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Assessment of Microwave/UV/O$_3$ in the Photo-Catalytic Degradation of Bromothymol Blue in Aqueous Nano TiO$_2$ Particles Dispersions

Sung Hoon Park · Sun-Jae Kim · Seong-Gyu Seo · Sang-Chul Jung

Abstract In this study, a microwave/UV/TiO$_2$/ozone/H$_2$O$_2$ hybrid process system, in which various techniques that have been used for water treatment are combined, is evaluated to develop an advanced technology to treat non-biodegradable water pollutants efficiently. In particular, the objective of this study is to develop a novel advanced oxidation process that overcomes the limitations of existing single-process water treatment methods by adding microwave irradiation to maximize the formation of active intermediate products, e.g., OH radicals, with the aid of UV irradiation by microwave discharge electrodeless lamp, photo-catalysts, and auxiliary oxidants. The results of photo-catalytic degradation of BTB showed that the decomposition rate increased with the TiO$_2$ particle dosages and microwave intensity. When an auxiliary oxidant such as ozone or hydrogen peroxide was added to the microwave-assisted photo-catalysis, however, a synergy effect that enhanced the reaction rate considerably was observed.

Keywords Photo-catalysts · Microwave · UV · Ozone · Dye

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Introduction

Azo dye is the most widely used one of those synthesized organic dyes, whose market share is about 50% of the whole dye market. The high market share of azo dye is due to its relatively low production cost and easy supply of raw materials. When discharged, however, it causes unpleasant deep color and is reduced to toxic amines. Therefore, wastewater treatment is necessary after a use of azo dye.

The treatment of wastewater containing dyes is difficult. Generally, adsorption using activated carbon and biological treatment using microorganisms are used to remove organic pollutants such as dyes contained in waste water. However, these methods do not easily remove the complex aromatic compounds with various substitutions contained in dye wastewater and causes generation of large amount of sludge and solid waste leading to high treatment cost. Oxidation has been widely used to convert toxic non-biodegradable materials into biodegradable forms. Conventional oxidation processes using ozone or hydrogen peroxide (H$_2$O$_2$), however, have limits in treating a number of different kinds of pollutants, calling for a more efficient oxidation process. Traditional methods (for example adsorption on activated carbons [1]) only transfer contaminations from one phase to another. The most promising way for removing dyes is photo-catalysis, because this process decomposes the end dyes to water and carbon dioxide [2]. Application of TiO$_2$ photo-catalyst in water treatment has recently been investigated widely [3, 4]. There are still many problems yet to be solved, however, in the application of TiO$_2$ photo-catalyst in the treatment of non-biodegradable materials. First, photo-catalysis has usually been used in air pollutants treatment because it is suitable for treatment of low-concentration pollutants. Concentrations of water pollutants, however, are much

higher than those of air pollutants. Thus, their treatment by photo-catalysis is difficult compared to that of air pollutants. Second, polluted water often contains mixture of hydrophilic and hydrophobic materials. Therefore, it is not easy for the pollutants to be adsorbed on the photo-catalyst surface. Third, polluted water has high turbidity, hence low transparency, hindering activation of photo-catalysts by ultraviolet (UV) rays. Fourth, some materials are not easily degraded by photo-catalysis only. Fifth, the amount of oxygen available for photo-catalytic oxidation is very low in water compared to in air. Due to these reasons, photo-catalytic oxidation of water pollutants has not received large attention thus far. Recently, researches have been conducted actively to improve oxidative degradation performance by adding microwave irradiation as an effort to utilize TiO_2 photo-catalyst in water treatment more efficiently [5–10].

In this study, a microwave/UV/TiO_2/ozone/H_2O_2 hybrid process system, in which various techniques that have been used for water treatment are combined, is evaluated to develop an advanced technology to treat non-biodegradable water pollutants efficiently. In particular, the objective of this study is to develop a novel advanced oxidation process that overcomes the limitations of existing single-process water treatment methods by adding microwave irradiation to maximize the formation of active intermediate products, e.g., OH radicals, with the aid of UV irradiation by MDEL, photo-catalysts, and auxiliary oxidants.

