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Kinetics analysis for development of a rate constant estimation model for ultrasonic degradation reaction of methylene blue

Daisuke Kobayashi [a,*], Chiemi Honma [b], Hideyuki Matsumoto [c], Tomoki Takahashi [a], Chiaki Kuroda [c], Katsuto Otake [a], Atsushi Shono [a]

[a] Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan
[b] Department of Chemical Science and Technology, Graduate School of Chemical Science and Technology, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan
[c] Department of Chemical Engineering, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152-8550, Japan

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ABSTRACT

Ultrasound has been used as an advanced oxidation method for wastewater treatment. Sonochemical degradation of organic compounds in aqueous solution occurs by pyrolysis and/or reaction with hydroxyl radicals. Moreover, kinetics of sonochemical degradation has been proposed. However, the effect of ultrasonic frequency on degradation rate has not been investigated. In our previous study, a simple model for estimating the apparent degradation rate of methylene blue was proposed. In this study, sonochemical degradation of methylene blue was performed at various frequencies. Apparent degradation rate constant was evaluated assuming that sonochemical degradation of methylene blue was a first-order reaction. Specifically, we focused on effects of ultrasonic frequency and power on rate constant, and the applicability of our proposed model was demonstrated. Using this approach, maximum sonochemical degradation rate was observed at 490 kHz, which agrees with a previous investigation into the effect of frequency on the sonochemical efficiency value evaluated by KI oxidation dosimetry. Degradation rate increased with ultrasonic power at every frequency. It was also observed that threshold power must be reached for the degradation reaction to progress. The initial methylene blue concentration and the apparent degradation rate constant have a relation of an inverse proportion. Our proposed model for estimating the apparent degradation rate constant using ultrasonic power and sonochemical efficiency value can apply to this study which extended the frequency and initial concentration range.

1. Introduction

Ultrasound is used in various applications such as medical imaging, non-destructive testing of materials, underwater ranging, welding of thermoplastics, and chemical reactions. The frequency range of ultrasound is roughly defined to be between 20 kHz and 10 MHz. Optimal frequency changes with respect to the applied field. The frequency ranges from 20 to 100 kHz, 20 kHz to 2 MHz, and 5 to 10 MHz are used for conventional power ultrasound, extended range for sonochemistry, and diagnostic ultrasound, respectively [1]. In chemical processes such as polymerization, degradation, and emulsification, a frequency between 20 kHz and 2 MHz is mainly used.

Recently, ultrasound has been used as an advanced oxidation method for wastewater treatment [2,3]. Ultrasonic irradiation of a liquid causes formation, growth, and collapse of microbubbles, a process referred to as cavitation. Rapid collapse of bubbles creates an unusual environment for a chemical reaction. These localized hot spots have temperatures of 5000 K, pressures of 500 atm, and lifetimes of a few microseconds [4]. Hydroxyl and hydrogen radicals are formed by pyrolysis of water vapor inside collapsing bubbles [5,6]. 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 case of volatile or hydrophobic compounds, degradation proceeds not only via reaction with hydroxyl radicals but also via a direct pyrolysis reaction. Degradation of phenol and some of its derivatives, including chlorophenol and nitrophenol, has been investigated by many researchers [7]. Ultrasonic degradation of dyes has been studied [8–11], and ultrasonic degradation of water-soluble-polymer has also been studied [12].

Sonochemical degradation kinetics of hazardous organic compounds has also been investigated, and some kinetics models have

* Corresponding author. Tel.: +81 3 5228 8310; fax: +81 3 5261 4631.
E-mail address: dkobayashi@ci.kagu.tus.ac.jp (D. Kobayashi).

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Nomenclature

C	concentration of methylene blue (mol/m^3)	k_0	degradation rate in the bulk solution (mol/m^3 s)
C_0	initial concentration of methylene blue (mol/m^3)	k_{app}	apparent degradation rate constant (s^{-1})
c_p	heat capacity of water (J/kg)	M	mass of water (kg)
f	ultrasonic frequency (kHz)	P	ultrasonic power (W)
L_1	distance between the ultrasonic transducer and bottom of reactor (mm)	P_0	threshold power (W)
		r	degradation rate (mol/m^3 s)
L_2	distance between the ultrasonic transducer and level of water bath (mm)	SE_{KI}	sonochemical efficiency value of KI oxidation (mol/J)
		T	temperature of water bath (K)
K	equilibrium constant of adsorption and desorption (m^3/mol)	t	ultrasonic irradiation time (s)
		V	sample solution volume (L)
k	pseudo rate constant (mol/m^3 s)	α	constant of proportionality (–)

been proposed. Okitsu et al. [8,13,14] have proposed a Langmuir type kinetic model based on a heterogeneous reaction system, and this model is applicable to the analysis of sonochemical degradation of azo dyes, butyric acid, and benzoic acid. In this model, the degradation rate (r) is represented as shown in Eq. (1):

$$r = \frac{kKC_0}{1 + KC_0} \tag{1}$$

Here, k is a pseudo rate constant, K is the equilibrium constant of adsorption and desorption, and C_0 is the initial concentration of the material being degraded. Priya and Madras [15] have also developed a Langmuir–Hinshelwood kinetic model, which is similar to the model of Okitsu et al., for sonochemical degradation of two Rhodamine dyes: Rhodamine B and Rhodamine blue.

