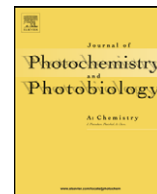




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## Investigation of the roles of active oxygen species in photodegradation of azo dye AO7 in TiO<sub>2</sub> photocatalysis illuminated by microwave electrodeless lamp

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## ABSTRACT

A novel microwave electrodeless lamp (MWL) was used as the light source for microwave assisted TiO<sub>2</sub> photocatalysis to degrade azo dye Acid Orange 7 (AO7). This technique aims to provide a new way to study the synergetic effect of both UV–vis light and microwave irradiations on aqueous solution of catalysts. The roles of active oxygen species in the photodegradation of AO7, such as hydroxyl radical (HO•), positive holes (h<sup>+</sup>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), were investigated to understand the photodegradation mechanism. The presence and roles of these oxidative species were examined using appropriate quenchers. It was found that the degradation of AO7 proceeded via three pathways, namely, UV-induced photocatalytic degradation, visible light-induced dye self-photosensitized degradation and direct photolytic degradation. The percentages of dye degradation by the three pathways were about 31.1%, 39.0% and 19.5%, respectively.

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### 1. Introduction

Much attention has been focused on photocatalytic degradation of organic pollutants mediated by TiO<sub>2</sub> particles in the past two decades. A large extent of evidence has proven the effectiveness of this method in the mineralization of a wide variety of harmful/toxic organic pollutants in wastewaters and towards the purification of drinking water [1]. At present, limited commercial application of this technology is available due to its low quantum efficiency. Most of the photogenerated positive holes (h<sup>+</sup>) and electrons (e<sup>-</sup>) are recombined before they are trapped by hydroxyls or oxygen adsorbed on the catalyst surface. Microwave energy has exhibited its great ability to accelerate reactions and to improve yields and selectivity on synthetic organic chemistry [2]. Recently, microwave irradiation has been used to assist photochemical reactions in the degradation of organic pollutants [3–10]. The results of these experiments showed that microwave irradiation could considerably accelerate the photodegradation of organic pollutants. Horikoshi et al. [11] has reported that specific interactions of

microwave irradiation with the UV-illuminated TiO<sub>2</sub> particle surface have resulted in the increase of photocatalytic oxidation. Such interactions may give rise to the generation of additional surface defects that can directly increase the concentration of hydroxyl radicals or equivalent reactive oxygen species. They have proved using ESR that 20% more hydroxyl radicals were generated by microwave-assisted photocatalysis as compared to sole photocatalysis [12]. Booske et al. [13] suggested that microwave irradiation can generate a non-thermal distribution which enhances ion mobility and diffusion of charge carriers.

Because microwave irradiation is harmful for traditional electrode lamps, more researchers now use microwave electrodeless lamp (MWL) as the light source in microwave-assisted photocatalysis system, which is more compatible with microwave irradiation [11,14,15]. MWL not only avoids the conflict between traditional electrode lamp and microwave irradiation, but also provides a convenient way to study the synergetic effect of UV–vis irradiation and microwave irradiation on photochemical reactions. Moreover, in our earlier studies, it was discovered that MWL was different from traditional lamps in photochemical degradation processes [16–18]. As compared to traditional lamps, MWL results in faster decolorization and complete mineralization of dyes in irradiated homogeneous solutions. In this study, the roles of active oxygen species, hydroxyl radicals, holes and hydrogen dioxide were investigated in the photodegradation of organic pollutants, in an attempt to understand the mechanism of TiO<sub>2</sub> photocatalysis as illuminated