Experimental

Microwave/UV-TiO$_2$ System

Figure 1 shows the schematic of the Microwave/UV-TiO_2 experimental apparatus used in this study. Microwave radiation was carried out with a Microwave system manufactured by Korea microwave instrument Co. Ltd. It consisted of a microwave generator (frequency, 2.45 GHz; maximal power, 1 kW), a three-stub tuner, a power monitor, and a reaction cavity. Microwave radiation (actual power used, 200–600 W) used to irradiate the organic dye aqueous solution containing TiO_2 nano particles was delivered through a wave-guide. Microwave irradiation was continuous, and the microwave intensity was adjusted by connection to a power monitor. Optimal low reflection of the microwave radiation was achieved using the three-stub tuner. The UV sensor and the microwave generator were located on the right side and left side of the microwave cavity, respectively. Both devices were set at 180° to each other as illustrated in the Fig. 1. A stirrer was installed on the back side in the reaction cavity (Fig. 1) to enhance the transfer of microwave. As the microwave-irradiated

reactant solution is heated steadily, it was not possible to carry out experiments at constant temperature without a cooling system. In this study, the reactant solution was stored in a stainless steel beaker installed in a constant-temperature equipment. A roller pump was used to circulate the heated reactant solution through a cooling system to keep the reaction temperature constant at 298 K. In this study, ozone was added as an auxiliary oxidant to increase the efficiencies of the decomposition reactions of organic compounds. Ozone was produced by feeding oxygen gas with the flow rate of 500 cc/min to an ozone generator (Lab-1, Ozonetech Co. Ltd) as is shown in Fig. 1. The ozone production rate was adjusted between 0.75 and 3.26 g/hr by controlling the power consumption.
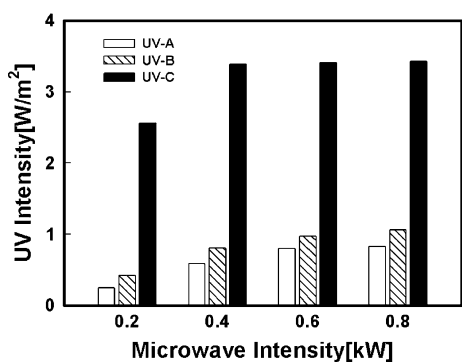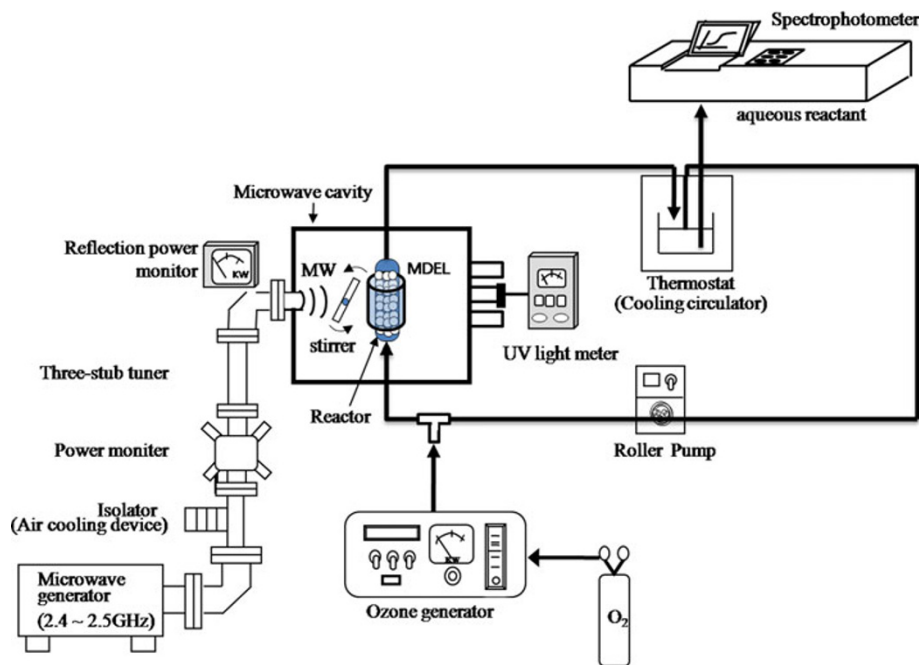
Double-Tube Type MDEL

