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## Photocatalytic degradation of 4-*tert*-octylphenol in water and the effect of peroxydisulfate as additives

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### ABSTRACT

Photocatalytic degradation of 4-(*tert*-octyl)phenol (4-OP) has been investigated by recirculating the aqueous solution through a packed bed reactor with TiO<sub>2</sub>. The first-order rate constant  $k$  for the degradation of 4-OP was evaluated to be  $5.40 \times 10^{-3} \text{ min}^{-1}$  and an activation energy of  $18.6 \text{ kJ mol}^{-1}$  was obtained. The rate constant  $k$  was not dependent of the flowrate but a decrease in total organic carbon (TOC) became smaller as the flowrate increased. Under the illumination for 6 h at the flowrate of  $28.5 \text{ ml min}^{-1}$ , 83.2% of 4-OP was degraded but 60.7% of the initial TOC was remained. Measurements of LC/MS using electrospray ionization revealed the formation of byproducts having molecular weights of 136, 178, 192, 220 and 222. Possible candidates for these byproducts were proposed. The degradation rate of 4-OP was remarkably accelerated by addition of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>: 4-OP was completely disappeared under irradiation of 4 or 2 h, respectively, in the presence of  $4 \times 10^{-3}$  or  $2 \times 10^{-2} \text{ mol dm}^{-3}$  K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. In the latter case, the TOC decreased to 34.6% by continuing the irradiation even after 4-OP was disappeared. In the presence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, 4-OP was degraded without TiO<sub>2</sub>, which is attributable to the reaction by SO<sub>4</sub><sup>-</sup> radicals. We demonstrated that the UV/TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system was more appropriate than the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> for decontamination of 4-OP in water.

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### 1. Introduction

Alkylphenol ethoxylates (APE) are a group of nonionic surfactants that have been used for many years as detergents, emulsifiers, and dispersing agents [1,2]. During the biodegradation of APE in sewage treatment plants, alkylphenols are produced as metabolites, which have been shown to have a higher toxicity, estrogenic activity [3–5], persistence, and tendency toward bioaccumulation than the parent substrate. Especially, nonylphenols and octylphenols have been reported to bioaccumulate in the lipids of water organisms [6–8].

Several oxidative methods have been proposed for the remediation of water and wastewater effluents contaminated with alkylphenol. Degradation of 4-(*tert*-octyl)phenol (4-OP) under ultrasonic irradiation [9], photocatalytic degradation of alkylphenols on TiO<sub>2</sub> [10], microbial degradation of nonylphenol [11] and removal of alkylphenols during ozonation [12,13] have been inves-

tigated. Among them, TiO<sub>2</sub> photocatalysis has more advantages over other techniques because it is faster than biodegradation and cheaper than ozonation or sonication. Furthermore TiO<sub>2</sub> can be activated by solar energy.

It is well known that most organic compounds can be oxidized to CO<sub>2</sub> by TiO<sub>2</sub> photocatalysis [14–17]. Previously, we have reported that trichloroethylene in water was mineralized on porous TiO<sub>2</sub> pellets prepared by sol–gel method [18] and 4-chlorophenol was completely dechlorinated and partially mineralized in highly dispersed TiO<sub>2</sub> sols [19]. We have also reported that the addition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> remarkably accelerated the degradation rate of TCE because S<sub>2</sub>O<sub>8</sub><sup>2-</sup> acted as an electron acceptor to inhibit the recombination process between the photogenerated electrons and holes [18]. Degradation of endocrine disrupting chemicals including alkylphenols using TiO<sub>2</sub> photocatalyst has been reported [10] but the experiments were performed at very low concentrations such as  $100 \mu\text{g L}^{-1}$  and intermediates as well as degradation pathway have not been discussed in details. In this study, we examined the photocatalytic degradation of 4-OP in order to clarify the intermediates and effect of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> to accelerate the degradation rate.

