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Degradation of methylene blue under multibubble sonoluminescence condition

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Abstract

Methylene blue (MB) is one of typical textile dyestuffs that cannot be degraded by a conventional method such as biological treatment. In this study, degradation of MB in aqueous solution under ultrasonic field at the multibubble sonoluminescence (MBSL) condition was tried for the first time. At the optimum condition of MBSL, 0.1 mM MB solution was degraded completely within 30 min, which is quite faster than the reaction rate for the photocatalytic degradation of MB in aqueous TiO_2 dispersions under UV-irradiation. The sonochemical degradation of MB at the MBSL condition was found to be first-order with respect to MB concentration. Also, it has been found that MB was degraded by the oxidation process by OH radicals.

Keywords: Hydroxyl radical; Multibubble sonoluminescence (MBSL); Methylene blue (MB); Sonochemical reaction; Ultrasound

1. Introduction

Methylene blue (MB) is a typical dyestuff that cannot be degraded by a conventional method such as biological treatment. Dye-containing wastewater should be treated properly to convert the highly toxic dye in the wastewater to harmless products for environment remediation. Recently, photocatalytic degradation of MB has been studied in a colloidal TiO_2 solution under UV-irradiation [1–3], even though this technology needs to develop an effective means of separating the photocatalyst nanoparticles from the treated solution [4]. One of the mechanisms of the photocatalytic degradation of MB is that the dye in solution is oxidized by OH radicals [3,5]. In fact, a passway of *N*-demethylation of MB [3] was found to be due to a series attack by OH radicals on MB in aqueous solution. Such observed results indicate that MB in water solution may be degraded under sonoluminescence condition, which provides OH radicals in the solution.

Sonoluminescence is a phenomenon of light emission associated with the catastrophic collapse of a microgas bubble under ultrasound [6]. The light emission from a well-controlled single bubble under ultrasound is characterized by picosecond flashes of continuous spectrum with no major peaks [7–9]. Hydrodynamic solutions for the oscillating gas bubble yield gas temperature of 10,000–30,000 K and pressure of 10,000 atm at the collapse [10–12], at which the bubble wall acceleration exceeds 10^{12} m/s^2 [11,13]. Consequently, the bubble collapse produces a liquid zone at high temperature of 1000 °C and pressure of 500 atm [10], where high-energy chemical reaction can be made [14]. Rather than a single bubble, a lot of transient bubbles can be generated by the irradiation of high-intensity ultrasound into aqueous solution. The collapse of these cavitated bubbles produces intense local heating and high pressure inside the bubbles where hydroxyl radicals OH can be generated [15,16] and diffused into water so that organic materials in the bubble–liquid interface or in water solution can be oxidized.

In this study, the degradation of MB under multibubble sonoluminescence (MBSL) condition was examined for the first time. Also, we investigated the oxidization mechanism

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of MB in water solution due to hydroxyl radicals produced at MBSL condition when a strong bubble collapse occurs. As expected, at the optimum condition of MBSL, 0.1 mM MB solution was oxidized completely in less than 30 min, which is quite faster than the complete reaction time by photocatalytic degradation of MB in aqueous TiO_2 dispersion under UV-irradiation [3], a well-known method of MB treatment.

2. Chemical kinetics

MBSL spectra of water exhibits a strong peak at 350 nm due to emission from the excited hydroxyl radicals [17]. The spectra peak becomes prominent when the bubble size becomes rather large [18] or the amplitude of ultrasound decreases [19]. It was suggested that the three-body recombination pathway [20] such as $O + H + M \rightarrow OH^{\bullet} + M$ is the origin of the molecular emission of $OH^{\bullet}$, where $OH^{\bullet}$ represents an excited state of OH under MBSL. The kinetic scheme [20] developed by this idea for $OH^{\bullet}$ molecular emission was adopted in this study, which are as follows.