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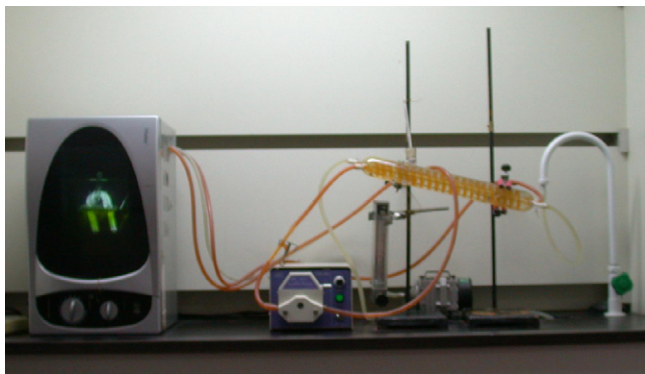


Fig. 1. Experimental setup for TiO<sub>2</sub>/MWL photocatalytic degradation of AO7.

by MWL (TiO<sub>2</sub>/MWL). The azo dye Acid Orange 7 (AO7) was chosen as a typical organic pollutant, and monitored using the UV–vis spectrophotometer and TOC analyzer to evaluate the performance of TiO<sub>2</sub>/MWL in photocatalytic oxidation.

## 2. Experimental

### 2.1. Materials and analysis

AO7 was obtained from Beijing Xuanwu Chemistry Co. and used without further purification. The TiO<sub>2</sub> used was Degussa P-25 (BET area, ca. 50 m<sup>2</sup>/g; TEM particle size, 20–30 nm). KI and isopropanol (*i*-PrOH), which were of analytical-grade, were purchased from Beijing Chemicals Co. Catalase (1870 units/mg) from bovine liver was purchased from Sigma Co. Other chemicals used were of analytical-grade.

The samples were analyzed after removal of catalyst using a syringe filter (0.2 μm). The UV–vis spectrum of the samples was recorded from 200 nm to 650 nm using a U-3010 UV-Vis spectrophotometer (Hitachi Co., Japan). The concentration of AO7 was determined by measuring the absorbance at a fixed wavelength (485 nm) according to the calibration curve established. Total organic carbon (TOC) in solution was measured by a Phoenix 8000 TOC analyzer (Tekmar-Dohrmann Co., USA). The concentration of ozone in solution was measured by the indigo colorimetric method. The concentration of hydrogen peroxide in solution formed during reaction was determined by a colorimetric method [19]. The roles of active oxygen species in dye degradation processes, such as OH•, h<sup>+</sup> and H<sub>2</sub>O<sub>2</sub>, were investigated indirectly with the use of appropriate species quenchers. A series of comparison experiments were made between the original decolorization curves of AO7 solution in TiO<sub>2</sub> and those obtained after addition of quenchers in the initial solution, under otherwise identical conditions. KI, *i*-PrOH and catalase were used as quenchers of these oxidative species. The dosages of KI, *i*-PrOH and catalase were 0.1 mmol/L, 0.1 mmol/L and 500 mg/L, respectively, with reference to previous research works [19–21].

### 2.2. Degradation procedures

The microwave source was from a domestic microwave oven (Haier. Co. Ltd.; power, 700 W; frequency, 2.45 GHz). A cylindrical glass reactor (*D*: 10 cm; *H*: 15 cm) was employed throughout the experiments. Air (0.15 m<sup>3</sup>/h) was bubbled through a sintered glass filter fixed at the bottom of the reactor to homogenize the solution. The reactor was placed inside of the microwave oven as illustrated in Fig. 1. Solution is circulated via a cooler, using a peristaltic pump, and its temperature was kept at 38 ± 1 °C. The whole system was filled with 750 mL of AO7 (100 mg/L) solution, of which 125 mL was

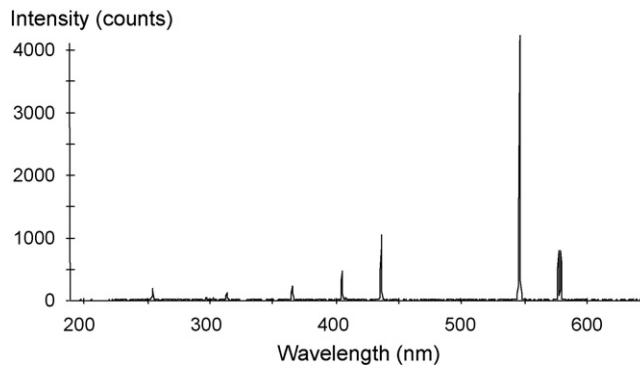


Fig. 2. Emission spectra of MWL.