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## 2. Materials and methods

### 2.1. Chemicals

4-OP for environment analysis grade was obtained from Wako Pure Chemical Industries (Osaka, Japan). TiO<sub>2</sub> powder (Degussa P-25) was purchased from Japan Aerosil and TiO<sub>2</sub> immobilized ceramic balls, ST-B21 (0.5 mm in diameter) and ST-B23 (3.0 mm in diameter), were from Ishihara Sangyo (Tokyo, Japan). The TiO<sub>2</sub> amount loaded on these balls was 23 wt% and their BET surface area was 70 m<sup>2</sup> g<sup>-1</sup> according to the data given by the supplier. Other chemicals were of guaranteed reagent grade and used without further purification. Laboratory grade water was prepared with a Milli-Q pure water system.

### 2.2. Experimental procedures

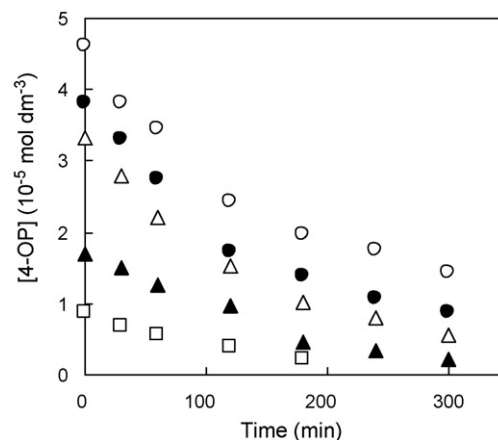
Aqueous solutions containing  $5 \times 10^{-5}$  mol dm<sup>-3</sup> 4-OP were prepared by dissolving the neat compound into water under sonication. Degradation experiments were performed by using a circulation system where the TiO<sub>2</sub> immobilized ceramic balls were packed in spiral glass tubing (Pyrex, inner diameter: 6 mm, outer diameter: 8 mm, total volumes: 28 cm<sup>3</sup>). A 6 W fluorescent black light bulb was located in the center of annulus of the spiral tubing. A peristaltic pump was used for circulating 1 L of aqueous 4-OP solution in a reservoir which was immersed in water thermostated at 30 °C. Glass inlet and outlet in the reservoir were connected by fluoroelastomer tubing (Fluran F-5500-A, NORTON) with the pump and the photoreactor. After the sample solution was circulated for 1 h, the lamp was ignited. Aliquot samples were withdrawn at appropriate times, filtrated by filter (0.45 μm) and analyzed by a high performance liquid chromatograph (HPLC, Shimadzu) and total organic carbon analyzer (TOC 5000A, Shimadzu).

Analyses by liquid chromatography-mass spectrometry (LC/MS 2010, Shimadzu) were performed with a C18 column (Waters, XTerra MS 2.1 mm i.d. × 150 mm) by using methanol as a mobile phase at a flow rate of 0.2 ml min<sup>-1</sup>. The mass spectrometry was operated in negative mode electrospray ionization (ESI). For analyzing particles which were formed during the reaction, a GC/MS instrument (6890N/5973, Agilent Technologies) equipped with a capillary column (DB-5MS, 30 m × 0.25 mm i.d., film thickness 0.25 μm) was used.

## 3. Results and discussion

### 3.1. Comparison of the photocatalytic activity of various TiO<sub>2</sub>

Photodegradation experiments were performed by packing 12 g of ST-B21 or ST-B23 or circulating the 4-OP aqueous solution suspended with 2 g of P-25 powders in the spiral photoreactor tubing. Before irradiation, a decrease in the 4-OP concentration due to the adsorption on TiO<sub>2</sub> surface was observed to be less than 6% of the initial concentration ( $5 \times 10^{-5}$  mol dm<sup>-3</sup>). 4-OP was effectively photodegraded in the following order: P-25 powder > ST-B21 > ST-B23. (The first rate constant  $k$  which was described in the following section was evaluated to be  $1.80 \times 10^{-2}$ ,  $1.34 \times 10^{-2}$  and  $5.40 \times 10^{-3}$  min<sup>-1</sup>, respectively.) The P-25 powders are very fine particles and the ST-B21 (0.5 mm in diameter) is smaller than ST-B23 (3 mm in diameter). Thus, the difference in the activity might be due to the effective surface area exposed to light. Hereafter, ST-B23 was used in the experiments, since centrifugation is needed for P-25 before HPLC measurements and packing the photoreactor tightly with ST-B21 prevented the reaction solution from flowing.



