Research Article

Effect of Oxygen and Hydrogen Peroxide on the Photocatalytic Degradation of Monochlorobenzene in TiO₂ Aqueous Suspension

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The influences of oxygen and hydrogen peroxide (H₂O₂) on the degradation and mineralization of monochlorobenzene (MCB) during UV/TiO₂ process were investigated. Experimental results indicated that oxygen was a determining parameter for promoting the photocatalytic degradation. The presence of oxygen reduced the illumination time needed for the complete decay of MCB from 240 to 120 min. The photocatalytic degradation of MCB in UV/TiO₂/O₂ photocatalysis followed a simplified two-step consecutive kinetics. The rate constants of degradation (k_1) and mineralization (k_2) were increased from 0.016 to 0.046 min⁻¹ and from 0.001 to 0.006 min⁻¹, respectively, as the initial concentration of dissolved oxygen (DO) was increased from 1.6 to 28.3 mg L⁻¹. Owing to the fact that H₂O₂ acted as an electron and hydroxyl radicals ($\cdot$ OH) scavenger, the addition of H₂O₂ should in a proper dosage range to enhance the degradation and mineralization of MCB. The optimal H₂O₂ dosage for MCB degradation was 22.5 mg L⁻¹, whereas the most efficient H₂O₂ dosage for MCB mineralization was 45.0 mg L⁻¹. In order to minimize the adverse effects of higher H₂O₂ dosage, including the capture of $\cdot$ OH radicals and competitive adsorption, and to improve the photocatalytic degradation of MCB, the sequential replenishment of H₂O₂ was suggested. For the stepwise addition of a total H₂O₂ dosage of 45.0 mg L⁻¹, a complete destruction of MCB was observed within 120 min of irradiation. Additionally, the mineralization efficiency was about 87.4% after 240 min of illumination time.

1. Introduction

During last several decades, the control of organic pollutants has received much attention for its considerable amount and variety. However, the conventional biological, physical, and chemical technologies are ineffective and limitative toward the destruction of toxic and recalcitrant organic pollutants. Heterogeneous photocatalysis, one of the so-called Advanced Oxidation Processes (AOPs), offers an advanced oxidation capable of pollutant abatement [1, 2]. Many researchers have concluded that the UV/TiO₂ process is a promising technology for the degradation and mineralization of organic substrates to harmless final products in air and water media [3–6].

The mechanism of the UV/TiO₂ process has been discussed extensively in the literature [7–9]. When TiO₂ is irradiated with light energy equal to or higher than its band-gap,

an electron (e⁻) can be excited from the valence band to the conduction band and leaving a hole (h⁺) in the valence band

If charge separation is maintained, the paired e⁻-h⁺ may migrate to the surface of the photocatalyst. In aqueous phase, the photoinduced h⁺ is apparently able to oxidize surface hydroxyl groups or surface-bond water molecules to produce highly reactive and nonselective hydroxyl radicals ($\cdot$ OH) (2). The $\cdot$ OH radicals are considered to be the dominant oxidizing species contributing to the photocatalytic degradation of organic substrates [10–12]. Nevertheless, the e⁻ can

recombine with the h^+ (3), causing a decrease in the availability of the photoinduced h^+ [13, 14]. Without electron acceptors, the limitation attributed to the recombination of e^- - h^+ pairs would reduce the photocatalytic efficiency and cause radiation energy loss. Therefore, suppressing the recombination of e^- - h^+ pairs is an important consideration in enhancing the performance of photocatalytic degradation.

In this study, both oxygen and hydrogen peroxide (H_2O_2) were selected as electron acceptors. Monochlorobenzene (MCB), one of the hydrophobic and volatile organic compounds (VOCs), was chosen as a model compound. The objectives of the present work were to evaluate the effect of oxygen and H_2O_2 on the photocatalytic degradation of MCB. The change in the concentration of MCB with various oxygen concentrations and H_2O_2 dosages was examined. Additionally, the extent of mineralization was also estimated by measuring the concentration of total organic carbon (TOC) in MCB solution.

