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Photo-catalytic degradation of rhodamine B using microwave powered electrodeless discharge lamp

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Abstract−A microwave discharge electrodeless lamp (MDEL) was used as the light source for microwave assisted TiO_2 photo-catalysis to degrade rhodamine B. A MDEL filled with low pressure mercury gas has been developed for the photo-catalytic treatment of water pollutants over TiO_2 balls. TiO_2 balls produced by the chemical vapor deposition method were used. The degradation reaction rate was shown to be higher with higher microwave intensity and with a larger amount of O_2 gas addition. The effect of addition of H_2O_2 was not significant when photo-catalysis was used without additional microwave irradiation or when microwave was irradiated without the use of photo-catalysts. When H_2O_2 was added under simultaneous use of photo-catalysis and microwave irradiation, however, considerably higher degradation reaction rates were observed. This result suggests that there is a synergy effect when the constituent techniques are applied together.

Key words: Photo-catalyst, Microwave, UV, Dye, Chemical Vapor Deposition

INTRODUCTION

Azo dye is the most widely used of the 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 an unpleasant deep color and is reduced to toxic amines. Therefore, wastewater treatment is necessary after the use of azo dye.

The treatment of wastewater containing dyes is difficult. Generally, adsorption using activated carbon, biological treatment using microorganisms, and photochemical treatment 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 generate a 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_2O_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 application of TiO_2 photo-catalyst in the treatment of non-biodegradable materials. First, photo-catalysis has usually been used in air pollutant 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 a 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. For these reasons, photo-catalytic oxidation of water pollutants has not received much 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].

In many photo-decomposition reaction systems, TiO_2 powders are often used as a photo-catalyst [6]. However, powder catalysts have several problems, such as (1) difficulties in the separation of the catalyst from suspension after the reaction, (2) difficulties in the prevention of aggregation in high concentration suspensions. To avoid such agglomeration, suspension must be diluted. Then the overall reaction rate tends to be slow. On the one hand, these problems can be solved by the use of immobilized (i.e., coated) catalyst particles. However, the coated catalysts are easily detached from the supports. To avoid these problems, TiO_2 thin films have been prepared by the Sol-Gel method [7], the sputter method [8] and the chemical vapor deposition (CVD) method [9]. Among these, CVD

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is considered as a promising method to prepare high-quality thin films over large surface area with a well-controlled composition and low defect density [10,11].

The objective of this study is to evaluate the efficacy of microwave-assisted photo-catalytic degradation of rhodamine B using TiO_2 photo-catalyst ball by CVD, and hydrogen peroxide and oxygen gas were also added to improve the decomposition efficiency in the microwave/UV-TiO_2 process.

EXPERIMENTAL

1. TiO_2 Photo-catalyst Balls

TiO_2 Photo-catalyst balls prepared by a low pressure metal organic chemical vapor deposition (LPMOCVD) method were used. Titanium tetraisopropoxide ($Ti(OC_3H_7)_4$, TTIP) was used as the precursor to generate a TiO_2 film on alumina balls (Nikkto, HD-11) with 8 mm diameter. Details of the apparatus were described in our previous paper [12]. The CVD conditions used for the preparation of TiO_2 films are as follows: total flow rate of gas fed to the reactor 1,500 sccm, oxygen concentration at the reactor inlet 50 mol%, operating pressure 1 Torr, deposition temperature 773 K, TTIP evaporator temperature 323 K. Anatase TiO_2 films were prepared on the alumina balls with a thickness of 3-5 μm indicate X-ray diffraction pattern and SEM [10].

2. Microwave/UV-TiO_2 System

Fig. 1 shows a schematic of the Microwave/UV-TiO_2 experimental apparatus used in this study. It consists of a microwave irradiation equipment generated by modifying a commercial microwave oven, a high-frequency power generator (Korea microwave instrument Co.), a MDEL, a pyrex reactor tube (30ID, 250 mm length) in which photo-catalytic oxidative degradation of water pollutants takes place, a roller pump that circulates the reactant solution and a gas-providing equipment. The maximum power capacity and the frequency of the irradiated microwave are 1 kW and 2.45 GHz, respectively. A stirrer was installed on the other side of microwave irradiating part in the microwave irradiation equipment 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.

3. 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 the 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 MDEL (170 mm length, 36 mm inner diameter, 55 mm outer diameter) 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 gas was doped between the tubes inside the double-tube UV lamp that was kept vacuumed. This is a UV-C type lamp that emits UV light in a plasma phase when it is irradiated by microwave. Fig. 2 shows a photograph of the double-tube type MDEL emitting UV light by microwave irradiation in the microwave oven.