$$H_2O + M \xrightarrow{k_1} OH + H + M \tag{1.1}$$

$$OH + M \xrightarrow{k_2} O + H + M \tag{1.2}$$

$$O + H + M \xrightarrow{k_3} OH^{\bullet} + M \tag{1.3}$$

$$OH^{\bullet} + M \xrightarrow{k_4} OH + M \tag{1.4}$$

The overall reaction can be represented by Eq. (1.1). For each species appearing in Eq. (1), the rate equations may be written as

$$\frac{d[H_2O]}{dt} = -k_1[H_2O][M] \tag{2.1}$$

$$\frac{d[OH]}{dt} = k_1[H_2O][M] - k_2[OH][M] + k_4[OH^{\bullet}][M] \tag{2.2}$$

$$\frac{d[O]}{dt} = k_2[OH][M] - k_3[O][H][M] \tag{2.3}$$

$$\frac{d[OH^{\bullet}]}{dt} = k_3[O][H][M] - k_4[OH^{\bullet}][M] \tag{2.4}$$

$$\frac{d[H]}{dt} = \frac{d[OH]}{dt} + \frac{d[OH^{\bullet}]}{dt} + 2\frac{d[O]}{dt} \tag{2.5}$$

$$\frac{d[M]}{dt} = -3\frac{\rho_0}{R}\frac{dR}{dt}\left(\frac{R_0}{R}\right)^3 \tag{2.6}$$

The reaction rates in Eq. (2) can be parameterized in the modified Arrhenius form such as

$$k_i = A_i\left(\frac{298}{T}\right)^{N_i}\exp\left(-\frac{E_i}{T}\right) \tag{3}$$

The constants A_i, N_i and $E_i(K)$ were taken from Bernstein et al. [20]. It is noted that they used constant bubble wall velocity of $dR/dt = 400$ m/s in their study. However, the chemical reaction rate depends crucially on the time rate change of gas temperature and pressure inside the bubble, one should use more rigorous approach to determine the bubble wall velocity near the collapse.

The kinetic scheme given in Eq. (1) may be right because any indication of presence of H or HO_2 radicals cannot be found in the electron spin resonance (ESR) experiment [21]. The OH radicals produced inside the bubbles diffuse into the solution and react with MB. However, there is a possibility of recombination of OH and H radicals at the cooled interface, where the concentration of MB is small. The reactions are given by

$$2OH \rightarrow H_2O_2 \tag{4}$$

$$2H \rightarrow H_2 \tag{5}$$

3. Experimental apparatus and procedures

An experimental apparatus for multibubble sonoluminescence consists of a cylindrical quartz cell into which a 5 mm diameter titanium horn (Misonix XL2020, USA) is inserted, as shown in Fig. 1. The system was operates at 20 kHz and power input of 165 W, which is about 30% of the maximum power of 500 W. An adapter was used to connect the titanium horn and the cylindrical cell whose diameter and height are 25 and 93 mm, respectively. Three-*O*-rings provide a seal between the horn and the cell and environment. The cell has two ports: one is for a temperature sensor and the other is for the input of argon gas. The solution in the test cell was kept at constant pressure with argon atmosphere. Continuous circulation of water to the bath in which the cell is immersed keeps the temperature of the solution inside the cell around 20 °C. The MBSL condition can be found by trial and error at a proper ultrasound intensity, liquid temperature and distance between the horn tip and the bottom of the cell. The emission of the blue light concentrated around the horn tip by the argon bubble cloud in water is shown in Fig. 2. The applied sinusoidal signal from the sonicator and the signal at the bottom of the test cell and the sonoluminescence pulse from the bubble clouds were measured simultaneously as can be seen in Fig. 3.

Aqueous MB solution was prepared by mixing MB (Sigma Chemical, 99%) with deionized and distilled water. The aqueous solutions were prepared containing MB in the range of 0.08–0.14 mM. The solution was stirred for 24–26 h for MB to dissolve into water. The solution in the test cell was saturated with argon gas of 1.5 atm during irradiation of ultrasound. The solution temperature was maintained at 20 °C by circulating the constant cold-water stream of 0.7 °C from to the water bath. After sonicating aqueous MB solution at the sonoluminescence condition, a 3 ml sample solution was taken for analysis at desired times. Variation in the concentration of MB was monitored by UV–vis spectroscopy (Hitachi, U-3300).