2. Materials and Methods

2.1. Materials. Anatase TiO_2 powder with a specific BET surface area of $9.3\text{ m}^2\text{ g}^{-1}$ and a primary particle size of 150 nm was purchased from Acros Organics and used as received. Reagent grade MCB (C_6H_5Cl , MW = 112.56, density = 1.106 g mL^{-1} , vapor pressure = 12 mm Hg at 25°C , and water solubility = 494 mg L^{-1} at 25°C) with a purity over 99% was obtained from Merck. H_2O_2 (30%) was obtained from Fluka Chemical. Other chemicals used for analysis, including acetonitrile, acetic acid, potassium hydrogen phthalate, phosphoric acid, and sodium peroxydisulfate were of analytical grade. Pure N_2 and O_2 gases and air were used to adjust the initial dissolved oxygen (DO) concentration to the desired levels. Deionized water was employed for solution preparation.

2.2. Experimental Apparatus and Procedure. A hollow cylindrical photoreactor with a working capacity of 2.5 l and equipped with a water jacket was used in this study. Cooling water from a thermostatic bath (TUNGTEC BL-20) was circulated through the photoreactor jacket to keep the temperature at 30°C . Irradiation was performed using a 15 W blacklight lamp (F15T8 BLB, UVP) with a maximum emission at 365 nm. The UV lamp was vertically immersed in a quartz tube placed in the center of the photoreactor. The light intensity inside the photoreactor, as measured by potassium ferrioxalate actinometry, was $5.68\text{ }\mu\text{ Einstein s}^{-1}$. The reaction mixture was continuously agitated by a magnetic stirrer to keep the TiO_2 particles suspended.

Two series of experiments were carried out to examine the effects of oxygen and H_2O_2 on the photocatalytic degradation of MCB. Prior to MCB solution preparation, all deionized water was first purged by N_2 gas for 30 min to minimize the amount of DO. Subsequently, the deionized water was purged with either air or O_2 gas to obtain the predetermined DO concentration. The initial concentration of MCB was fixed at 0.1 mM and the TiO_2 dosage was 1.0 g L^{-1} unless otherwise stated. The initial pH of solution

was adjusted to 7 by adding an appropriate volume of dilute NaOH or HNO_3 solutions. After 30 min of premixing in the dark, the UV lamp was switched on to initiate the photocatalytic degradation.

The experimental procedure for the H_2O_2 -assisted batch was similar to the oxygen-assisted batch. In this case, the MCB solution was prepared using deionized water that had been deoxygenated by N_2 gas. After TiO_2 powder was added into the solution, the solution pH was adjusted to 7 with dilute NaOH or HNO_3 solutions. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min. After the addition of H_2O_2 into the suspension, the UV lamp was turned on.

At given irradiation time intervals, samples were withdrawn from the irradiated suspension. These collected samples were immediately centrifuged and filtered through a $0.22\text{ }\mu\text{m}$ Millipore filter for further analysis.

2.3. Analytical Methods. The residual MCB measurement was carried out by HPLC (Biotronik HPLC BT 7900) equipped with a Linear UVIS 200 UV detector and an ODS2 C18 column (length 25 cm, inner diameter 4.6 mm). The mobile phase was composed of acetonitrile (70%), water (29%), and acetic acid (1%) and the flow rate was kept at 1.5 mL min^{-1} . The detection wavelength selected for detecting MCB was 265 nm. A TOC analyzer (O. I. Analytical Model 700) equipped with a nondispersive infrared detector (NDIR) was employed to monitor the concentration of TOC. The DO concentration was quantified by an oxygen membrane electrode (Oxi 320, WTW).