TiO_2 photo-catalysts are excited by UV light, producing strong oxidants that can degrade organic compounds. Therefore, provision of UV is essential for a use of TiO_2 photo-catalysts. Typical UV lamps, however, have metal electrodes, which prevents them from being used in the microwave-irradiation equipment. Therefore, a double-tube type microwave discharge electrodeless lamp (170 mm length, 44 mm inner diameter, 60 mm outer diameter, hereafter MDEL) that emits UV upon the irradiation of microwave was developed in this study. It was made of quartz to maximize the reaction efficiency. Small amount of mercury was doped between the tubes inside the double-tube UV lamp that was kept vacuumed. The lamp used in this study is UV-C type lamp although a little amount of UV-A and UV-B wavelength lights are emitted as well. Figure 2 compares the UV intensities radiated at different microwave intensities. The sensor of the UV radiometer (HD2102-2, Delta OHM) was installed on the right-hand-side port of the microwave cavity (Fig. 1). The distance between MDEL and the sensor was about 30 cm. The ranges of wavelength detected by UV-A, UV-B, and UV-C sensors are 315–400, 280–315 nm, and 220–280 nm, respectively. At all microwave intensities tested in this study, UV-C exhibited much larger intensity than UV-A and UV-B. The UV-A and UV-B intensities increased with the microwave intensity, whereas the UV-C intensity showed little change at microwave intensity larger than 0.4 kW. Figure 3 shows the MDEL emitting UV light upon microwave irradiation in the microwave cavity.

Evaluation of Photo-Catalytic Reaction Activity

The photo-catalyst was Degussa P-25 TiO_2 (specific surface area 53 m^2g^{-1} by the BET method, particle size 20–30 nm by TEM, composition 83% anatase and 17% rutile by X-ray diffraction). In this study, the photo-
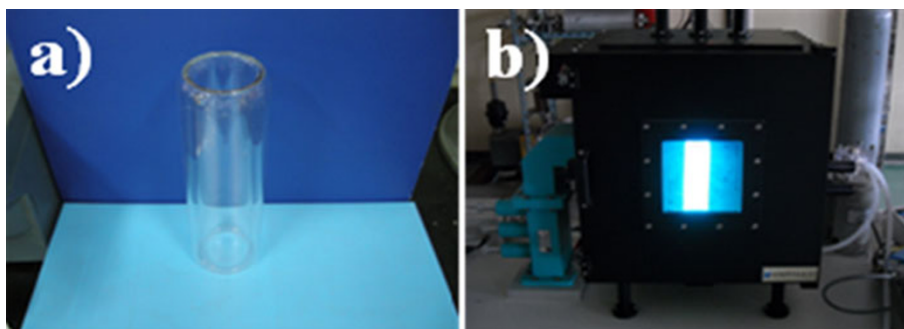
concentration of BTB was about 3.0×10^{-5} mol/l, and 1,000 ml of solution was circulated into the quartz reactor tube (230 mm length, 40 mm diameter) by a flow rate of 300 cc/min. Double distilled water was employed in these studies to make a solution for the degradation experiments. The decomposition rate was evaluated from the change in BTB concentration at the reactor outlet as a function of irradiation time. The concentration of BTB was measured by the absorbance at 420 nm using a spectrophotometer (UV-1601, Shimadzu).

catalytic activity of TiO$_2$ nano particle was investigated with the photo-catalytic decomposition of bromothymol blue (hereafter BTB) in its aqueous solution. BTB was chosen since it does not show strong absorption (and photo-decomposition) of UV-A light. High purity grade BTB was purchased from Daejung Chem. Co. Ltd. Initial

