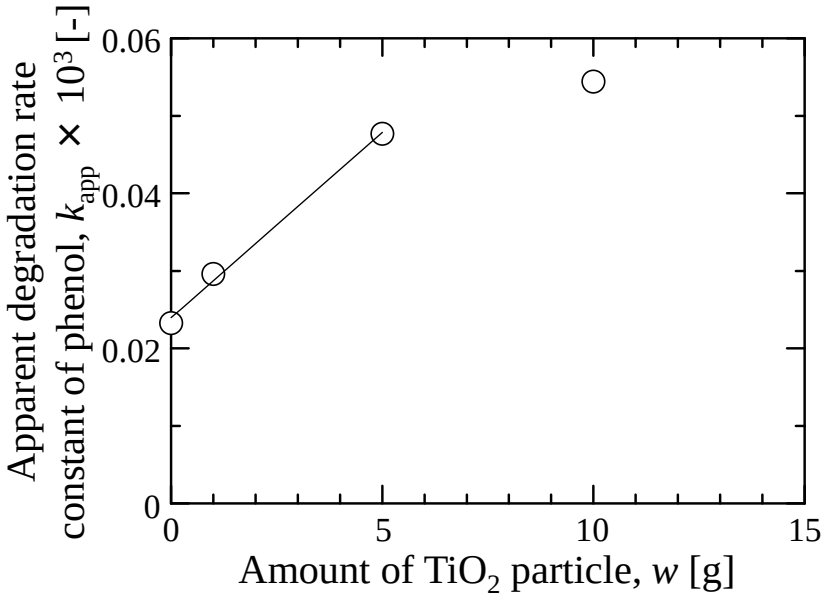

Figure 4: Effect of amount of TiO_2 particle addition on the apparent degradation rate constant of phenol (f = 20 kHz, P = 50 W)

Figure 5 shows the effect of amount of Al_2O_3 particle addition on the apparent degradation rate constant of chlorobenzene. Here, ultrasonic frequency, ultrasonic power, initial concentration of chlorobenzene, volume of sample solution, and Al_2O_3 particle diameter were 20 kHz, 300 W, 4.3 mM, 35 mL, and 2 mm, respectively. The apparent degradation rate constant is proportional to the increase in amount of Al_2O_3 particle, and optimal concentration of Al_2O_3 is higher than 450 g/L.
From the comparison of previous work and our results, the optimal concentration of particles of low frequency such as 20 kHz is higher than that of high frequency. It is guessed that ultrasonic physical effects such as mixing is effective at low frequency, and the particles are used effectively.

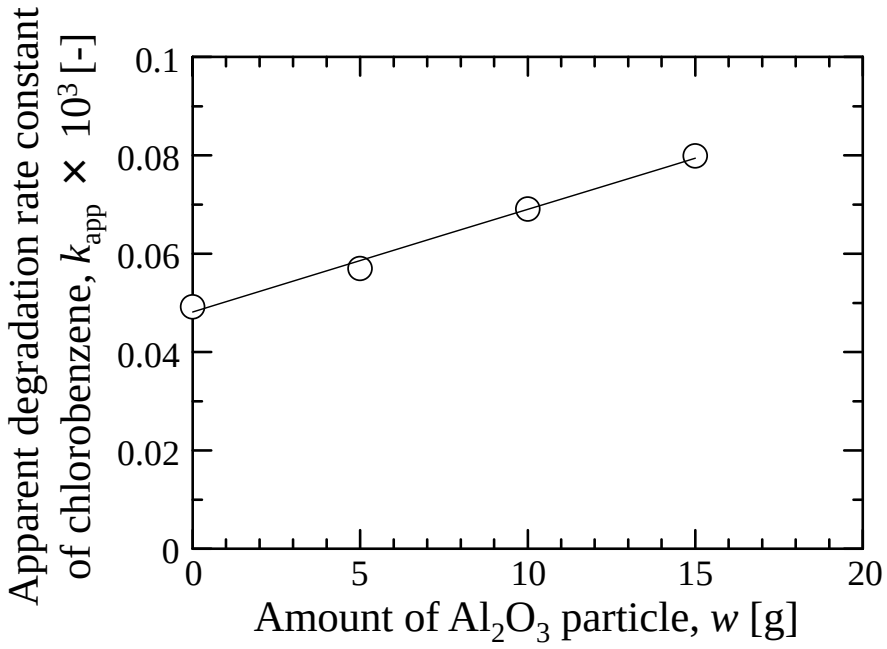

Figure 5: Effect of amount of Al_2O_3 particle addition on the apparent degradation rate constant of chlorobenzene (f = 20 kHz, P = 300 W)

3.3 Effects of particle addition on Enhancement factor of degradation reaction

The degradation reactions of methylene blue in this study, phenol, and chlorobenzene were enhanced by particle addition, and it is observed that there is a linear relationship between the apparent degradation rate constant and amount of particle. Therefore, we simply expressed the apparent degradation rate constants in the presence of particles as the following empirical relation Equation (1).

$$k_{\mathrm{app}} = k_{\mathrm{app},0} + aw \tag{1}$$

Here, *a* represents the constant of proportionality. In order to ignore the influence of degraded substance and ultrasonic frequency on degradation rate constant, Equation (2) is obtained by transforming Equation (1).

$$\frac{k_{\mathrm{app}}}{k_{\mathrm{app},0}} = 1 + bw \tag{2}$$

Here, *b* represents the constant of proportionality.
Table 2 shows the effects of degradation conditions on degradation rate constants without particle addition, and constant of proportionality (*b*). It is found that the constant of proportionality is not influenced by degraded material and ultrasonic frequency.
However, particle type influences the constant of proportionality, and the value of TiO_2 particle is about 6 times as large as that of Al_2O_3 particle. On the other hand, the particle amount used for enhancement of reaction is considered to be influenced by ultrasonic frequency and ultrasonic power.

Table 2: Experimental conditions of ultrasonic degradation of methylene blue

degraded material	particle	*f* [kHz]	*P* [W]	*V* [mL]	*w* [g]	$k_{app,\,0}$ [s^{-1}]	*b* [g^{-1}]
methylene blue	TiO_2	490	8	100	0 - 2	0.00045	0.33
methylene blue	Al_2O_3	490	8	100	0 - 2	0.00045	0.058
chlorobenzene	Al_2O_3	20	300	35	0 - 15	0.048	0.044
phenol	TiO_2	20	50	25	0 - 10	0.000024	0.20

4. Conclusions

The ultrasonic degradation of methylene blue at a frequency of 490 kHz was carried out in the absence and presence of TiO_2 or Al_2O_3 particles. The degradation reaction rate increased with amount of particles addition, and ultrasonic degradation reaction was enhanced by particle addition. In addition, the apparent degradation rate constant is proportional to the increase in amount of particle. The simple model for the relationships between enhancement factor of ultrasonic degradation and amount of particles addition was proposed, and this model applied to our results and the results of previous study by other researchers. The constant of proportionality is not influenced by degraded material and ultrasonic frequency. However, particle type influences the constant of proportionality.

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