in the circulation pipe and 625 mL was contained in the reactor. The dosage of P-25 TiO<sub>2</sub> was 0.5 g/L. The U-shaped MWL was made of quartz and filled with mercury and argon. The UV–vis spectrum emitted by the MWL is depicted in Fig. 2. The MWL was suspended at the surface of the solution and about 60% was immersed. During the reaction, power of the MWL measured to be less than 28.1 W [17].

## 3. Results and discussions

### 3.1. The performance of decolorization and mineralization in TiO<sub>2</sub>/MWL

The typical UV–vis spectra obtained during TiO<sub>2</sub>/MWL degradation of AO7 aqueous solutions are shown in Fig. 3. It was observed that MWL irradiation on the aqueous TiO<sub>2</sub> dispersion during a 120 min period led to a continued diminution of the AO7 dye concentration in the solution. No new absorption bands appeared either in the visible region or in the ultraviolet region. The absorption bands of the dye in the visible region decreased with time and finally disappeared at 120 min, resulting in complete decolorization of the solution, which indicated the destruction of its chromophoric structure in the vicinity of the azo-linkage. This was accompanied by a parallel decrease in the intensity of the bands at the ultraviolet region, which indicated that mineralization also occurred. The photodegradation of AO7 was well described by pseudo-first-order

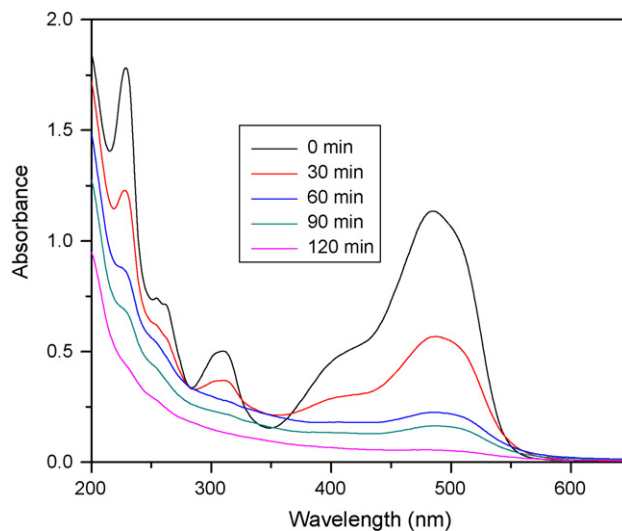


Fig. 3. Absorption spectrum of AO7 solution as a function of irradiation time after 2.5-fold dilution.

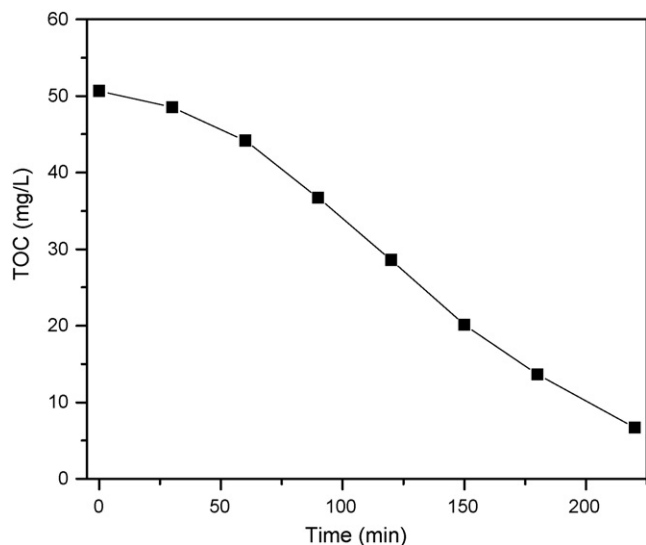


Fig. 4. The change of TOC of the solution as a function of irradiation time.