4. Evaluation of Photo-catalytic Reaction Activity

The degradation experiment was performed to evaluate the activity of photo-catalytic reaction for Rhodamine B (hereafter RB). Initial concentration of RB was about 5.0×10^{-6} mol/liter and 700 ml of solution was circulated into the reactor by a flow rate of 300 cc/min. High purity grade RB was purchased from Junsei Chem. Co. Ltd. Double distilled water was employed in these studies to make a solution for the degradation experiments. The decomposition rate was evaluated from the change of RB concentration at the reactor outlet as a function of irradiation time. The concentration of RB was measured by the absorbance at 550 nm by using a spectrophotometer (UV-1601, Shimadzu). Microwave and UV were irradiated

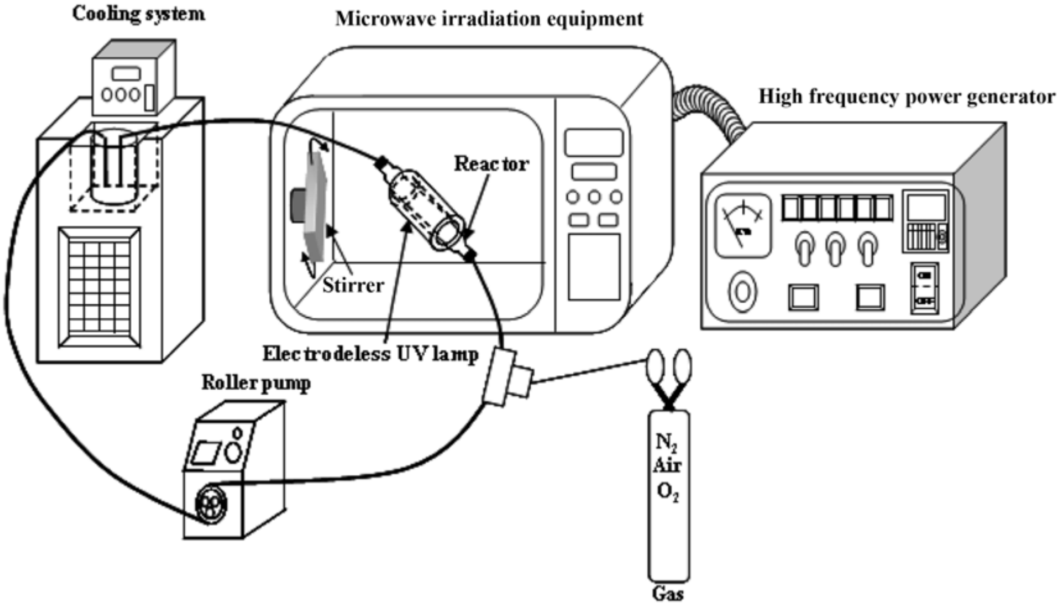

Fig. 1. The microwave/UV-TiO_2 photo-catalytic degradation system.

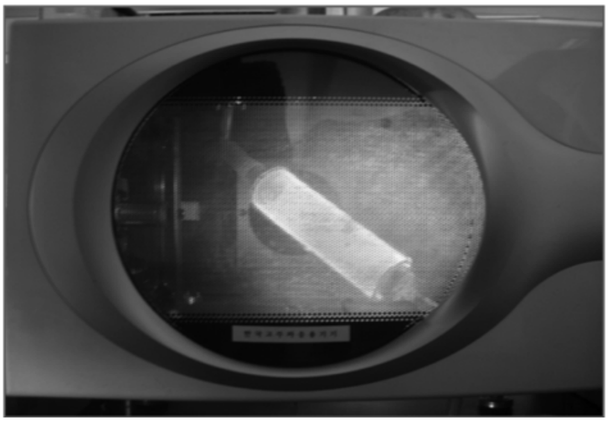

Fig. 2. Snapshot of the double-tube type MDEL emitting UV light by microwave irradiation in the microwave oven.