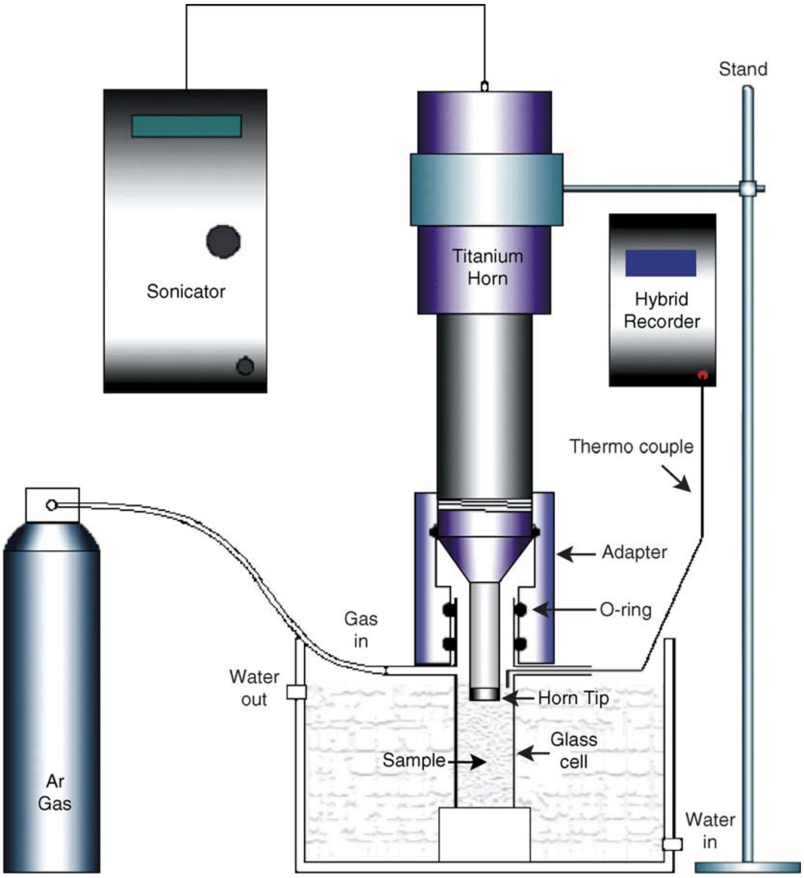

Fig. 1. Experimental set-up for MBSL experiment.

4. Results and discussion

4.1. Decomposition of MB at MBSL condition

Temporal change in the concentration of MB depending on the irradiation time of ultrasound at MBSL condition was monitored by examining the variation in the maximal absorption in UV–vis spectrum at 660 nm. Typical MB solution displays the maximal absorption at 664 and at 600 nm as shown in Fig. 4. No appreciable spectral shift of the peak during the decomposition process was observed for 0.10 mM MB solution as shown in Fig. 4, a result which is certainly differ-

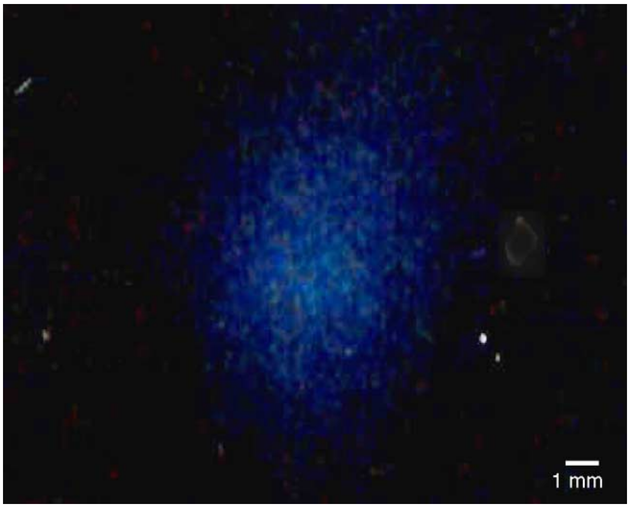

Fig. 2. Sonoluminescence from bubble clouds.