3. Results and Discussion

3.1. Direct Photolysis and H_2O_2 -Assisted Photolysis. Two preliminary experiments were carried out to estimate the contribution of direct photolysis and H_2O_2 -assisted photolysis for the removal of MCB. The variation in the MCB concentration during irradiation can be seen in Figure 1. For the direct photolysis, there was about 42.8% degradation of MCB after 240 min of illumination time. This result implied that the UV light had evident contribution on the degradation of MCB which was in agreement with the observation reported by other researcher [15]. The change in the MCB concentration fitted an exponential decay curve, suggesting the direct photolysis of MCB followed the pattern of pseudo first-order kinetics. A linear regression was obtained with natural logarithmic normalized concentration against illumination time. The degradation rate constant was calculated to be 0.002 min^{-1} .

In order to evaluate the degradation ability of H_2O_2 -assisted photolysis, an irradiation experiment was conducted under the condition of H_2O_2 dosage equal to 22.5 mg L^{-1} . Corresponding to the obtained experimental result recorded in Figure 1, it was found that the concentration of MCB decreased gradually during the period of irradiation. The extent of MCB degradation in the H_2O_2 -assisted photolysis within 240 min of irradiation was approximately 60.2% and the pseudo first-order degradation rate constant was

FIGURE 1: Direct photolysis and H₂O₂-assisted photolysis of MCB.

0.004 min⁻¹. The typical time-dependent MCB concentration in the presence of both UV light and H₂O₂ was similar to that under the UV irradiation only. It was stated that H₂O₂ has an extremely low absorption at UV light of 365 nm [16], therefore, the generation of ·OH radicals due to the photolysis of H₂O₂ would be insignificant. As a result, the observable MCB decay can mainly be ascribed to the direct photolysis. Moreover, the additional MCB degradation can be explained by the oxidative ability of H₂O₂.

3.2. UV/TiO₂/O₂ Photocatalysis

3.2.1. Degradation of MCB. The dependency of the photocatalytic degradation of MCB on the initial DO concentration was studied in the range from 1.6 to 28.3 mg L⁻¹. Typical time-dependent MCB concentration during photocatalytic degradation is illustrated in Figure 2(a). As can be seen, when TiO₂ suspension was exposed to UV light, the MCB concentration decreased markedly with illumination time in comparison with the same experiment performed in the absence of TiO₂. The difference between direct photolysis and UV/TiO₂/O₂ photocatalysis revealed that UV light and TiO₂ photocatalyst together had a significant effect on the degradation of MCB. Since ·OH radicals were the key feature of UV/TiO₂ process, the degradation of MCB was primarily related to the generated ·OH radicals.

Referring to Figure 2(a), the presence of oxygen was contributed to the photocatalytic degradation. Complete destruction of MCB was observed after 240 min of irradiation when the experiment was performed under initial DO concentration equal to 1.6 mg L⁻¹. In addition, for the initial DO concentration of 28.3 mg L⁻¹, the illumination time required for complete decay of MCB was reduced to 120 min. The depletion of the DO concentration during irradiation, as recorded in Figure 2(b), confirmed that oxygen was involved in the photocatalytic degradation. Accordingly, the improvement of the degradation of MCB, which is related

to the increasing initial DO concentration, can be attributed to the fact that oxygen acted as electron acceptor to trap the photoinduced e⁻ [17, 18]

Through the reduction of oxygen with e⁻, reactive superoxide radical anions (O₂^{·-}) was produced (4). Simultaneously, the e⁻-h⁺ pair recombination was restrained. Stabilizing the primary carrier led to promote the generation of ·OH radicals. Moreover, other oxidizing species such as HO₂[·] and H₂O₂ were also formed (5)–(7). It was believed that additional ·OH radicals would be generated through sequential reactions [11, 19–21]. Consequently, an increase in the DO concentration would accelerate the degradation of MCB.

3.2.2. Mineralization of MCB. The decay of TOC during photocatalytic degradation was monitored to evaluate the mineralization of MCB. From the plot shown in Figure 2(c), the improvement of the mineralization of MCB in the presence of oxygen was observed. The mineralization efficiency increased from 42.6 to 93.1% within 240 min of irradiation as initial DO concentration varied from 1.6 to 28.3 mg L⁻¹. Similar observations have been reported in the literature for other model compounds [22–24].