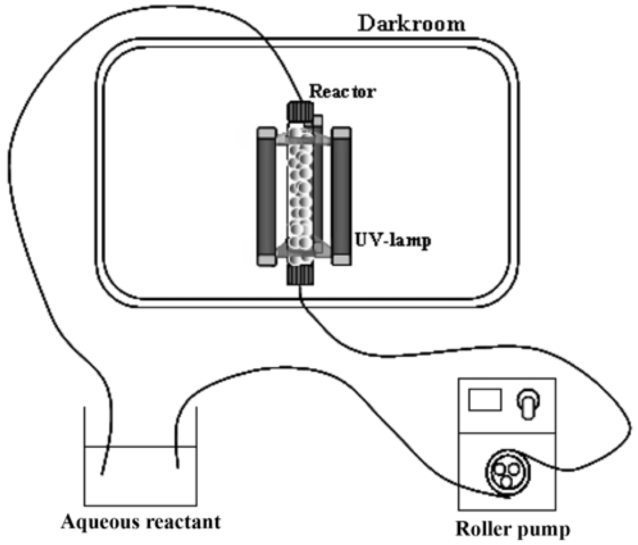

Fig. 3. The UV-TiO$_2$ experimental apparatus.

simultaneously by the MDEL installed in the vicinity of the reactor leading to photo-catalytic degradation reactions. The apparatus shown in Fig. 3 was used to evaluate the effects of each constituent technique on the degradation reaction rate. It is not possible to separate the effects of microwave and UV using the experimental setup shown in Fig. 1 because microwave and UV were inevitably irradiated together in that setup. To measure the photo-catalytic degradation rate under the condition of no microwave irradiation, three 4-Watt UV-C lamps (Sankyo denki, Germicidal, G15TB-AN) were used to irradiate UV on the reactor.

RESULTS AND DISCUSSION

1. Effect of Microwave Intensity

The decomposition rate was evaluated from the rate of the change in dye concentration as a function of irradiation time. The concentration of the RB was measured by the absorbance with a spectrophotometer. The results shown in Fig. 4 indicate that decomposition of the RB by photo-catalytic reaction in presence of TiO$_2$ catalyst is approximated by a pseudo first-order reaction model:

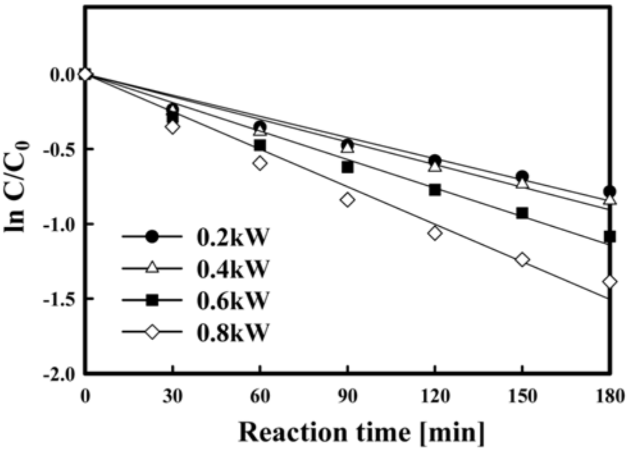

Fig. 4. Degradation rate of the RB at various microwave intensity.

$$C/C_0=\exp(-Kt) \tag{1}$$

Where C is the RB concentration at time t, C$_0$ the initial concentration, and *K* the over-all rate constant. The overall 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 microwave intensity. Microwave, which is a kind of electromagnetic wave with a very small wavelength, causes about 2.45 billion times of vibrations/translations/rotations of water molecules [13]. These kinds of molecular movements can contribute to increasing the temperature, hence increasing the degradation reaction rate. In this study, however, the temperature effect was excluded by maintaining the reaction temperature at 298 K to deduce, from analysis of the effect of microwave intensity, how microwave participates in the degradation reaction.

2. Effects of Addition Gases

Water treatment using photo-catalysts is an advanced technology that oxidizes organic and toxic compounds by producing strong oxidants, OH radicals, as intermediate products. As various new kinds of water pollution sources appear, however, non-biodegradable materials that would not be degraded easily even with photo-catalysts have recently been reported. In particular, water treatment using TiO$_2$ photo-catalysts has the disadvantage of using a small amount of oxygen dissolved in water [14]. In this study, the effect of provision of additional oxygen gas was investigated. Fig. 5 shows the effects of the addition of different gases for the microwave-assisted TiO$_2$ photo-catalytic degradation reaction of RB. The results obtained with the addition of O$_2$, N$_2$, and air with the flow rate of 500 cc/min were compared with those obtained with no gas added. The microwave intensity was 0.4 kW and the initial concentration of the RB solution was 5.0×10^{-6} mol/liter for all cases. The degradation rate was highest when O$_2$ was added, followed by the case of air addition. The degradation rate obtained with N$_2$ addition was lower than that obtained with no gas added. It can be deduced from this result that oxygen added in water treatments can help increase the photo-catalytic degradation rate by playing a role as auxiliary oxidants. Addition of nitrogen, an inert gas that does not positively affect the degradation reaction, was shown to rather decrease the degradation rate.