Results and Discussion

Effect of TiO$_2$ Nano Particle Dosages

Figure 4 shows the results of decomposition experiments of BTB obtained at three different TiO$_2$ nano particle dosages. The microwave intensity was 0.4 kW, and the circulation rate was 300 cc/min. The addition of a larger
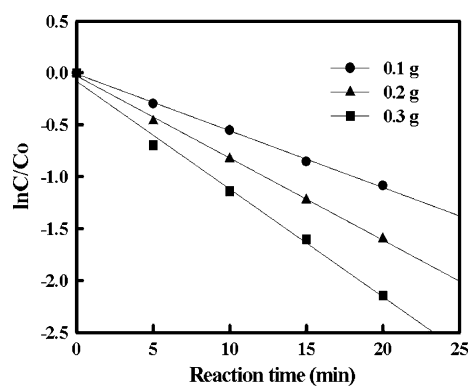
Fig. 4 Effect of TiO$_2$ particle dosages for decomposition of BTB in aqueous solutions

Fig. 5 Effect of microwave intensity for decomposition of BTB in aqueous solutions

amount of TiO$_2$ nano particle resulted in a higher decomposition rate. The plots for the three cases were all fitted well by linear line, which indicates that decomposition of BTB in the presence of TiO$_2$ catalyst can be approximated by a pseudo first order reaction model:

$$c/c_0 = \exp(-Kt) \qquad (1)$$

where C is the BTB concentration at time t, C_0 the initial concentration, and K the over-all rate constant. Over-all rate constant K is determined as the slope of the line in Fig. 4 by regression analysis. It is clearly shown in this figure that the degradation rate increases with amount of TiO$_2$ nano particle dosages.

Effect of Microwave Intensity

The results are shown in Fig. 5 as a function of microwave intensity. The experiments were carried out with the 0.1 g TiO$_2$ nano particle. Three different microwave powers were used: 0.2, 0.4, and 0.6 kw. It is clearly shown in this figure that the degradation rate increases with microwave intensity. Microwave has thermal effect and non-thermal effect. The thermal effect means selective, fast, uniform increase in temperature by microwave. The non-thermal effect represents the enhancement of the chemical reaction rate resulting from increased collision frequency. Sometimes, the thermal effect and the non-thermal effect can create a synergy effect.

In this study, a short wavelength electromagnetic wave UV is emitted by MDEL upon the irradiation of microwave. Therefore, the intensity of UV increases with the microwave power. UV, which carries intense energy, is used for exciting photo-catalyst. It can also contribute to degrading BTB directly. It was not possible to figure out the detailed mechanism how microwave took part in the degradation of BTB. Nevertheless, it can be inferred from the experimental result, which showed higher degradation efficiency at higher microwave intensity, that microwave
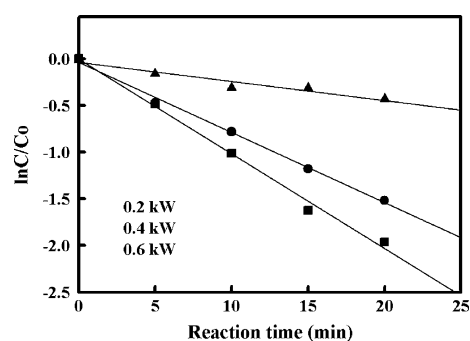
contributed to degradation of BTB indirectly by increasing UV intensity. The thermal and non-thermal effects of microwave are also presumed to have contributed directly to the degradation reaction.