For the initial DO concentrations of 17.9 and 28.3 mg L⁻¹, there were still measurable DO concentrations after 240 min of illumination time. Since there was sufficient oxygen in the photocatalytic system, the TOC decreased abidingly during photocatalytic degradation. Moreover, besides the electron acceptor function, oxygen can also participate in the oxidative reaction to promote the mineralization of organic substrates and intermediates [25, 26]. Consequently, the depression of TOC decay was ascribed to the lack of oxygen involved in the photocatalytic degradation afterward in the case of lower initial DO concentration.

A comparison of Figures 2(a) and 2(c) indicated that the TOC decayed with illumination time in parallel with the MCB degradation. However, it should be noted that complete disappearance of MCB occurred within 120 to 240 min of irradiation under various initial DO concentrations, whereas residual TOC was still observed. This phenomenon implied that transient organic intermediates were likely to present in the photocatalytic system.

3.2.3. Two-Step Consecutive Kinetics. Based on the total organic carbon concentration in the photocatalytic system, the mass balance can be expressed as [27, 28]

$$[\text{TOC}]_t = [\text{MCB}]_{c,t} + [\text{Inter}\cdot]_{c,t}, \quad (8)$$

where [TOC]_t is the total organic carbon concentration in the system, [MCB]_{c,t} is the carbon concentration in the MCB

FIGURE 2: Concentration profiles of (a) MCB, (b) DO, (c) TOC, and (d) intermediates during photocatalytic degradation of MCB at various initial DO concentrations: (●) 1.6 mg L⁻¹, (▼) 3.9 mg L⁻¹, (■) 9.0 mg L⁻¹, (◆) 17.9 mg L⁻¹, and (▲) 28.3 mg L⁻¹.

at time t , and $[\text{Inter}\cdot]_{c,t}$ is the carbon concentration in the intermediates at time t . Correspondingly, the carbon concentration in the intermediates can be determined from the concentrations of MCB and TOC. Figure 2(d) illustrates the variation of carbon concentration in the intermediates for different initial DO concentration during the photocatalytic degradation of MCB. As can be seen, the intermediates accumulated first and decomposed thereafter.

Since the mineralization of MCB occurs through the intermediates, a simplified two-step consecutive kinetics can be used to describe the photocatalytic degradation [29, 30]

where k_1 is the degradation rate constant of MCB and k_2 is the mineralization rate constant of the intermediates. The ultimate product of the photocatalytic degradation can

be CO₂, H₂O, and relevant inorganic ions. Each step in (9) is assumed to be a first-order and irreversible reaction. Applying the two-step consecutive kinetics, the carbon concentrations in the MCB and the intermediates can be expressed by

$$[\text{MCB}]_{c,t} = [\text{MCB}]_{c,o} e^{-k_1 t} \quad (10)$$

$$[\text{Inter}\cdot]_{c,t} = \frac{k_1 [\text{MCB}]_{c,o}}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}). \quad (11)$$

Accordingly, the two rate constants k_1 and k_2 can be derived from the disappearance of MCB and the intermediates.

As listed in Table 1, the increase in the value of k_1 was proportional to the initial DO concentration. The enhancement of k_1 was about 3 times higher when the initial DO concentration was 28.3 mg L⁻¹ rather than 1.6 mg L⁻¹. Take the calculated k_1 and the determined $[\text{Inter}\cdot]_{c,t}$ into (11),

TABLE 1: Determination of the two-step consecutive kinetic constant for the photocatalytic degradation of MCB at different DO concentration.

DO concentration, mg L ⁻¹	k_1 , min ⁻¹	R^2	k_2 , min ⁻¹	R^2
1.6	0.016	0.9915	0.001	0.9843
3.9	0.020	0.9884	0.003	0.9787
9.0	0.025	0.9940	0.003	0.9681
17.9	0.038	0.9975	0.007	0.9591
28.3	0.046	0.9977	0.006	0.9685

TABLE 2: Determination of the two-step consecutive kinetic constant for the photocatalytic degradation of MCB at different H₂O₂ dosage.