Fig. 6 shows the results of RB degradation obtained using three

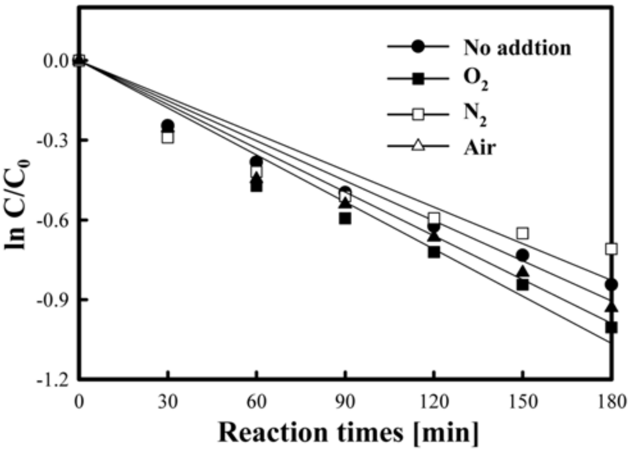

Fig. 5. Effect of into gases for decomposition of RB in aqueous solution.

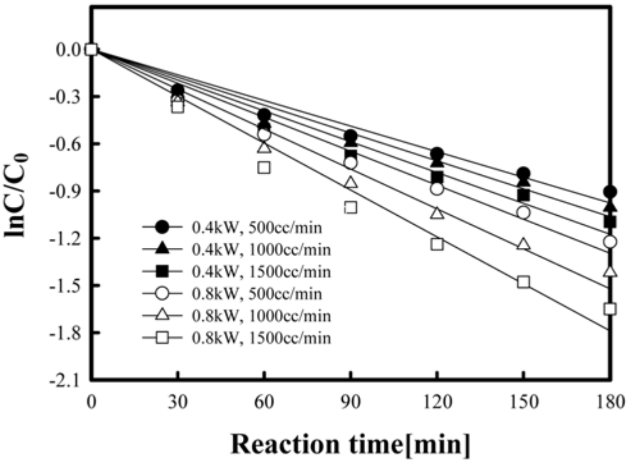

Fig. 6. Photo-catalytic degradation of RB at various oxygen gas flow rate.

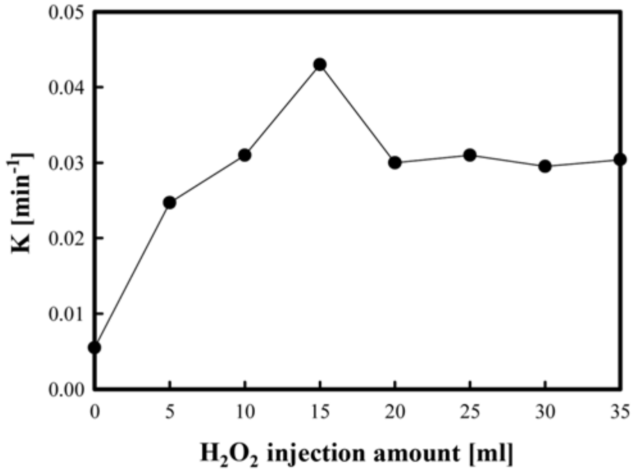

Fig. 7. Effect of injection H_2O_2 for decomposition of RB in aqueous solutions.

different O_2 flow rate, 500, 1,000, and 1,500 cc/min, with the microwave intensity of 0.4 and 0.8 kW. The degradation rate was higher with the higher microwave intensity and with a higher O_2 flow rate. The effect of O_2 flow rate can be explained as follows. UV irradiated on TiO_2 photo-catalysts causes excitation, leading to movement of electrons in the valance band towards the conduction band [14]. If the reaction does not follow immediately, however, recombination occurs. By playing a role as electron capturers, oxygen molecules can slow down the recombination rate and help produce peroxide and hydroperoxy radicals, and therefore enhance the degradation reaction rate [15].

3. 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 [16]. 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 ($OH^-+h^+ \rightarrow OH^{\cdot}$). Second, H_2O_2 may split photo-catalytically to produce hydroxyl radicals directly, as 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 [17]. Fig. 7 shows how the photo-catalytic degradation rate of the RB 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 [18]. H_2O_2 is known to form a surface complex on TiO_2 [19]. 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+•OH $HO_2^{\cdot}$+H_2O).