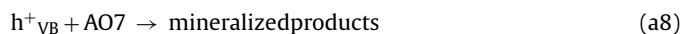
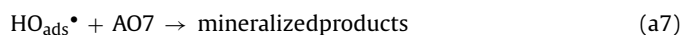
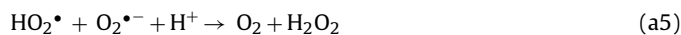
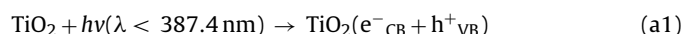
model ( $R^2=0.994$ ) and the rate constant ( $k$ ) was  $0.0212 \text{ min}^{-1}$ . Results of TOC measurements obtained during  $\text{TiO}_2/\text{MWL}$  treatment of the dye solution are presented in Fig. 4. It was proved that  $\text{TiO}_2/\text{MWL}$  also had a good performance on mineralization. The removal of 87% TOC was observed after 220 min.

### 3.2. The possible pathway of AO7 degradation in $\text{TiO}_2/\text{MWL}$

As depicted from Fig. 2, it was found that the wavelength range of MWL light was from 250 nm to 600 nm. Lights appeared at wavelengths 254, 365, 404, 435, 546, and 579 nm, respectively. Because the band gap of anatase  $\text{TiO}_2$  is 3.2 eV (corresponds to  $\lambda = 387.4 \text{ nm}$ ), among these different wavelength lights emitted by the MWL, only the lights at 254 nm and 365 nm could excite  $\text{TiO}_2$  to generate the valence band electrons and the conduction band holes. The light (at 254 nm and 365 nm) emitted by the MWL were over 10 times smaller than those above 387.4 nm, which showed consistency with other results [12,14]. As shown, this part of light (at 254 nm and 365 nm) might play a minor role in the photochemical process. It has been proved that dyes could be degraded under irradiation of visible light in aqueous  $\text{TiO}_2$  suspensions by dye self-photosensitization [22,23]. Horikoshi et al. [12] also have identified that both UV-induced photocatalytic degradation and visible light-induced dye self-photosensitization degradation occurred in the degradation of dye in microwave-assisted photocatalysis by illuminated by electrodeless lamp. Our earlier research [16,17] showed that the degradation of AO7 by direct photolysis under MWL irradiation was also significant. Therefore, the photodegradation of AO7 in  $\text{TiO}_2/\text{MWL}$  might have proceeded via three pathways, UV-induced photocatalysis, visible light-induced dye self-photosensitization degradation and direct photolysis.

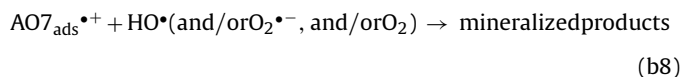
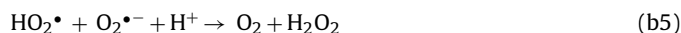
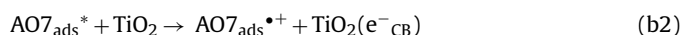
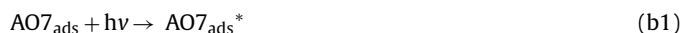
#### 3.2.1. UV-induced photocatalytic degradation ( $\lambda < 387.4 \text{ nm}$ )

The valence band electrons and the conduction band holes can be generated by the excited catalyst under UV light (Eq. (a1)). A series of reactions (Eqs. (a2)–(a6)) followed subsequently to yield active oxygen species, such as the  $\text{HO}^\bullet$  radicals, which led to the oxidative degradation of AO7 [1].



