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Comparison of Activation Energy of Ultrasonic Degradation of Methylene Blue between Oxidation Degradation and Pyrolysis

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Highlights

- The ultrasonic degradation was carried out in the absence and presence of DMSO.
- The apparent degradation rate constant was influenced by ultrasonic frequency.
- The activation energy of hydroxyl degradation was higher than that of pyrolysis.

1. Introduction

Ultrasound is known to be useful in initiating reactions, enhancing reaction rates and improving selectivity in many chemical reactions. Especially, ultrasound is considered to be one of the attractive advanced oxidation technologies for waste water treatment by degradation of hazardous organic compounds in water [1]. Ultrasonic degradation of phenol and some of its derivatives has been investigated by many researchers [2]. Ultrasonic degradation of organic dyes has also been investigated [3]. In these studies, the effects of operational conditions such as frequency on degradation rate have been investigated, and ultrasonic degradation reactions are considered to occur in three different regions, i.e., on the inside of collapsing bubbles, at the interfacial region surrounding collapsing cavitation bubbles, and in the bulk solution in which they are mediated by hydrogen peroxide (formed by recombination of hydroxyl radicals). In this study, the ultrasonic degradation of methylene blue as a model hazardous organic compound was carried out in the absence and presence of dimethyl sulfoxide (DMSO) as a radical scavenger for various frequencies and temperatures, and the effects of DMSO addition on the degradation rate constant estimated by assuming first-order kinetics were investigated. In addition, activation energy of ultrasonic degradation was estimated.

2. Methods

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) 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

Figure 1 shows the effect of frequency on apparent degradation rate constant of methylene blue (k_{app}) and degradation rate constant of methylene blue by pyrolysis ($k_{app,\ pyrolysis}$). Here, $k_{app,\ pyrolysis}$ was estimated using the pseudo-first-order reaction model for the experimental data of the temporal change of methylene blue concentration in the presence of DMSO. The ultrasonic power, concentration of DMSO, and temperature were 7 W, 705 mol/m^3, and 298 K, respectively. The apparent degradation rate was influenced by ultrasonic frequency, and this behavior agrees with previous study. On the other hand, the apparent degradation rate constant by pyrolysis ($k_{app,\ pyrolysis}$) was not found to be influenced by ultrasonic frequency. We also investigate the effect of temperature on apparent degradation rate constant in the presence and absence of DMSO in order to estimate the activation energy. Figure 2 shows the effects of degradation mechanism on Arrhenius plot at the frequencies of 490 kHz and 1640 kHz, and Table 1 shows the effects of frequency and

degradation mechanism on activation energy. The activation energy of hydroxyl degradation was higher than that of pyrolysis both 490 kHz and 1640 kHz.

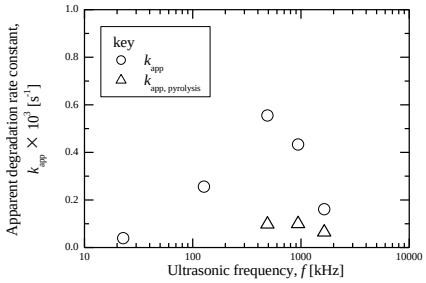

Figure 1. Effect of frequency on apparent degradation rate constant of methylene blue and degradation rate constant of methylene blue by pyrolysis.

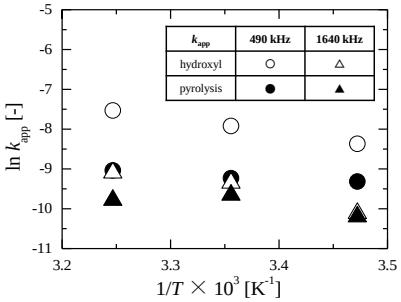

Figure 2. Effects of frequency and degradation mechanism on Arrhenius plot.

Table 1. Effects of frequency and degradation mechanism on activation energy.

	490 kHz		1640 kHz	
	hydroxyl	pyrolysis	hydroxyl	pyrolysis
E_A [kJ/mol]	30.9	10.4	37.6	15.9

4. Conclusions

The ultrasonic degradation of methylene blue was carried in the absence and presence of DMSO as a hydroxyl radical scavenger for various frequencies and temperatures. The degradation reaction mainly proceeds via oxidation reaction with hydroxyl radicals, but also proceeds via a direct pyrolysis reaction. Also, the apparent degradation rate constant increased with increasing temperature both in the absence and presence of DMSO. The effects of degradation mechanism of activation energy was investigated, and the activation energy of hydroxyl degradation was higher than that of pyrolysis.

References

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Keywords
Ultrasonic degradation, Degradation rate constant, Activation energy