**Fig. 1.** Variations of the 4-OP concentration against irradiation time. Aqueous solutions containing  $4.6$  (○),  $3.8$  (●),  $3.3$  (△),  $1.7$  (▲) or  $0.87$  (□)  $\times 10^{-5}$  mol dm<sup>-3</sup> 4-OP were circulated through 12 g of TiO<sub>2</sub> at the flowrate of 100 ml min<sup>-1</sup> and 30 °C.

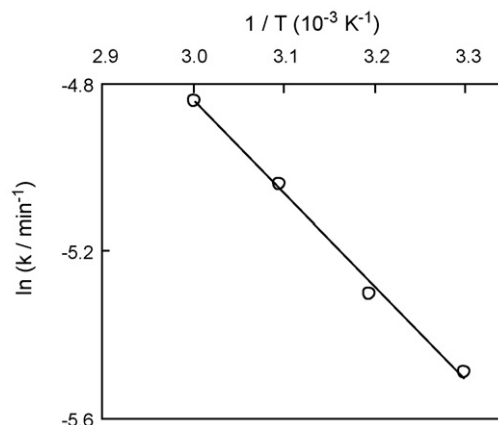
### 3.2. Kinetic aspects

Fig. 1 showed the time course of the photodegradation of 4-OP at various initial concentrations. Plots of  $\ln[4\text{-OP}]$  vs. irradiation time showed straight lines and thus the reaction follows the first-order kinetics.

$$\text{Rate} = k[4\text{-OP}] \quad (1)$$

The first-order rate constant  $k$  was estimated to be  $5.40 \times 10^{-3}$  min<sup>-1</sup> from the slope of the plots of  $\ln[4\text{-OP}]$  vs. irradiation time. Fig. 2 depicted an Arrhenius plot where  $k$  values were obtained from the experiments under the reaction temperature of 30, 40, 50 and 60 °C. The apparent activation energy was calculated to be 18.6 kJ mol<sup>-1</sup>. Such a small value suggests that the photocatalytic degradation of 4-OP is not sensitive to temperature. The charge separation by absorbing photon occurs at high speeds. Since photocatalytic reaction occurs on the TiO<sub>2</sub> surface, the apparent activation energy is related to the activation energy of the surface reaction and the enthalpy changes accompanying the adsorption of reactants. Apparent activation energy as low as 10 kJ mol<sup>-1</sup> was obtained for the photocatalytic degradation of phenol over anatase TiO<sub>2</sub> [20].

Fig. 3 indicated the effect of flowrate (28.5, 60.5, 88.0 and 115 ml min<sup>-1</sup>) on the rate constants  $k$  and TOC decreased ( $[\text{TOC}]_{\text{decreased}}$ ) during the irradiation for 4 h. The value of  $k$  was not dependent on the flowrate but that of  $[\text{TOC}]_{\text{decreased}}$  decreased



**Fig. 2.** Arrhenius plots.

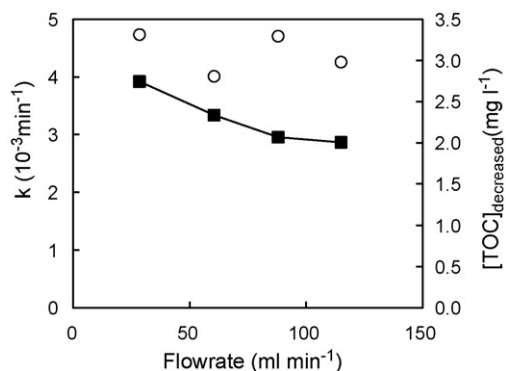


Fig. 3. Effect of flowrate on the rate constant  $k$  (○) and TOC decreased (■) for 4 h.