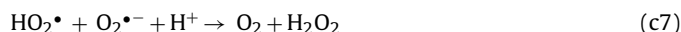
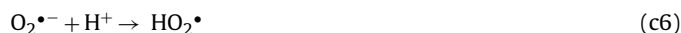
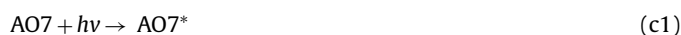
#### 3.2.2. Visible light-induced dye self-photosensitization degradation ( $\lambda > 387.4 \text{ nm}$ )

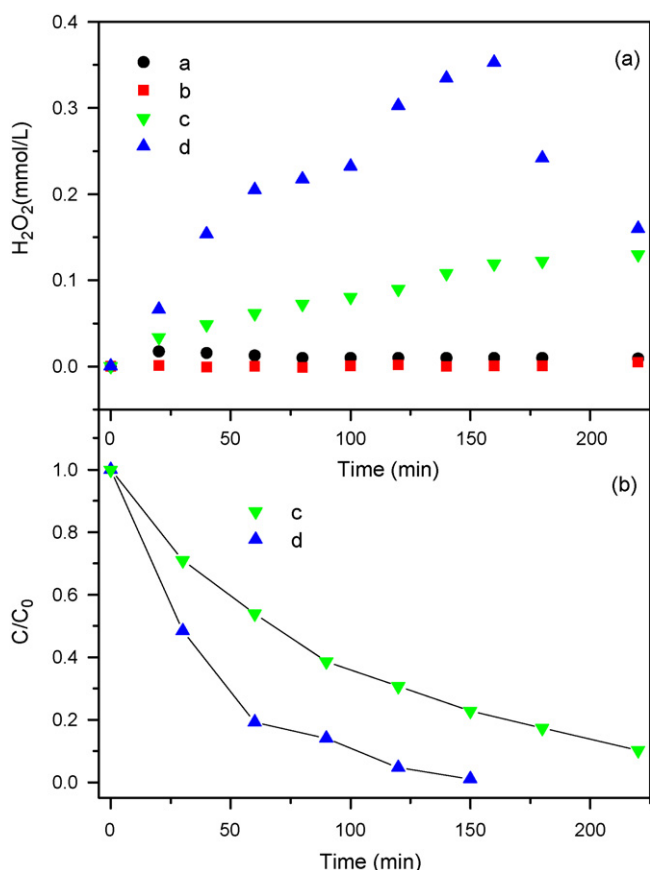
Under visible light irradiation, the  $\text{TiO}_2$  semiconductor is not excited. However, the AO7 is excited under this irradiation to produce singlet and triplet states (Eq. (b1);  $\text{AO7}_{\text{ads}}^*$ ). Subsequently,  $\text{AO7}_{\text{ads}}^*$  injects an electron into the conduction band of the semiconductor with  $\text{AO7}_{\text{ads}}^*$  being converted to  $\text{AO7}_{\text{ads}}^{\bullet+}$  (Eq. (b2)). In turn, the injected electron on the  $\text{TiO}_2$ ,  $\text{TiO}_2(e^-)$ , reacts with adsorbed  $\text{O}_2$ , to produce active oxygen radicals (Eqs. (b3)–(b7)), which resulted in the oxidative degradation of AO7 [22,23].



