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

Daisuke Kobayashia,\*, Hideyuki Matsumotob

aDepartment of Applied Chemistry, Tokyo Denki University, Adachi, Tokyo 120-8551, Japan

bTokyo Institute of Technology, Meguro, Tokyo 152-8552, Japan

 kobayashi@mail.dendai.ac.jp

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). Especially, degradation of phenol and some of its derivatives such as chlorophenol and nitrophenol using ultrasound has been investigated by many researchers. The ultrasonic degradation of dyes has also been investigated. 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 TiO2 particles has been investigated in complete darkness (Kubo *et al.*, 2005). Sekiguchi and Saita (2001) have been investigated the effect of Al2O3 particles on the degradation of chlorobenzene in an ultrasonic field.

In our previous study, 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 TiO2 or Al2O3 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.

* 1. 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 (TiO2 or Al2O3) 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 TiO2 and Al2O3 using this study were 300 nm and 50 μm, respectively.

*Table 1: Experimental conditions of ultrasonic degradation of methylene blue*

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *f* | *P* | *L*1 | *L*2 | *T* | *C*0 | *t* | *V* | *w* |
| [kHz] | [W] | [mm] | [mm] | [K] | [mM] | [min] | [mL] | [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.

* 1. Results and discussion
		1. Degradation of methylene blue

Figure 2 shows the effects of amount of TiO2 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 TiO2 particle addition. Therefore, the ultrasonic degradation is enhanced by TiO2 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 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 TiO2 and Al2O3.

The apparent degradation rate constant is proportional to the increase in amount of TiO2 particle until amounts of particle is approximately 1.3 g, and concentration of TiO2 particle is approximately 13 g/L. The optimal concentration of TiO2 was 0.25 g/L in the photocatalytic irradiation system, because the UV light was hindered by the excess TiO2 particles [23]. However, such a phenomenon is not observed in this ultrasonic irradiation system. Thus, TiO2 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 Al2O3 particles, and the apparent rate constant is also proportional to the increase in amount of Al2O3 particle. Moreover, the enhancement of degradation rate constant by TiO2 particle addition is more effective than that by Al2O3 particle addition. It is guessed that the presence of the reactive particles of TiO2 enhances OH radical generation.



*Figure 2: Effects of amount of TiO2 particle addition on the time dependence of methylene blue concentration (f = 490 kHz, P = 8 W)*



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

* + 1. Degradation of phenol and chlorobenzene

Kubo *et al*. (2005) have been investigated the degradation of phenol in the presence of TiO2 particles. The degradation reaction rate of phenol was enhanced by TiO2 particle addition and degradation was a pseudo-first-order reaction. Figure 4 shows the effect of amount of TiO2 particle addition on the apparent degradation rate constant of phenol. Here, ultrasonic frequency, ultrasonic power, initial concentration of phenol, volume of sample solution, and TiO2 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 TiO2 particle until amounts of particle is approximately 7 g, and concentration of TiO2 particle is approximately 280 g/L.

Sekiguchi and Saita (2001) have been investigated the degradation of chlorobenzene in the presence of Al2O3 particles. The degradation reaction rate of chlorobenzene was also enhanced by Al2O3 particle addition and degradation was a pseudo-first-order reaction. Figure 5 shows the effect of amount of Al2O3 particle addition on the apparent degradation rate constant of chlorobenzene. Here, ultrasonic frequency, ultrasonic power, initial concentration of chlorobenzene, volume of sample solution, and Al2O3 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 Al2O3 particle, and optimal concentration of Al2O3 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 4: Effect of amount of TiO2 particle addition on the apparent degradation rate constant of phenol (f = 20 kHz, P = 50 W)*



*Figure 5: Effect of amount of Al2O3 particle addition on the apparent degradation rate constant of chlorobenzene (f = 20 kHz, P = 300 W)*

* + 1. 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).

$k\_{app}=k\_{app, 0}+aw$ (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).

$\frac{k\_{app}}{k\_{app, 0}}=1+bw$ (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 TiO2 particle is about 6 times as large as that of Al2O3 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 1: Experimental conditions of ultrasonic degradation of methylene blue*

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| degraded material | particle | *f* | *P* | *V* | *w* | *k*app, 0 | *b* |
| [kHz] | [W] | [mL] | [g] | [s-1] | [g-1] |
| methylene blue | TiO2 | 490  | 8  | 100  | 0 - 2 | 0.00045  | 0.33  |
| methylene blue | Al2O3 | 490  | 8  | 100  | 0 - 2 | 0.00045  | 0.058  |
| chlorobenzene | Al2O3 | 20  | 300  | 35  | 0 - 15 | 0.048  | 0.044  |
| phenol | TiO2 | 20  | 50  | 25  | 0 - 10 | 0.000024  | 0.20  |

* 1. Conclusions

The ultrasonic degradation of methylene blue at a frequency of 490 kHz was carried out in the absence and presence of TiO2 or Al2O3 particles. 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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