as the flowrate increased. These findings indicate that 4-OP was effectively degraded on the TiO<sub>2</sub> surface but mineralization of the produced intermediates required an enough time to contact the TiO<sub>2</sub>. Fig. 4 showed the time course of the concentration of 4-OP and TOC at the flowrate of 28.5 ml min<sup>-1</sup>. Under the illumination for 6 h, 83.2% of 4-OP was degraded but 4-OP mineralized to CO<sub>2</sub> was only 39.3%. In order to identify byproducts, the reaction solution after the photocatalytic experiment was analyzed by LC/MS but no peaks were detected. Thus, the LC/MS analysis was performed after concentrating the solution as follows: 100 ml of the reaction solution was extracted with 30 ml of dichloromethane and the obtained extract was dehydrated with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated and dried. The resulting residue was dissolved into 1 ml of methanol and analyzed by LC/MS using methanol as a mobile phase. In total ion chromatogram in the range of  $m/z$  50–500, three peaks were detected. Mass spectra of three peaks were showed in Fig. 5. One of

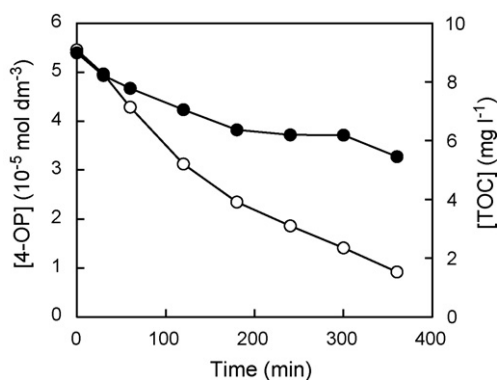


Fig. 4. Variations of 4-OP concentration (○) and TOC (●) against irradiation time. Conditions were the same as in Fig. 3 except for the flowrate of 28.5 ml min<sup>-1</sup>.

them was identified to be unreacted 4-OP because its mass spectrometry (Fig. 5(c)) coincided with that of the authentic sample of 4-OP. Since electrospray is a soft ionization method, the negative mode scan for alkylphenols shows the deprotonated molecule to be the most abundant [21,22]. In Fig. 5(C), most abundant ion was observed at  $m/z$  205, which is ascribed to the deprotonated molecule of 4-OP (molecular weight, MW: 206). The intensity of the peak was larger by a factor of 2.3 than the peak at  $m/z$  237. The latter peak was attributable to attachment of methanol as a solvent (4-OP-H+CH<sub>3</sub>OH). If we assume that byproducts show peaks at  $m/z$  of MW – 1 and MW – 1 + 32 and the ratio of intensities at both peaks was the same as that obtained in the mass spectrometry of 4-OP, the mass spectra in Fig. 5(a) and (b) suggest that the MWs of the byproducts were 136, 178, 192, 220 and 222. The possible candidates for byproducts were listed in

