P-3: Rate Constants Estimation Model of Ultrasonic Degradation Reaction of Methylene Blue

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In this study, the degradation process of methylene blue was investigated using ultrasound. This study focused on the effects of frequency and power on the degradation reaction rate constant. The apparent degradation rate constants were estimated based on time dependence of methylene blue concentration assuming pseudo-first-order kinetics. A simple model for estimating the apparent degradation rate constant using power and SE value is proposed in this study.

1. Introduction

Many organic compounds acting as environmental pollutants are released in water. Techniques such as solvent extraction, incineration, chemical dehalogenation, and biodegradation have been investigated for the degradation of hazardous organic compounds. We found ultrasound to be an attractive, advanced technology for the degradation of hazardous organic compounds in water (Hoffmann *et al*., 1996). However, the effects of ultrasonic frequency on degradation rate constants were not investigated quantitatively. In this study, the degradation process of a model for hazardous organic compound methylene blue was investigated using ultrasonic irradiation. The apparent degradation rate constant was estimated assuming that the degradation of methylene blue is a first-order reaction. In particular, this study focused on the effects of ultrasonic frequency and ultrasonic power on the apparent degradation rate constant.

2. Experimental

2.1. Degradation of methylene blue

Figure 1 shows the entire experimental apparatus. A stainless steel vibration plate attached with a PZT transducer (Honda Electronics Co., Ltd.) was installed in the center of the water bath at the bottom. The temperature of the water bath was maintained constant. Table 1 shows the experimental conditions for methylene blue degradation.

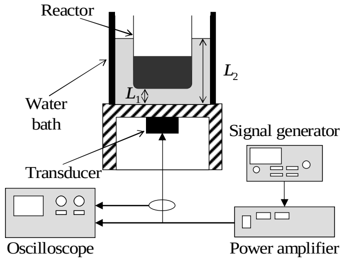

Figure 1: Experimental setup

Table 1

Operational conditions for methylene blue degradation

frequency	ultrasonic power	reactor's position		temperature	initial concentration of methylene blue	irradiation time	sample solution volume
f	P	L_1	L_2	T	C_0	t	V
[kHz]	[W]	[mm]	[mm]	[K]	[mM]	[min]	[L]
22.8	0 – 20	45	80	298	0.0105	0 – 120	0.1
127		10	60				
490		10	60				
940		10	60				
1640		10	60				

2.2. Analysis

After ultrasonic irradiation, the methylene blue concentration (C) was determined by measuring the absorbance of the sample at a wavelength of 665 nm using a UV-Vis spectrometer (Agilent 8453, Agilent Technologies). The ultrasonic power in the reactor was measured by calorimetry. The SE value, estimated in this study, was approximately equal to that reported by Koda et al. (2003). Thus, in order to improve the flexibility of the model proposed in this study, the reported SE value was used for kinetic analysis.

3. Results and discussions

3.1. Effects of operational conditions on degradation of methylene blue

Figure 2 shows the effects of ultrasonic power on the time dependence of methylene blue concentration at 490 kHz. Plots denote the experimental data. Lines are the calculated results discussed later. The degradation rate increased with increasing ultrasonic power due to an increase in the generation of OH radicals. The degradation rate was also influenced by frequency. Our observation regarding the influence of frequency on sonochemical degradation agrees with the previously reported results and suggests a relationship between the degradation rate and the SE value.

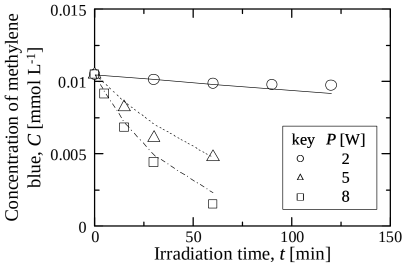

Figure 2: Effects of ultrasonic power on time dependence of methylene blue concentration at 490 kHz

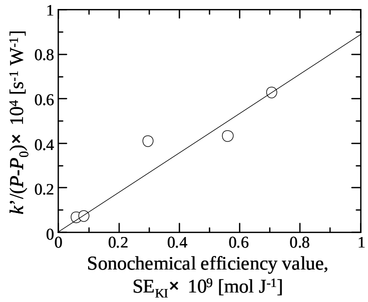

Figure 3: Relationship between SE_{KI} value and the apparent degradation rate constant per unit of ultrasonic power

Kinetic model for degradation of methylene blue

The sonochemical degradation of methylene blue is reported to be a pseudo-first-order chemical reaction, and we propose the formula for estimating the degradation rate constant as shown in Eq. (1) (Kobayashi *et al.*, 2012). Here, P_0 and α represents the threshold power and ratio of SE value of methylene blue degradation and KI oxidation.

$$k_{\mathrm{app}} = \alpha \times \frac{SE_{\mathrm{KI}} \times (P - P_0)}{C_0 \times V} \quad (1)$$

Figure 3 shows the relationship between the SE_{KI} value and the apparent rate constant per unit of ultrasonic power. It can be observed that the SE_{KI} value and the apparent rate constant per unit power have a linear relationship. Thus, the apparent degradation rate constant of methylene blue for 0.01 mM initial concentration and 0.1 L sample solution volume was able to estimate using Eq. (2).

$$k_{\mathrm{app}} = 8.98 \times 10^4 \times SE_{\mathrm{KI}} \times (P - P_0) \quad (2)$$

Conclusions

Methylene blue degradation using an ultrasound was performed, and we proposed a simple model for estimating the apparent degradation rate constant of methylene blue based on ultrasonic power and the SE_{KI} value.

References

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