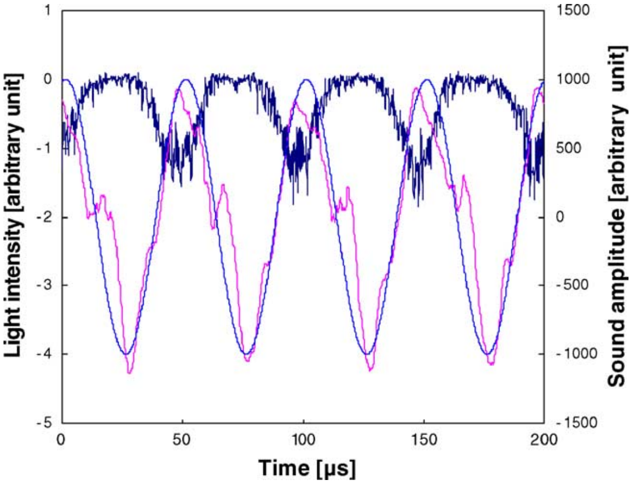

Fig. 3. Input signal to the transducer, received signal at the bottom of the cell (distorted signal) and the MBSL received by PMT (fluctuating signal).

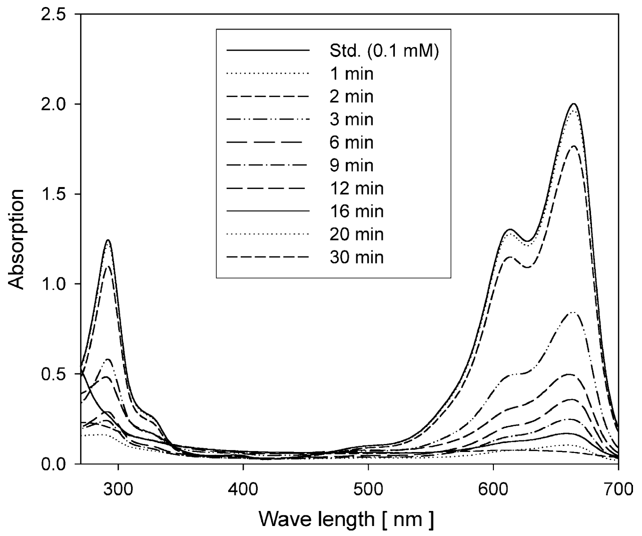

Fig. 4. Temporal spectral changes of MB under ultrasound at the MBSL condition. Initial concentration of MB is 0.10 mM.

ent from the case of decomposition of MB in aqueous TiO_2 dispersions under UV-irradiation [3].

Degradation of MB under ultrasound at the MBSL condition for various initial concentrations of MB is shown in Fig. 5. At lower concentrations, the degradation proceeded more rapidly. A concentration dependence of MB degradation was also observed in the photocatalytic oxidation of MB in heterogeneous catalysis system [22] and in dispersed TiO_2 system [3]. Even at a larger concentration of 0.14 mM, MB under ultrasound was degraded faster than the case in the presence of TiO_2 in 50 ml dispersion under UV-irradiation.

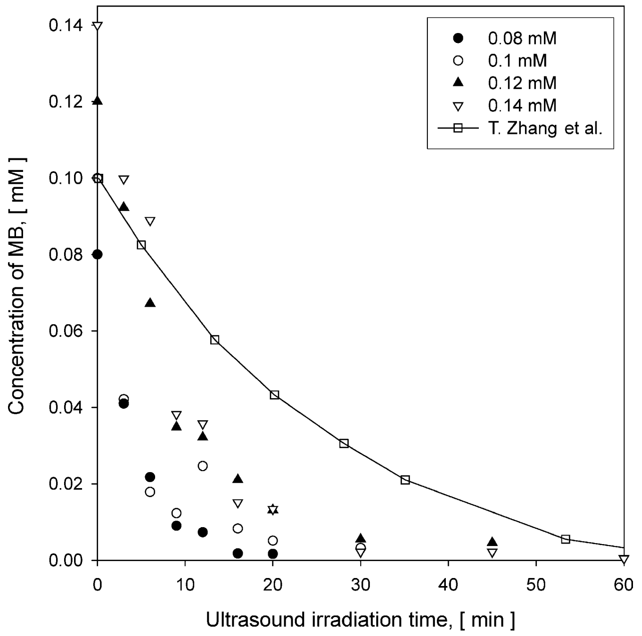

Fig. 5. Degradation rate of MB under ultrasound at the MBSL condition with various initial concentrations. Zhang et al. data are those of degradation of MB under UV-irradiated TiO_2 dispersions.