Effects of Ozone

Ozone, a strong oxidant with the electric potential difference of 2.07 V, has widely been used in water treatment because it can effectively remove taste, odor, and precursors of trihalomethanes. However, the direct ozone reaction is relatively selective in oxidation of organic compounds because ozone has very low reactivity on single-bond chemicals and aromatic compounds with specific functional groups such as –COOH and –NO$_2$. On the contrary, the hydroxyl radical (·OH), which has a higher oxidation potential (2.80 V) than ozone and reacts with organic compounds unselectively, can be applied to oxidation treatment effectively. Therefore, large attention is being given to the advanced oxidation processes (AOPs), in which the organic compounds are decomposed using OH radicals. The microwave/UV/TiO$_2$/ozone hybrid process used in this study is an AOP that can overcome the limitations of the single-process ozone water treatment by using microwave and UV irradiations and resulting activation of photo-catalysts to maximize the formation of OH radicals. Figure 6 compares the results of the decomposition of BTB in aqueous solution obtained with different experimental conditions. The circulation flow rate of the solution was set at 300 ml/min for all the experiments. Three different levels of ozone addition were tested: 0.75, 1.78, and 3.26 g/hr. The TiO$_2$ nanoparticles mass and the microwave irradiation intensity were 0.1 g and 0.4 kW, respectively, when they were applied. At all experimental conditions, the decomposition rate increased with the ozone injection rate. When only microwave irradiation was added on top of ozone injection, the decomposition rate showed little change. On the other hand, when microwave irradiation was used to assist the UV-TiO$_2$ photo-catalysis
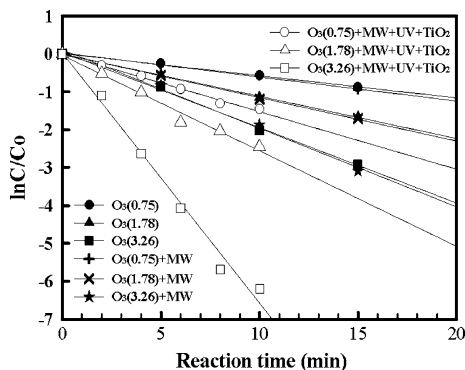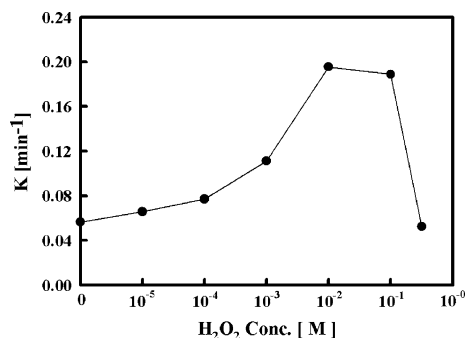
Fig. 6 Photo-catalytic degradation of BTB at various ozone injection rates

by MDEL together with ozone injection, the decomposition rate increased significantly.

Effect of Addition H_2O_2

The effect of H_2O_2 has been investigated in numerous studies, and it was reported that it increases the photo-catalytic degradation rate of organic pollutants [11]. The enhancement of the degradation rate with addition of H_2O_2 can be rationalized in terms of several reasons. First, it increases the rate by removing the surface-trapped electrons, hence by lowering the electron-hole recombination rate and increasing the efficiency of hole utilization for reactions such as ($OH^- + h^+ \rightarrow OH^\bullet$). Second, H_2O_2 may split photo-catalytically to produce hydroxyl radicals directly, as a cited in studies of homogeneous photo-oxidation using $UV/(H_2O_2 + O_2)$. Because H_2O_2 seems to be an efficient electron acceptor in TiO_2 photo-catalytic systems, its effect on photo-catalytic degradation reactions was tested [12]. Figure 7 shows how the photo-catalytic degradation rate of the BTB is affected by the addition of H_2O_2 in the microwave-assisted photo-catalytic system. The H_2O_2 addition to reactant solution increases the photo-catalytic degradation rate to a maximum, but further

addition of H_2O_2 above this level decreases the efficiency [13]. H_2O_2 is known to form a surface complex on TiO_2 [14]. The reduced photo-catalytic degradation rate in the presence of excess H_2O_2 can be ascribed to both the blocking of surface sites by H_2O_2 and the OH radical scavenging by H_2O_2 ($H_2O_2 + \bullet OH \rightarrow HO_2\bullet + H_2O$).

Comparison of the Effects of the Constituent Techniques

The decomposition rate constants obtained at different experimental conditions are shown in Fig. 8. The results of six different experiments are compared in this figure: microwave irradiation only (M); ozone injection only (O); microwave irradiation on top of ozone injection (MO); microwave-assisted UV-TiO_2 photo-catalysis by MDEL (MUP); MUP on top of ozone injection (MUPO); and MUP on top of hydrogen peroxide injection (MUPH). Information on detailed experimental conditions is as follows: TiO_2 nanoparticles mass of 0.1 g; microwave irradiation intensity of 0.4 kW; solution circulation flow rate of 300 ml/min; ozone injection rate of 0.75 g/hr; hydrogen peroxide addition amount of 1 ml (1.1632×10^{-2} mol).