H ₂ O ₂ dosage, mg L ⁻¹	k_1 , min ⁻¹	R^2	k_2 , min ⁻¹	R^2
5.6	0.018	0.9966	0.002	0.9836
11.2	0.023	0.9932	0.002	0.9568
22.5	0.026	0.9956	0.002	0.8682
45.0	0.024	0.9872	0.001	0.8519
78.0	0.011	0.9972	<<0.001	0.9631

the value of mineralization rate constant k_2 was obtained. It was evident that the mineralization rate constant depended on the initial DO concentration. The value of k_2 increased with increasing initial DO concentration to a certain level and thereafter remained almost constant. The k_2 increased 8 times when the initial DO concentration was increased to 17.9 mg L⁻¹ rather than 1.6 mg L⁻¹. Interestingly, the values of k_2 were lower than those of k_1 , this revealed that the mineralization may be the rate-limiting step in the photocatalytic degradation of MCB. Therefore, prolonged illumination time would be reasonable for complete mineralization.

3.3. UV/TiO₂/H₂O₂ Photocatalysis

3.3.1. Degradation of MCB. According to its high oxidation potential and electrophilic, H₂O₂ is a stronger electron acceptor than oxygen [31–33]. A series of experiments were conducted with deoxygenated TiO₂ suspension in order to evaluate the effect of H₂O₂ dosage on the photocatalytic degradation of MCB. The examined range of H₂O₂ dosage was varied from 5.6 to 78.0 mg L⁻¹. From the typical temporal file exhibited in Figure 3(a), it can be seen that the degradation of MCB was sensitive to the variation of H₂O₂ dosage. A pseudo first-order kinetic model was provided to simulate the degradation of MCB. Table 2 summarizes the degradation rate constant k_1 derived from the gradient of the plot of the natural logarithm of the normalized MCB concentration against the illumination time. When the H₂O₂ dosage increased from 5.6 to 22.5 mg L⁻¹ the value of k_1 increased from 0.018 to 0.026 min⁻¹. A further increase in the H₂O₂ dosage from 22.5 to 78.0 mg L⁻¹, however, led to a significant decline in the k_1 from 0.026 to 0.011 min⁻¹. The optimum H₂O₂ dosage for the degradation of MCB was around 22.5 mg L⁻¹ which was similar to that observed by other researchers [20, 34–36].

The influence of H₂O₂ dosage on the degradation of MCB can be explained in terms of the number of generated ·OH radicals and the capture of ·OH radicals [36–39]. It is well known that H₂O₂ can trap photoinduced e⁻ to stabilize the paired e⁻-h⁺

Additional ·OH radicals could be yielded via the reaction between H₂O₂ and e⁻ or O₂·⁻ (12) and (13). As a result, the addition of H₂O₂ into the photocatalytic system was expected to promote the degradation of MCB. Exceeding the optimum dosage, however, the excess H₂O₂ would trap the ·OH radicals to form weaker oxidant HO₂· radicals. Accordingly, the capture of ·OH radicals was occurred through (14) and (15). The decline in the ·OH radical concentration, triggered by the higher H₂O₂ dosage, restrained the degradation of MCB.

The variation of DO concentration during the UV/TiO₂/H₂O₂ photocatalysis for a variety of H₂O₂ dosage is illustrated in Figure 3(b). It was found that the DO concentration increased markedly with illumination time to reach a maximum value and decreased thereafter. The increase in the DO concentration was related to the decomposition of H₂O₂ [39, 40]

Correspondingly, the addition of H₂O₂ seemed to act as an oxygen source. The later decrease in the DO concentration implied that the generated oxygen was involved in the mineralization.