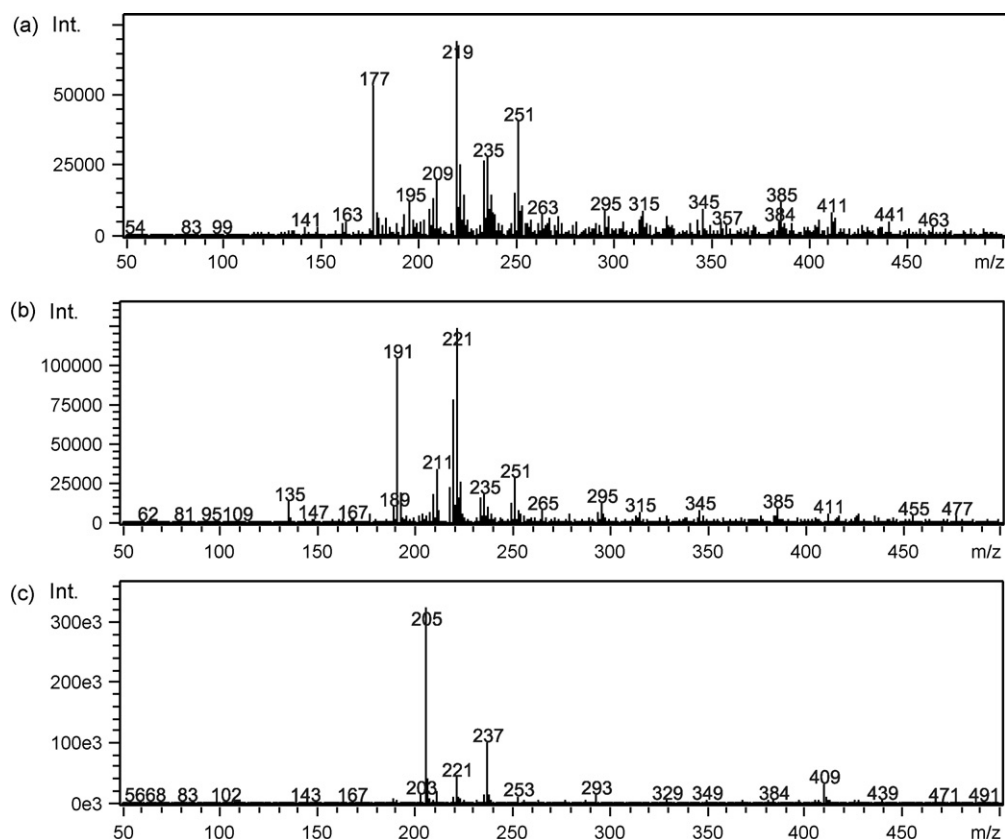
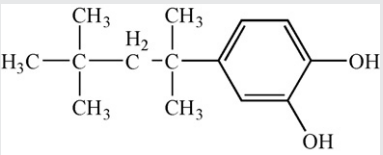
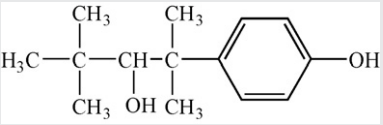
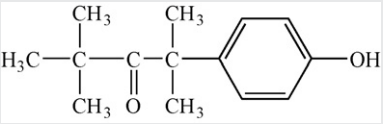
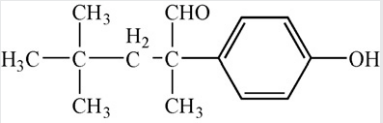
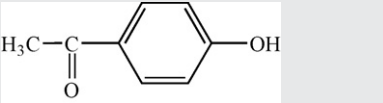
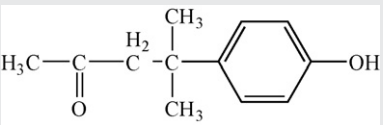
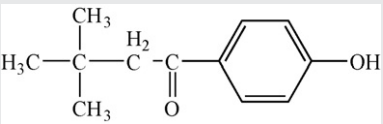
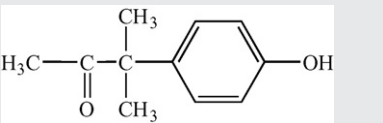


Fig. 5. Mass spectra of the three peaks (retention time: (a) 2.1 min, (b) 2.3 min, (c) 2.6 min) obtained in LC/MS chromatogram of the reaction solution after irradiation for 6 h.