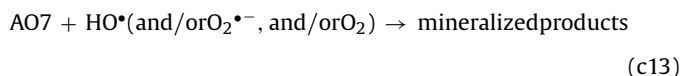
#### 3.2.3. Direct photolysis

Our earlier study [16] showed that direct photolysis of AO7 under MWL irradiation can result in complete decolorization and mineralization. The AO7 was firstly excited to produce singlet and triplet states dye, as in the case of dye self-photosensitization degradation pathway. The difference is that  $\text{AO7}^*$  is subsequently involved in reactions (Eqs. (c2)–(c4)) to generate the hydrated electron ( $e_{\text{aq}}^-$ ) rather than the injection of an electron into the conduction band of the semiconductor. Reactions (Eqs. (c5)–(c7)) took place to yield  $\text{H}_2\text{O}_2$ , which are then decomposed into  $\text{HO}^\bullet$  radicals. Oxidation by these  $\text{HO}^\bullet$  radicals is the major degradation process in direct photolysis. It was also proved that a small amount of  $\text{O}_3$  could be generated in solution under MWL irradiation (Eqs. (c9) and (c10)). Through the photolysis of  $\text{O}_3$ , degradation of AO7 takes place by direct oxidation and  $\text{HO}^\bullet$  oxidation. However, as compared to  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$  has a neglectable role in the degradation of dye in direct photolysis process.



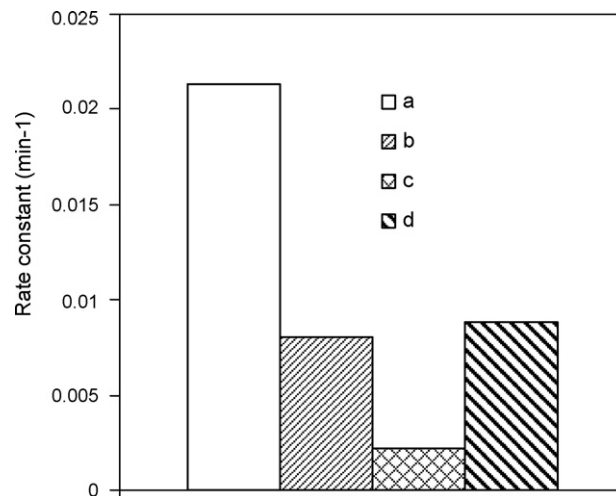


**Fig. 5.** The concentration of H<sub>2</sub>O<sub>2</sub> (a) and AO7 degradation (b) in TiO<sub>2</sub>/MWL and MWL irradiation alone. a – Pure water in MWL; b – pure water in TiO<sub>2</sub>/MWL; c – AO7 solution in MWL; d – AO7 solution in TiO<sub>2</sub>/MWL.



### 3.3. The formation of H<sub>2</sub>O<sub>2</sub>

As discussed above, H<sub>2</sub>O<sub>2</sub>, one of the critical active oxygen species, will be generated in the three degradation pathways. In order to investigate the contributions of the three degradation pathways to H<sub>2</sub>O<sub>2</sub>, the concentrations of H<sub>2</sub>O<sub>2</sub> in AO7 solution were expressed as a function of irradiation time in two processes; under sole MWL irradiation and TiO<sub>2</sub>/MWL. They were measured and their results shown in Fig. 5. The concentrations of H<sub>2</sub>O<sub>2</sub> in pure water under same conditions were also monitored in the two processes, under otherwise identical conditions, in order to estimate the roles of AO7 in the formation of H<sub>2</sub>O<sub>2</sub>. As shown in Fig. 5(a), H<sub>2</sub>O<sub>2</sub> concentration in pure water under sole MWL irradiation was very low. However, H<sub>2</sub>O<sub>2</sub> concentration in AO7 solution under sole MWL irradiation was higher than that in pure water and H<sub>2</sub>O<sub>2</sub> concentration increased with irradiation time. It is thus evident that the formation of H<sub>2</sub>O<sub>2</sub> was related with AO7. As discussed earlier, an amount of H<sub>2</sub>O<sub>2</sub> would be generated through UV photocatalysis in pure water under TiO<sub>2</sub>/MWL. However, experimental results



**Fig. 6.** Effects of quenchers on degradation rate of AO7 in TiO<sub>2</sub>/MWL: (a) without quenchers; (b) with [i-PrOH] = 0.10 mmol/L; (c) with [KI] = 0.10 mmol/L; (d) with [catalase] = 500 mg/L.

showed that the H<sub>2</sub>O<sub>2</sub> concentration was very low in pure water under TiO<sub>2</sub>/MWL. It can therefore be deduced that H<sub>2</sub>O<sub>2</sub> produced through UV photocatalysis in AO7 solution under TiO<sub>2</sub>/MWL would be very low as well.