FIGURE 3: Concentration profiles for (a) MCB, (b) DO, (c) TOC, and (d) intermediates during photocatalytic degradation of MCB at various H_2O_2 dosages: (○) 5.6 mg L^{-1} , (▽) 11.2 mg L^{-1} , (□) 22.5 mg L^{-1} , (◇) 45.0 mg L^{-1} , and (△) 78.0 mg L^{-1} .

3.3.2. Mineralization of MCB. Similar to the degradation of MCB, the mineralization of MCB also took place throughout the entire irradiation. Figure 3(c) shows the concentration of TOC as a function of illumination time under various H_2O_2 dosages. As can be seen, the extent of TOC decay increased from 44.4 to 74.1% with H_2O_2 dosage increased from 5.6 to 45.0 mg L^{-1} after 240 min of irradiation. At higher dosage, however, the mineralization efficiency decreased to 62.5%. Reviewing the result shown in Figure 3(a), there was still observable MCB throughout the entire irradiation period in the case of H_2O_2 dosage equal to 78.0 mg L^{-1} . This meant that the constraint on the mineralization efficiency may be ascribed to the competitive MCB.

Based on (8), the carbon concentration in the transient organic intermediates was determined as shown in Figure 3(d). Interestingly, the maximum value of intermediate concentration was decreased when the H_2O_2 dosage

varied from 5.6 to 78.0 mg L^{-1} . When H_2O_2 dosage was 5.6 mg L^{-1} , the intermediates accumulated abidingly to its maximum value of 5.6 mg L^{-1} as TOC and then decreased. Similarly, the maximum values were 4.7, 3.5, 3.2, and 3.0 mg L^{-1} as TOC in the cases of H_2O_2 dosage equal to 11.2, 22.5, 45.0, and 78.0 mg L^{-1} , respectively. The decline in the maximum concentration of the intermediates revealed that some fraction of mineralization was occurred in parallel with the degradation of MCB.

Applying two-step consecutive kinetic model to the determined intermediate concentration, the mineralization rate constant k_2 was calculated as summarized in Table 2. It can be seen that the value of k_2 was decreased with increasing H_2O_2 dosage. The highest k_2 value was 0.002 min^{-1} under the experimental conditions of H_2O_2 dosage equal to 5.6, 11.2, and 22.5 mg L^{-1} . Notably, when the H_2O_2 dosage was 78.0 mg L^{-1} , the determined k_2 value was lower than

0.001 min^{-1} . According to the principle of the two-step consecutive kinetics, the calculation of k_2 value was depend on the concentration of the intermediates and the value of k_1 . Consequently, the decline of the maximum intermediates concentration as H_2O_2 dosage was increased led to a lower k_2 value.

3.4. Evaluation of Oxygen and H_2O_2 as Electron Acceptors. According to its characteristics as electron acceptor and oxidizing agent, the presence of oxygen in photocatalytic system was beneficial for the photocatalytic degradation of MCB. The experimental results confirmed that the photocatalytic degradation of MCB in the presence of oxygen followed a simplified two-step consecutive kinetics. For kinetic analysis, both degradation and mineralization rate constants had been demonstrated to increase with increasing DO concentration. However, this is an important consideration to bear in mind that the DO concentration in contaminated water may be limited and aeration would cause the stripping of volatile organic compound such as MCB.

It is preferential to use H_2O_2 where there is a limited availability of oxygen. Considering its hydrophilic property, the H_2O_2 would come into contact with the hydroxylated TiO_2 particles in aqueous solution and trap the photoinduced e^- . Furthermore, H_2O_2 could also serve as an oxygen source to improve the mineralization. Excess H_2O_2 , however, could act as $\cdot\text{OH}$ radical scavenger in the photocatalytic system. Moreover, the H_2O_2 may compete with MCB for the active sites of TiO_2 particle [32, 41–44] to suppress the photocatalytic degradation of MCB. To avoid the capture of $\cdot\text{OH}$ radical and competitive adsorption under high H_2O_2 dosage, sequential replenishment of H_2O_2 into UV/ TiO_2 system was suggested.