Serpone et al. [16] have investigated sonochemical degradation of three monochlorophenols and proposed the degradation rate model described by Eq. (2):

$$r = k_0 + \frac{kKC_0}{1 + KC_0} \tag{2}$$

Here, k_0 is the degradation rate in the bulk solution. In this model, degradation rate is the sum of rates in the bulk solution and interfacial region surrounding collapsing cavitation bubbles.

In the above mentioned models, the effect of ultrasonic frequency on degradation rate has not been investigated. On the other hand, a simple pseudo-first-order reaction model is typically suggested [17–19]. Pétrier and Francony [20] have investigated degradation of phenol and carbon tetrachloride at different frequencies: 20, 200, 500, and 800 kHz. Degradation rate of phenol reaches a maximum value at 200 kHz. In general, the most suitable frequencies for degradation of hydrophobic organic compounds with a high vapor pressure lie between 20 and 100 kHz because these compounds can be easily degraded inside collapsing bubbles and/or at the interfacial region surrounding collapsing cavitation bubbles. Hydrophilic compounds, particularly at low concentration, can be degraded in the bulk solution by hydrogen peroxide at suitable frequencies, which lie between 200 and 800 kHz. Therefore, the effect of ultrasonic frequency on degradation of phenol correlates with the degree of hydrogen peroxide formation. Ultrasonic degradation of phenol at 20, 300, and 520 kHz has been investigated by Kidak and Ince [21], and maximum degradation efficiency occurs at 300 kHz. However, there have been few quantitative analyses of the effect of ultrasonic frequency on degradation rate.

On the other hand, effects of ultrasonic frequency on chemical reaction efficiency have been investigated for various reactions [22,23], and Koda et al. proposed a standard method for calibrating the sonochemical efficiency value (SE_{KI}) using KI oxidation dosimetry [24]. SE_{KI} is defined as the number of reacted molecules per unit of ultrasonic energy and is considered to quantitatively measure the influence of ultrasonic frequency on the sonochemical effect. In addition, recently, Tran et al. have investigated the effect of frequency on ultrasonic physical effect [25]. A simple quantification method of acoustically induced physical effect is proposed and the ultrasonic physical effect decreases with increasing ultrasonic frequency.

In our previous study, ultrasonic degradation of methylene blue as a model hazardous organic compound was performed at frequencies of 22.8, 127, and 490 kHz. Apparent degradation rate constants were evaluated using a pseudo-first-order reaction model, and we have proposed a simple model for estimating the apparent degradation rate constant of methylene blue on the basis of SE_{KI} [11]. In this study, degradation of methylene blue was performed at various frequencies, especially in the high frequency region around 1 MHz. Effects of ultrasonic irradiation conditions on degradation rate were investigated. In particular, this study focused on effects of ultrasonic frequency and power on apparent degradation rate constant, which was estimated assuming that degradation of methylene blue, using ultrasonic irradiation, is a first-order reaction. Moreover, the effects of initial concentration of methylene blue on degradation rate constant were also investigated at the frequency of 490 kHz. The purpose of this study is to determine whether the operable frequency region of our proposed model can be extended to increase its versatility.

2. Experimental

2.1. Degradation of methylene blue

Fig. 1 shows the complete experimental apparatus. A stainless steel vibration plate with an attached PZT transducer (Honda

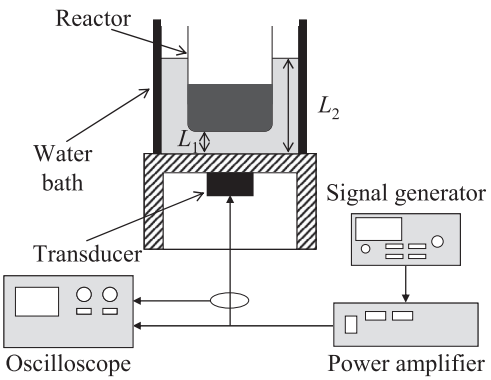

Fig. 1. Complete experimental apparatus.