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Effect of Radical Scavenger Addition on Ultrasonic Degradation of Methylene Blue

メチレンブルーの超音波分解にラジカル捕捉剤添加がおよぼす影響

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1. Introduction

Ultrasound has been used as am advanced oxidation method for degradation of hazardous organic materials[1, 2]. Sonochemical 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). Sonochemical degradation of organic compounds in an aqueous solution proceeds via their reaction with hydroxyl radicals.

In our previous study, 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 pseudo-first-order with respect to ultrasonic frequency, and degradation readily progresses at frequencies of 127, 490, and 940 kHz. In addition, it is found that the maximum degradation rate was observed at 490 kHz, and sonochemical efficiency value and the apparent degradation rate constant per unit power have a linear relationship[3, 4]. However, the degradation of methylene blue by ultrasonic physical effects has not been investigated.

In this study, the effect of radical scavenger addition on the ultrasonic degradation of methylene blue was investigated. At first, the effect of DMSO addition on the apparent degradation rate constant was investigated. The effect of frequency on degradation by ultrasonic physical effects was also investigated.

2. Experimental

Fig. 1 shows the experimental apparatus. A stainless steel 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 22.8 kHz, 127 kHz, 940 kHz and 1640 kHz. The transducers were driven by a power amplifier (1040L, E&J), 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.

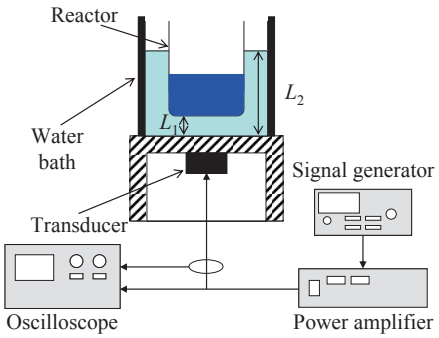

Fig. 1 Experimental apparatus

Table 1 shows experimental conditions for methylene blue degradation. Process variables are defined as follows: the ultrasonic frequency (f), ultrasound output power (P), initial methylene blue concentration (C_0), amount of DMSO addition (w), distance between the ultrasonic transducer and bottom of the reactor (L_1), distance between the ultrasonic transducer and level of the water bath (L_2), and irradiation time (t). The volume of the sample solution (V) and temperature of the water bath (T) were maintained constant. Before ultrasonic irradiation, the sample solution and remaining space in the reactor were deoxygenated

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with a nitrogen gas flow for 20 min at 298 K. After deoxygenation, the sample was irradiated with ultrasound under a continuous nitrogen gas flow (0.1 L/min).

Table 1 Experimental conditions

frequency	power	reactor's position		temperature	initial concentration	irradiation time	sample volume	amount of DMSO
f	P	L_1	L_2	T	C_0	t	V	w
[kHz]	[W]	[mm]	[mm]	[K]	[mol/m^3]	[min]	[m^3]	[mL]
22.8	0 - 20	45	80	298	0.01	0 - 60	0.1×10^{-3}	0 - 1
127		10	60					
490		10	60					
940		10	60					
1640		10	60					

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. The ultrasonic power in the reactor was measured by calorimetry[5]. The effects of frequency on sonochemical efficiency were also evaluated using SE_{KI} value[6].

3. Results and Discussions

Fig. 2 shows the effect of ultrasonic frequency on sonochemical efficiency value and apparent degradation rate constant of methylene blue per unit ultrasonic power without DMSO addition. For degradation of methylene blue, the apparent degradation rate constant at 490 kHz was approximately 15 times greater than that at 22.8 kHz under the same ultrasonic power. It has been reported that sonochemical efficiency in the frequency range of 200 – 500 kHz is 10 times greater than those in low and high frequency regions[6], and our results well agree with this phenomenon.

Fig. 3 shows the effect of amount of DMSO addition on apparent degradation rate constant of methylene blue at the frequency of 490 kHz, and at the ultrasonic power of 7 W. The apparent degradation rate constant decreases with increasing amount of DMSO. Therefore, degradation of methylene blue was mainly occurred by hydroxyl radicals.

On the other hand, it is found that the rate constant by ultrasonic physical degradation is not influenced by frequency.

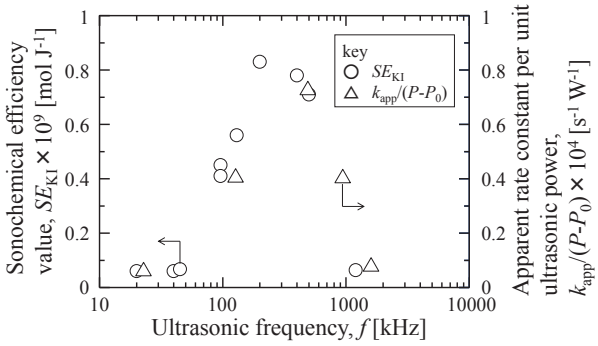

Fig. 2 Effect of ultrasonic frequency on sonochemical efficiency value and apparent degradation rate constant of methylene blue per unit ultrasonic power in the absence of DMSO

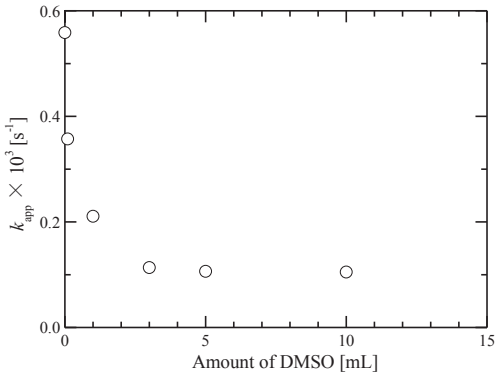

Fig. 3 Effect of DMSO addition on apparent degradation rate constant of methylene blue at f = 490 kHz and P = 7 W

4. Conclusions

The ultrasonic degradation of methylene blue was carried in the absence and presence of DMSO. The degradation rate constant decreases in the presence of DMSO. On the other hand, the degradation rate constant was not influenced by ultrasonic frequency in the presence of DMSO.

References

1. Y. G. Adewuri: Ind. Eng. Chem. Res. **40** (2001) 4681.
2. P. Chowdhury and T. Viraraghavan: Sci. Tot. Environ. **407** (2009) 2474.
3. D. Kobayashi, C. Honma, H. Matsumoto, T. Takahashi, C. Kuroda, K. Otake and A. Shono: Ultrason. Sonochem. **21** (2014) 1489.
4. D. Kobayashi, C. Honma, H. Matsumoto, T. Takahashi, Y. Shimada, C. Kuroda, K. Otake and A. Shono: Jpn. J. Appl. Phys. **53** (2014) 07KE03.
5. R. F. Contamine, A. M. Wilhelm, J. Berlan and H. Delmas: Ultrason. Sonochem. **2** (1995) S43.
6. S. Koda, T. Kimura, T. Kondo and H. Mitome: Ultrason. Sonochem. **10** (2003) 149.