As is shown in Fig. 8, the decomposition reaction seldom took place when only microwave was irradiated (M). The rate constant for the case M was much lower than the ozone addition only case (O) even with the smallest ozone addition amount of 0.75 g/hr, for which the rate constant was 0.0584 min^{-1}. When microwave irradiation and ozone addition were applied at the same time (MO), the rate constant (0.0588 min^{-1}) was almost same as that of the case O. Thus, microwave irradiation does not seem to play a significant role in the decomposition reaction without photo-catalysis. For the case of microwave-assisted UV-TiO_2 photo-catalysis using MDEL (MUP), the rate constant (0.0547 min^{-1}) was significantly higher than that of the microwave only case (M), but it was a little lower than the ozone only case (O). When the microwave-assisted UV-TiO_2 photo-catalysis was applied on top of ozone

Fig. 7 Effect of injection H_2O_2 for decomposition of BTB in aqueous solutions
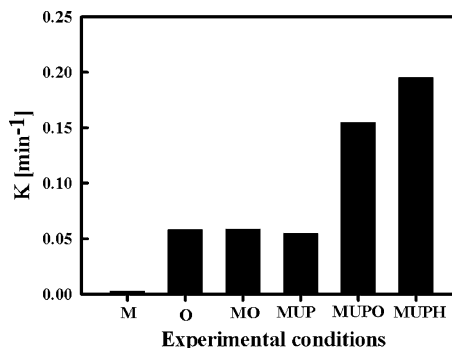
Fig. 8 Rate constants obtained under different experimental conditions

addition (MUPO), the decomposition rate constant was very high (0.1550 min^{-1}), which was even larger than the sum of the rate constants for the cases of MO and MUP. When hydrogen peroxide was added as the auxiliary oxidant, instead of ozone, to the microwave-assisted UV-TiO$_2$ photo-catalysis (MUPH), the decomposition rate still remained very high; the decomposition rate constant was 0.1954 min^{-1} with addition of 1.1632×10^{-2} mol hydrogen peroxide. The results of MUPO and MUPH indicate that there is a synergy effect when an auxiliary oxidant such as ozone or hydrogen peroxide is added to the microwave-assisted UV-TiO$_2$ photo-catalytic decomposition reaction.

Microwave, a kind of electromagnetic wave with a very short wavelength, excites polar molecules to cause them to rotate and vibrate back and forth rapidly: e.g., water molecules vibrate about 2.45×10^9 times per second upon microwave irradiation. The original objective of this study was to enhance the decomposition reaction rate by exciting pollutant molecules using microwave irradiation. According to the experimental results shown above, the effect of excitement of pollutant molecules was negligible. When an auxiliary oxidant such as ozone or hydrogen peroxide was added to the microwave-assisted photo-catalysis, however, a synergy effect that enhanced the reaction rate considerably was observed. This result suggests that microwave irradiation may enhance the production of active intermediate products, e.g., OH radicals, by activating the auxiliary oxidants. However, it is difficult to examine this hypothesis quantitatively using the limited experimental results obtained in this study. It is required to design a new experimental system and conduct more quantitative investigation into this question in the future.

Conclusion

To use the photo-catalysis system for advanced treatment of non-biodegradable water pollutants, a series of experiments were performed in which the effects of microwave irradiation and auxiliary oxidants were evaluated. The conclusions obtained from the experimental results are as follows:

1. The results of photo-catalytic degradation of BTB showed that the decomposition rate increased with the TiO$_2$ particle dosages.
2. For degradation of BTB, the decomposition rate increased with microwave intensity, from analysis of the effect of microwave intensity, how microwave participates in the degradation reaction.
3. When microwave irradiation was used to assist the UV-TiO$_2$ photo-catalysis by MDEL together with ozone injection, the decomposition rate increased significantly.
4. The H$_2$O$_2$ addition to reactant solution increases the photo-catalytic degradation rate to a maximum, but further addition of H$_2$O$_2$ above this level decreases the efficiency.
5. This result suggests that there is a synergy effect when the constituent techniques are applied together and that the additional irradiation of microwave can play a very important role in photo-catalysis of organic water pollutants.

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