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Effect of Particle Addition on Ultrasonic Degradation Reaction Rate

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Abstract

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 particle, and the effects of amounts of particle on the enhancement of degradation rate constant estimated by assuming first-order-kinetics were 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, and the value of TiO_2 particle is about 6 times as large as that of Al_2O_3 particle.

Keywords

Degradation, Methylene Blue, Frequency, Particle Addition

1. Introduction

Ultrasound has been found to be an attractive advanced oxidation technology for the degradation of hazardous organic compounds in water [1]-[6]. Especially, degradation of phenol and some of its derivatives such as chlorophenol and nitrophenol using ultrasound has been investigated by many researchers [7]-[11]. The ultrasonic degradation of dyes has also been investigated [12]-[18]. In these studies, the effects of ultrasonic frequency, power, dissolved gas and solution pH on degradation have been investigated. In addition, the sonochemical

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reaction is enhanced by particle addition. Especially, the combination of photocatalysis and ultrasound is considered to enhance the degradation rate [4] [5]. The degradation of phenol by ultrasonic irradiation in the presence of TiO_2 particles has been investigated in complete darkness [19]. Sekiguchi and Saita have investigated the effect of Al_2O_3 particles on the degradation of chlorobenzene in an ultrasonic field [20].

In our previous study, the ultrasonic degradation of methylene blue in the absence and presence of TiO2 or Al_2O_3 particles for various frequencies was carried out [21]. 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 at 298 K by a thermostat. In addition, the temperature of sample solution in the reactor was between 298 K and 303 K.

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 (P), 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 methylene blue concentration (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.

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). After ultrasonic irradiation, the methylene blue concentration (C)

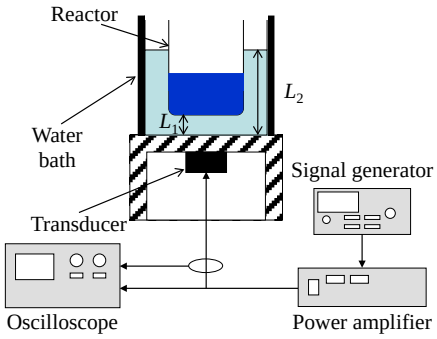

Figure 1. Experimental apparatus.

Table 1. Experimental conditions.

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

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. Before the analysis, the suspension was centrifuged to remove particles. The ultrasonic power in the reactor was measured by calorimetry [22].

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 methylene blue degradation is enhanced by TiO_2 particle addition, and the degradation rate increases with increasing TiO_2 particles amount. It is also found that the degradation of methylene blue in the presence of particles was also a pseudo-first-order reaction. **Figure 3** shows the effects of amount of TiO_2 or Al_2O_3 particles addition on the enhancement 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 and the apparent degradation rate constant in the absence of particles, respectively. 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. 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 [23]. 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.

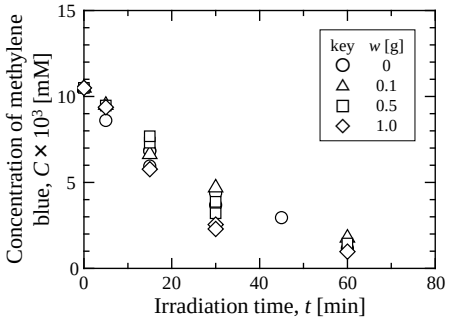

Figure 2. Effects of amount of TiO_2 particle addition on the time dependence of methylene blue concentration at a frequency of 490 kHz and an ultrasonic power of 8 W.

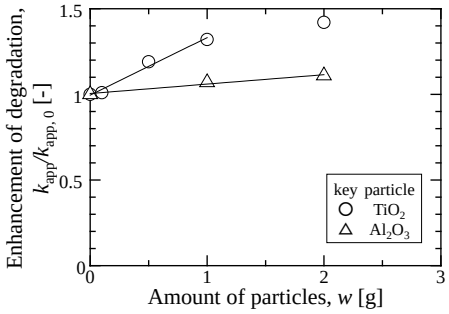

Figure 3. Effects of amount of TiO_2 or Al_2O_3 particles addition on the enhancement of degradation of methylene blue at a frequency of 490 kHz and an ultrasonic power of 8 W.