However, MB was degraded very slowly under ultrasound below the MBSL condition, which indicates that MB was hardly degraded by sonochemical action only, and that OH radicals produced at MBSL condition play a decisive role in the degradation of MB in solution.

4.2. Chemical kinetics for degradation of MB

Assuming that the hydroxyl radical OH is the primary oxidant for degradation of MB, a chemical kinetics for the process may be written as

$$\mathrm{OH} + \mathrm{MB} \rightarrow \text{products} \tag{6}$$

which allows an expression for the reaction rate of the degradation of MB such as

$$\frac{\mathrm{d[MB]}}{\mathrm{d}t} = -k[\mathrm{MB}][\mathrm{OH}] \tag{7}$$

Assuming that the concentration of the hydroxyl radicals remains to be constant, the concentration change during time t is given by

$$-\frac{1}{t}\ln\frac{[\mathrm{MB}]}{[\mathrm{MB}]_0} = k[\mathrm{OH}] = K \tag{8}$$

which shows the first-order chemical reactions.

In Fig. 6, the time-dependent concentrations of MB under ultrasound for various initial concentrations are given. The semi-log plots of $[\mathrm{MB}]/[\mathrm{MB}]_0$ against time for various initial concentrations are approximately linear, which show a case of the first-order reaction. From these observed values, apparent first-order rate constant for the degradation of MB may be estimated by using Eq. (8). As can be seen from Fig. 6, the degradation rate becomes faster at lower initial concentrations.

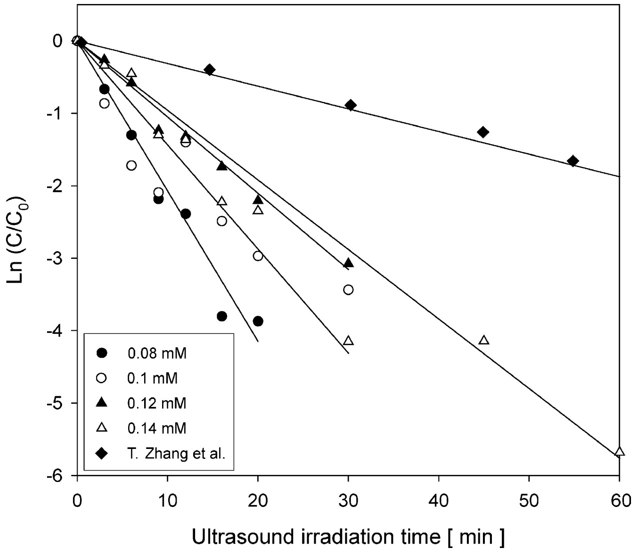

Fig. 6. Observed first-order kinetic plots for various initial concentrations for the degradation of MB under ultrasound at the MBSL condition.

Table 1
Concentration-dependent kinetics of degradation of MB under ultrasound at MBSL condition

$[MB]_0$ (mM)	K (min^{-1})	k ($mM^{-1}\ min^{-1}$)
0.08	0.2191	21.91
0.1	0.1535	15.35
0.12	0.1065	10.65
0.14	0.0825	8.25

With an upper bound value of the hydroxyl radical generation rate 0.01 mM/min [23], the values K in Eq. (8) and the reaction rates k for various initial concentrations are shown in Table 1. In this calculation, the final concentration of MB was taken to be 0.001 mM. The rate of degradation of MB under ultrasound is 4.6 times greater than the maximum rate of photocatalytic degradation of MB in UV-illuminated aqueous TiO_2 dispersion, which was achieved at pH 3.85 [3]. It should be noted that the kinetics of MB degradation under MBSL shows a reverse trend from the kinetics of the photodegradation of MB in UV-illuminated aqueous TiO_2 dispersions. Fig. 7 illustrates the relationship between the initial concentrations of $[MB]_0$ and the reaction rate k.