4. Comparison of the Effects of the Constituent Techniques

To compare the effects of the constituent techniques, experiments were performed under different experimental conditions. For the experimental condition in which microwave is not irradiated, the apparatus shown in Fig. 3 was used. The five conditions shown in Fig. 8 represent the photo-catalytic degradations under (1) irradiation of UV only using the setup shown in Fig. 4 (PU), (2) simultaneous irradiation of microwave and UV using the setup shown in Fig. 1 (PMU), (3) irradiation of UV only using the setup shown in Fig. 4 with addition of 15 ml of 0.18 M H_2O_2 (PUH), (4) irradiation of microwave only (without photo-catalysts) using the setup shown in Fig. 1 with addition of 15 ml of H_2O_2 (MUH), and (5) simultaneous irradiation of microwave and UV using the setup shown in Fig. 1 with addition of 15 ml of H_2O_2 (PMUH), respectively. One additional experiment was performed under irradiation of microwave only without photo-catalysts with the setup shown in Fig. 1, but none of the RB was degraded at all under this condition. For degradation reactions of RB, the reaction rate was higher when microwave was additionally irradiated (PMU) than the rate obtained under irradiation of UV only (PU). It is not straightforward to compare the results quantitatively because the intensities and wavelengths of UVs irradiated by setups shown in Fig. 1 and Fig. 4 are different from each other. Nevertheless, simply adding the microwave irradiation does not seem to increase the reaction rate very much. The effect of addition of H_2O_2 was not significant for UV-only (PUH)

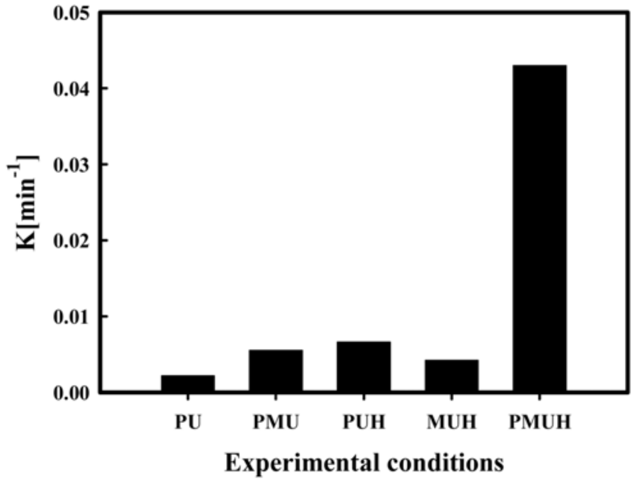

Fig. 8. Rate constants obtained under different experimental conditions.

Table 1. The over-all rate constants obtained at different experimental conditions

Conditions	PU	PMU	PUH	MUH	PMUH
[K]	0.0022	0.0055	0.0066	0.0042	0.0430

and microwave-only (MUH) cases. When H_2O_2 was added under simultaneous irradiation of UV and microwave (PMUH), however, considerably higher degradation reaction rates were observed. Table 1 summarizes the reaction rate constants obtained under different experimental conditions used in this study. The rate constants obtained under simultaneous irradiation of UV and microwave with addition of H_2O_2 (MPH) were 6-20 times higher than those obtained under other conditions. This result suggests that there is a synergy effect when the constituent techniques, i.e., photo-catalysis, microwave irradiation, and H_2O_2 addition, are applied together. This study was motivated by the expectation that additional irradiation of microwave in a conventional photo-catalysis system might enhance the degradation rate of organic pollutants by activating the photo-catalysts and pollutants. Without the use of additional oxidants, however, the effect of microwave irradiation was not very large. On the other hand, when H_2O_2 was added, the effect of microwave appeared to become significantly larger. One possible explanation for this result is that H_2O_2 is activated by microwave and produces more activation species participating in the degradation reaction. However, it is not possible to deduce more quantitative description about this phenomenon using the limited experimental results of the present study. Further experiments are required to investigate the interactions among the constituent techniques more quantitatively.

CONCLUSION

The photo-catalytic degradation of RB was carried out by MDEL and TiO_2 photo-catalyst balls prepared by CVD. For degradation reactions of RB, the reaction rate was higher when microwave was additionally irradiated than the rate obtained under irradiation of UV. Addition of oxygen gas in the photo-catalytic degradation of RB increased the reaction rate. With larger amount of oxygen added and with higher intensity of microwave irradiated, the reaction rate was increased more. The effect of addition of H_2O_2 was not significant when photo-catalysis was used without additional microwave irradiation or when microwave was irradiated without the use of photo-catalysts. When H_2O_2 was added under simultaneous use of photo-catalysis and microwave irradiation, however, considerably higher degradation reaction rates were observed. 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 H_2O_2-assisted photo-catalysis of organic water pollutants.

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