As shown in Fig. 5(a), the concentration of H<sub>2</sub>O<sub>2</sub> in AO7 solution in TiO<sub>2</sub>/MWL increased with irradiation time and reached 0.35 mmol/L at 160 min. Complete decolorization was achieved at this time and subsequently, the concentration of H<sub>2</sub>O<sub>2</sub> decreased with irradiation time. Because H<sub>2</sub>O<sub>2</sub> generated via UV photocatalysis was limited as discussed above, H<sub>2</sub>O<sub>2</sub> in AO7 solution in TiO<sub>2</sub>/MWL would be mainly generated via direct photolysis and visible light-induced dye self-photosensitization. The accumulation rate of H<sub>2</sub>O<sub>2</sub> at initial 160 min, in TiO<sub>2</sub>/MWL, was two times higher than that under MWL irradiation alone. The generation of H<sub>2</sub>O<sub>2</sub> in AO7 solution under sole MWL irradiation was totally attributed to direct photolysis. The amount of H<sub>2</sub>O<sub>2</sub> generated via direct photolysis in AO7 solution in TiO<sub>2</sub>/MWL could be considered the same as that in AO7 solution under sole MWL irradiation because both reaction conditions should be identical. Hence, it can be deduced that among the H<sub>2</sub>O<sub>2</sub> generated in AO7 solution in TiO<sub>2</sub>/MWL, about 1/3 of H<sub>2</sub>O<sub>2</sub> was generated through direct AO7 photolysis and the other 2/3 was generated via visible light-induced dye self-photosensitization.

### 3.4. The roles of the three degradation pathways

As discussed above, some active oxygen species, such as HO<sup>•</sup>, h<sup>+</sup> and H<sub>2</sub>O<sub>2</sub>, were formed during the reaction in TiO<sub>2</sub>/MWL. The roles of the three degradation pathways of AO7 in TiO<sub>2</sub>/MWL could be estimated by measuring the roles of these oxidative species. The effect of alcohols on the photocatalytic rate has been commonly used to estimate the oxidation mechanism [24–26]. Though direct oxidation of short aliphatic alcohols by photogenerated holes probably occurred, it was considered negligible because in aqueous media, they have very weak adsorption power on TiO<sub>2</sub> surfaces [20,24]. Therefore, alcohols are usually used as diagnostic tools of HO<sup>•</sup> radicals. In this experiment, *i*-PrOH was used as the quencher of HO<sup>•</sup> radicals. The rate constant of reaction between HO<sup>•</sup> radical and *i*-PrOH is 1.9 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, a rate almost of the diffusion limit [20]. The inhibitive effect of 0.1 mmol/L *i*-PrOH on photodegradation of the dye solution is shown in Fig. 6. It was observed that the degradation of AO7 was suppressed in the presence of *i*-PrOH. The

apparent rate constant ( $k$ ) of pseudo-first-order reaction decreased from  $0.0212 \text{ min}^{-1}$  to  $0.008 \text{ min}^{-1}$ . 62.3% decrease of  $k$  indicates that 62.3% of AO7 degradation in  $\text{TiO}_2/\text{MWL}$  was achieved by  $\text{HO}^\bullet$  radicals oxidation.