3.2. Degradation of Chlorobenzene and Phenol

Sekiguchi and Saita have been investigated the effects of Al_2O_3 particle addition on degradation of chlorobenzene [20]. The reaction rate of chlorobenzene was enhanced by Al_2O_3 particle addition and degradation was a pseudo-first-order reaction. **Figure 4** 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.

3.3. Effect of Particle Addition on Apparent Degradation Rate Constant

Kubo *et al*. have been investigated the effects of TiO_2 particles addition on degradation of phenol [19]. The reaction rate of phenol was enhanced by TiO_2 particle addition and degradation was a pseudo-first-order reaction. **Figure 5** 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.

3.4. Effect of Particle Addition on Enhancement of Degradation Reaction

The degradation reactions of methylene blue in this study, chlorobenzene, and phenol were enhanced by particle addition, and the apparent degradation rate constant is proportional to the increase in amount of particle. Therefore, we simply expressed the apparent degradation rate constants in the presence of particles as the following

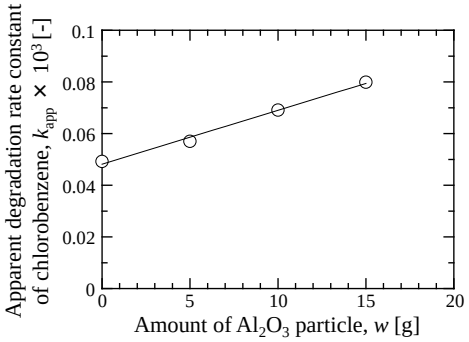

Figure 4. Effect of amount of Al_2O_3 particle addition on the apparent degradation rate constant of chlorobenzene at a frequency of 20 kHz and an ultrasonic power of 300 W.

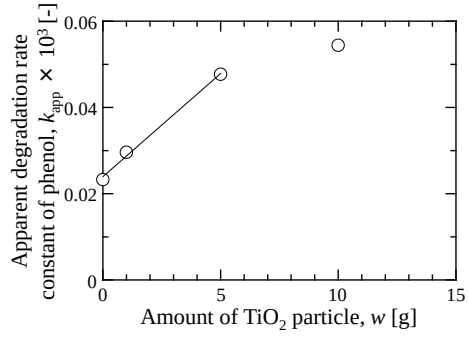

Figure 5. Effect of amount of TiO_2 particle addition on the apparent degradation rate constant of phenol at a frequency of 20 kHz and an ultrasonic power of 50 W.

Table 2. Effects of degradation conditions on degradation rate constants without particle addition and constant of proportionality (*b*).

Degraded material	Particle	*f* [kHz]	*P* [W]	*V* [mL]	*w* [g]	$k_{app,0}$ [s^{-1}]	*b* [g^{-1}]
Methylene blue (**Figure 3**)	TiO_2	490	8	100	0 - 2	0.00045	0.33
Methylene blue (**Figure 3**)	Al_2O_3	490	8	100	0 - 2	0.00045	0.058
Chlorobenzene (**Figure 4**)	Al_2O_3	20	300	35	0 - 15	0.048	0.044
Phenol (**Figure 5**)	TiO_2	20	50	25	0 - 10	0.000024	0.20

empirical relation Equation (1).

$$k_{app} = k_{app,0} + aw \quad (1)$$

Here, *a* represents 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).

$$\frac{k_{app}}{k_{app,0}} = 1 + bw \quad (2)$$

Here, *b* represents constant of proportionality. **Table 2** shows the effects of degradation conditions on deg- radation rate constants without particle addition and constant of proportionality (*b*). The constant of proportionality are calculated from lines in **Figures 3-5**. 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.

4. Conclusion

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 particle. 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.

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