Referring to Figure 3, the most efficient degradation was observed where the H_2O_2 dosage was 22.5 mg L^{-1} , whereas the optimal H_2O_2 dosage for MCB mineralization was 45.0 mg L^{-1} . Accordingly, total dosage of H_2O_2 equal to 45.0 mg L^{-1} was chosen for the evaluation of the photocatalytic degradation of MCB under various H_2O_2 addition sequences. In the experiment of stepwise addition of H_2O_2 , 22.5 mg L^{-1} of H_2O_2 was added into the TiO_2 suspension, once before irradiation and again after 40 min of illumination time. As the result illustrated in Figure 4(a), 120 min of irradiation was sufficient for complete elimination of MCB in the case when a two-step addition was made. On the contrary, 180 min of illumination time was needed for the one-time addition. The enhancement of the degradation efficiency was correlated to the higher degradation rate constant when the H_2O_2 dosage was 22.5 mg L^{-1} rather than 45.0 mg L^{-1} . Moreover, the second addition of H_2O_2 was attributed to sustain the suppression of the $e^- \cdot \text{h}^+$ pair recombination.

Monitoring the variation of DO concentration during photocatalytic degradation, it was observed that the oxygen accumulated continuously within 120 min of illumination time then decreased thereafter for both cases (Figure 4(b)). The concentration of the intermediates showed a similar tendency as depicted in Figure 4(c). Oxygen generated as a result

FIGURE 4: Comparison of the photocatalytic degradation of MCB under various H_2O_2 : (○) two-step addition and (◇) one-time addition.

of the decomposition of H_2O_2 whereas the accumulation of intermediates was due to the degradation of MCB. According to the effective degradation under the two-step addition of H_2O_2 , the concentration of intermediates increased faster than that under one-time addition of H_2O_2 . Furthermore, since oxygen would participate in the mineralization of MCB, both the concentrations of oxygen and intermediates declined afterward. A comparison of the experimental profiles shows that depletion of the intermediates concentration was shaper for the two-step addition of H_2O_2 than that for the one-time addition. Correspondingly, after 240 min of irradiation the mineralization efficiency of MCB in the case of two-step addition of H_2O_2 was 87.4% higher than the value of 74.1% in the case of one-time addition. The increment in the mineralization efficiency can be explained as due to the restraint of the capture of $\cdot\text{OH}$ radicals, the additional $\cdot\text{OH}$ radicals related with second dose of H_2O_2 , and the participation of oxygen in photocatalytic degradation. Accordingly, it was evident that the sequential

replenishment of H_2O_2 into UV/ TiO_2 system was advisable as a way to improve the efficiency of the photocatalytic degradation.

4. Conclusions

The direct photolysis and the oxidative potential of H_2O_2 were proven to have slight contribution on the degradation of MCB. Notably, UV light and TiO_2 together showed a marked effect. Increasing the DO concentration was beneficial for the photocatalytic degradation of MCB. Correspondingly, the degradation and mineralization rate constants increased with the DO concentration. Owing to the mineralization of MCB occurs through the intermediates, a simplified two-step consecutive kinetics can be used to describe the photocatalytic degradation in UV/ TiO_2/O_2 photocatalysis. For the UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ photocatalysis, H_2O_2 of lower dosage acted as electron acceptor to enhance the degradation efficiency. When the dosage was high, however, the degradation was suppressed due to the capture of $\cdot\text{OH}$ radicals and the competitive adsorption of H_2O_2 . In order to abate the disadvantages caused by using a higher H_2O_2 dosage, sequential replenishment of H_2O_2 into UV/ TiO_2 system was performed. Experimental results demonstrated that both degradation and mineralization efficiencies were enhanced by the restraint of the capture of $\cdot\text{OH}$ radicals, the additional $\cdot\text{OH}$ radicals caused from the second stage addition of H_2O_2 , and the participation of oxygen in photocatalytic degradation.

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