The number of OH radicals produced inside a bubble at its collapse was calculated by the chemical kinetics proposed by Bernstein et al. [20] and by a model for the bubble dynamics under ultrasound [11,12]. The calculation results shown in Fig. 8 are the case for an equilibrium radius of 10 μm at a frequency and an amplitude of 20 kHz and 1.2 atm, respectively. The species mole fractions were normalized to the initial H_2O mole fraction. An effective temperature to produce the hydroxyl radicals is about 4800 K, which is quite lower than the temperature of 6300 K calculated by a simplified bubble dynamics model with the adiabatic collapse of bubble of a constant contraction velocity [20]. The maximum relative mole fraction of the hydroxyl radicals at 4800 K, which is about 0.03, is similar magnitude to the value obtained at the temperature of 6300 K by Bernstein et al. [20]. Also, our calculation values for the temperature and the mole fraction of the hydroxyl radicals produced are close to those by Yasui et al. [24] who used complete chemical reaction scheme.

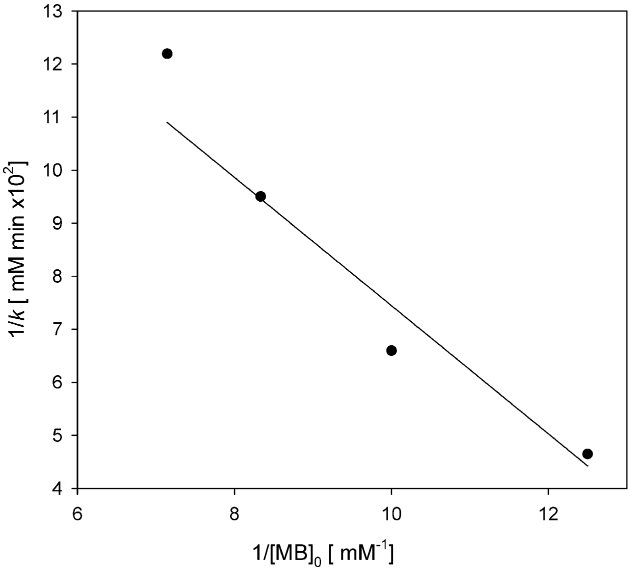

Fig. 7. Reciprocal plot of $1/k$ against $1/[MB]_0$.

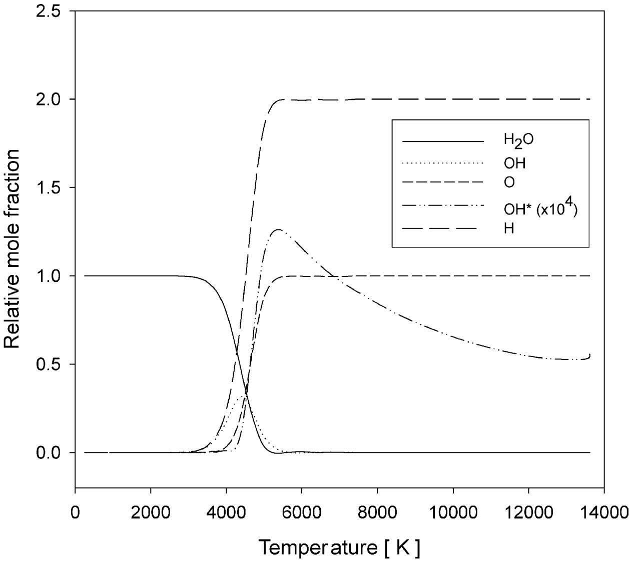

Fig. 8. Concentration of the chemical species depending on the gas temperature inside the bubble for the Ar/water system in the case of $R_0 = 10$ μm at $P_A = 1.2$ atm and $f = 20$ kHz.