**Table 1**  
Chemical structures of the byproducts

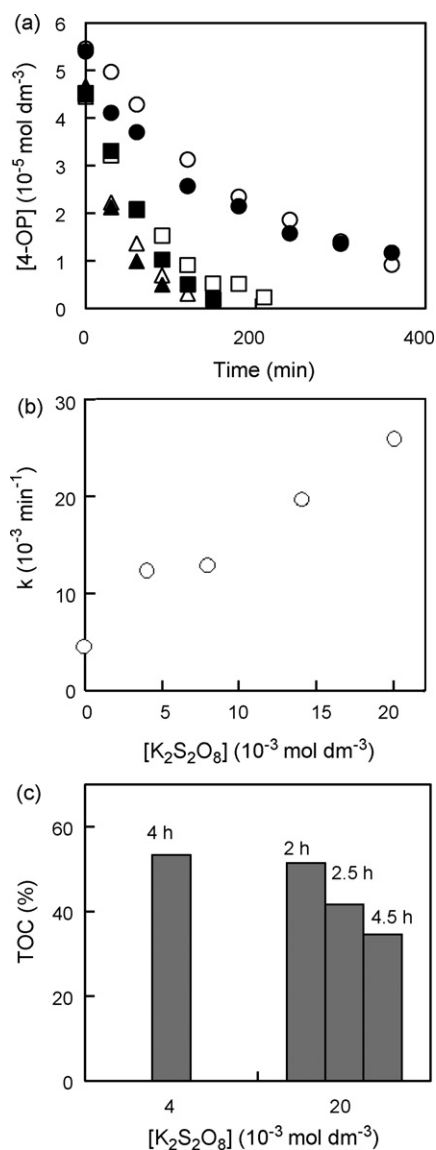
Chemical structures (MW)	
I	 (222)
II	 (222)
III	 (220)
IV	 (220)
V	 (136)
VI	 (192)
VII	 (192)
VIII	 (178)

**Table 1.** These compounds come from the oxidation on different sites of 4-OP alkyl chain. 4-*Tert*-octylcatechol (product I in Table 1) was identified as the product from photolysis of 4-OP by UV or H<sub>2</sub>O<sub>2</sub>/UV [23]. The compounds I–V in Table 1 were reported as byproducts from the degradation of 4-OP photoinduced by Fe(III) [24].

These products retain phenol moiety which is the essential functional group to exhibit the estrogenic property. The phenol moiety must be decomposed in order to weaken the estrogenic activity. It is well known that most organic compounds including phenols can be oxidized to CO<sub>2</sub> by TiO<sub>2</sub> photocatalysis because photogenerated holes exhibit strong oxidizing power. As mentioned in Fig. 3, the mineralization of byproducts was accelerated as the flowrate decreased although the degradation of 4-OP was not affected. This suggests that a longer the contact time of byproducts with TiO<sub>2</sub> is, more likely the complete mineralization occurs. If we could accelerate the degradation of 4-OP, degradation of byproducts would proceed more effectively after all of 4-OP is disappeared. Thus, we tried to accelerate the degradation rate of 4-OP.

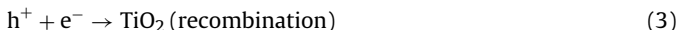
### 3.3. Acceleration of the degradation rate

Photocatalytic oxidation on TiO<sub>2</sub> occurs by photogenerated holes. It is well known that oxidation rate increases when recombination process between the photogenerated holes and electrons is suppressed. Oxygen dissolved in the reaction solution acts as an electron acceptor. Peroxydisulfate has been shown to be a more reliable and cheaper electron acceptor [25]. Effect of oxygen and peroxydisulfate as the electron acceptor was examined as shown in Fig. 6(a). The rate constant *k* under air bubbling was calculated to be  $7.62 \times 10^{-3} \text{ min}^{-1}$  which is higher by a factor of 1.4 than that without air purging. On the other hand, the degradation of 4-OP was remarkable accelerated by adding peroxydisulfate:  $5 \times 10^{-5} \text{ mol dm}^{-3}$  4-OP was completely disappeared under the irradiation of 4 or 2 h, respectively, in the presence of  $4 \times 10^{-3}$  or  $2 \times 10^{-2} \text{ mol dm}^{-3} \text{ K}_2\text{S}_2\text{O}_8$ . The degradation of 4-OP in the presence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> also followed the first-order kinetics. Fig. 6(b) depicted