KI is an excellent scavenger which can react with valence band holes and  $\text{HO}^\bullet$  radicals [27–29]. When iodide ion was used as a diagnostic tool for suppressing the hole and  $\text{HO}^\bullet$  process, the photocatalytic degradation of AO7 was largely inhibited, as shown in Fig. 6. In the presence of  $0.1 \text{ mmol/L}$  KI, the rate constant decreased to  $0.0022 \text{ min}^{-1}$ , which was only 10.4% of that in the absence of KI. This indicated that the total contribution of  $\text{HO}^\bullet$  radicals and holes to the degradation of AO7 was 89.6% and the total contribution of direct oxidation of other active species, such as  $\text{O}_2^{\bullet-}$ ,  $\text{HO}_2^{\bullet-}$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , was only 10.4%. Because the contribution of  $\text{HO}^\bullet$  radicals was 62.3%, it was deduced that the contribution of holes was 27.3%, obtained by subtracting the contribution of  $\text{HO}^\bullet$  radicals (62.3%) from the total contribution (89.6%).

The contribution of  $\text{H}_2\text{O}_2$  in  $\text{TiO}_2/\text{MWL}$  has been investigated using catalase, a quencher of  $\text{H}_2\text{O}_2$  [30,31]. A comparison was made between the original decolorization curves of AO7 solution which were obtained after adding catalase ( $500 \text{ mg/L}$ ) into the initial solution. It was observed that the decolorization rate decreased significantly and the  $k$ , which decreased by 58.5%, was  $0.0088 \text{ min}^{-1}$ . The degradation of AO7 by direct oxidation of  $\text{H}_2\text{O}_2$  was negligible due to its low reaction rate [32]. Therefore, the role of  $\text{H}_2\text{O}_2$  in the degradation of AO7 in  $\text{TiO}_2/\text{MWL}$  was to generate  $\text{HO}^\bullet$  radicals via decomposition. This also indicated that 58.5% AO7 degradation was achieved via oxidation of  $\text{HO}^\bullet$  radicals from the decomposition of  $\text{H}_2\text{O}_2$ . As discussed above, 2/3 of  $\text{H}_2\text{O}_2$  in AO7 solution was generated by visible light-induced dye self-photosensitization and 1/3 of  $\text{H}_2\text{O}_2$  was generated through direct AO7 photolysis. Moreover, the degradation of AO7 via visible light-induced dye self-photosensitization and direct photolysis were mainly achieved by oxidation of  $\text{HO}^\bullet$  radicals from the decomposition of  $\text{H}_2\text{O}_2$  generated in the two pathways. It could be estimated that the contribution of visible light-induced dye self-photosensitization degradation and direct photolysis to the degradation of AO7 in  $\text{TiO}_2/\text{MWL}$  was 39.0% and 19.5%, respectively.  $\text{H}_2\text{O}_2$  and holes are two sources of the  $\text{HO}^\bullet$  radicals in  $\text{TiO}_2/\text{MWL}$ . So, holes were the only source of  $\text{HO}^\bullet$  radicals in the presence of catalase. As discussed earlier, the total contribution of  $\text{HO}^\bullet$  radicals to AO7 degradation was 62.3% and it could be deduced that 3.8% of this AO7 degradation was attributed by  $\text{HO}^\bullet$  radicals from these holes. This figure was obtained by subtracting the contribution of  $\text{H}_2\text{O}_2$  (58.5%) from the total contribution of  $\text{HO}^\bullet$  radicals (62.3%). It was found that about 31.1% of the AO7 degradation in  $\text{TiO}_2/\text{MWL}$  was achieved via UV photocatalytic degradation and this was calculated by adding the direct contribution (27.3%) of holes to the indirect contribution (3.8%) of  $\text{HO}^\bullet$  radicals from these holes.

#### 4. Conclusion

$\text{TiO}_2/\text{MWL}$  had excellent performance on the decolorization and mineralization of AO7. A large amount of active oxygen species, such as  $\text{HO}^\bullet$ ,  $h^+$  and  $\text{H}_2\text{O}_2$ , were generated, resulting in the degradation of AO7. The degradation of AO7 in  $\text{TiO}_2/\text{MWL}$  proceeded via three pathways, UV-induced photocatalytic degradation, visible light-induced dye self-photosensitization and direct photolytic degradation. The respective percentages of dye degradation by the three pathways were about 31.1%, 39.0% and 19.5%.

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