All MB molecules in solution are assumed to be degraded by the oxidation process of hydroxyl radicals. For complete degradation of 0.08 mM MB solution during 20 min, the number of OH radicals needed for the degradation MB per second is about 6.0×10^{14}. Thus, the number of OH radicals generated per ultrasound cycle should be greater than 3.0×10^{10}. If 10% of OH radicals generated inside bubble diffuse into solution, the number of bubbles generated per ultrasound cycle should be greater than 3.0×10^3, which is a reasonable estimation for the MBSL equipment employed in this study.

In Table 2, the minimum number of bubbles produced per cycle for the complete degradation of MB for given initial concentrations is shown. Similar results of the minimum number of bubbles for various initial concentrations of MB were obtained. Smaller number of bubbles at higher concentrations may be due to the error in the estimation of the complete reaction time for given initial concentration. Degradation of polycyclic aromatic hydrocarbons (PAHs) of micromolar range in aqueous solution by ultrasonic irradiation was tried [25] in the presence of matrix components such as 1-butanol, NaCl and $FeSO_4$. However, 2 h is needed for complete degradation of such extremely small amount of PAHs, which is not the case of MBSL condition.

Another possibility of degradation of MB is the photobreaching of MB by O_2 under MBSL condition, which can be described as

$$C_{16}H_{18}SCl + 25\tfrac{1}{2}O_2 \rightarrow HCl + H_2SO_4 + 16CO_2 + 6H_2O \qquad (9)$$

Table 2
The number of MB molecules in a sample of 15 ml, the complete degradation time of MB and the minimum number of bubbles per cycle for complete degradation of MB given initial concentration of MB

Initial concentration (mM)	Number of MB molecules in a 15 ml sample	Complete degradation time (min)	Minimum number of bubble generated per cycle for complete reaction
0.08	7.22×10^{17}	20	2.77×10^{3}
0.1	9.03×10^{17}	30	2.35×10^{3}
0.12	1.08×10^{18}	45	1.90×10^{3}
0.14	1.26×10^{18}	60	1.67×10^{3}

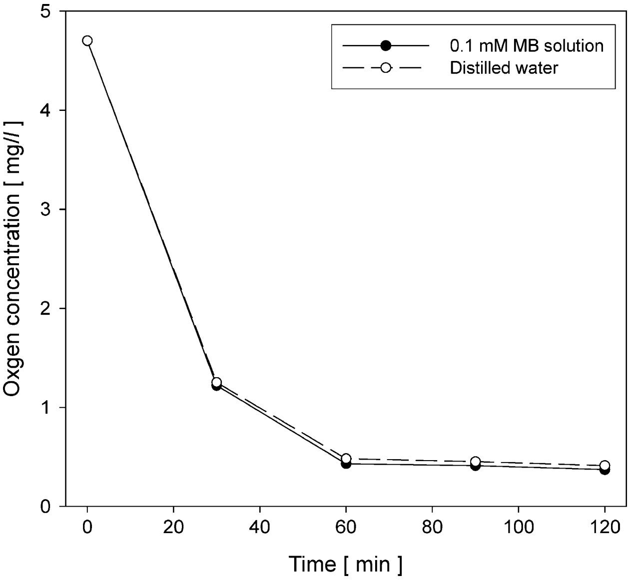

Fig. 9. Temporal reduction of oxygen concentration for the case of 0.1 mM MB solution and of water without MB due to ultrasound irradiation.

The above reaction, which can be possible by the photon energy greater than 3.2 eV [2], could be confirmed by the decrease in the oxygen concentration in the solution during the degradation of MB at the MBSL condition. However, as shown in Fig. 9, the temporal oxygen concentration in MB solution reduces similarly to the one in pure distilled water due to ultrasound irradiation so that the chemical reaction given in Eq. (9) was not occurred in our system.

5. Conclusion

Degradation of MB in aqueous solution under ultrasonic field at the MBSL condition was performed in this study. It has been confirmed, that MB under MBSL condition, is degraded mainly by the oxidation process by OH radicals produced inside the bubbles at their collapse. The sonochemical degradation of MB under MBSL condition, which was more effective method than the photocatalytic degradation of MB in aqueous TiO_2 under UV-irradiation, was found to be first-order rate model with respect to the MB concentration. The photobreaching process by O_2 with help of light energy from bubbles at the MBSL condition was confirmed to be not occurred.

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