**Fig. 6.** (a) Effect of air-bubbling and addition of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Conditions were the same as in Fig. 4 except for air-bubbling (●) and the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration was 0 (○), 4 (□), 8 (■), 14 (△) and 20 (▲) × 10<sup>−3</sup> mol dm<sup>−3</sup>. (b) Effect of the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration on the rate constant *k*. (c) TOC (%) remained in the solution after irradiation of 4 h in the presence of  $4 \times 10^{-3} \text{ mol dm}^{-3} \text{ K}_2\text{S}_2\text{O}_8$  or 2, 2.5, and 4.5 h in the presence of  $2 \times 10^{-2} \text{ mol dm}^{-3} \text{ K}_2\text{S}_2\text{O}_8$ .

the dependence of  $k$  on the concentration of  $S_2O_8^{2-}$ . The  $k$  value for  $2 \times 10^{-2} \text{ mol dm}^{-3} K_2S_2O_8$  was evaluated to be  $2.58 \times 10^{-2} \text{ min}^{-1}$  which is higher than that for  $4 \times 10^{-3} \text{ mol dm}^{-3}$  by a factor of 2.1. Fig. 6(c) indicated the TOC percent remained in the solution. Just after the peak of 4-OP in HPLC was completely disappeared (4 or 2 h, respectively, with  $4 \times 10^{-3}$  or  $2 \times 10^{-2} \text{ mol dm}^{-3} K_2S_2O_8$ ), 53.4% or 51.5% of the initial TOC was remained. By continuing the experiments in the presence of  $2 \times 10^{-2} \text{ mol dm}^{-3} K_2S_2O_8$ , the TOC decreased to 34.6% at the irradiation of 4.5 h.



If  $S_2O_8^{2-}$  acts only as the electron acceptor to suppress the recombination process, the  $k$  value must be the same as that with air-purging, in which oxygen acted as the electron acceptor. However, the  $k$  value even with  $4 \times 10^{-3} \text{ mol dm}^{-3} K_2S_2O_8$  was higher than that with air-purging by a factor of 1.61. Such a higher value suggests that the degradation of 4-OP by  $SO_4^-$  radicals occurred. The  $SO_4^-$  radical is a strong oxidant capable of mineralizing phenolic compounds such as butylated hydroxyanisole in water [26]. The produced  $SO_4^{2-}$  ion is not considered to be a pollutant.

#### 3.4. Comparison with homogeneous photolysis or thermal decomposition

Thermal or photochemical activated decomposition of  $S_2O_8^{2-}$  ion to  $SO_4^-$  radical has been reported. Usually, UV at 254 nm was used to decompose  $S_2O_8^{2-}$  to  $SO_4^-$  radical. Although the black light we used in this study emitted 365 nm, we examined the degradation of 4-OP in the presence of  $S_2O_8^{2-}$  under illumination (UV/ $S_2O_8^{2-}$ ). The degradation of 4-OP was performed by recirculation of the 4-OP aqueous solution containing 4, 8, 14 or  $20 \times 10^{-3} \text{ mol dm}^{-3} K_2S_2O_8$  through the spiral tubing which was not packed with  $TiO_2$ . Fig. 7(a) indicated that concentrations of 4-OP decreased linearly against the irradiation time. Fig. 7(b) showed the dependence of the slopes obtained from Fig. 7(a) on the initial concentration of  $S_2O_8^{2-}$ . Reaction mechanism in the UV/ $S_2O_8^{2-}$  system can be represented as follows:



In a similar manner, phenols, cresols, or benzyl alcohols have been shown to be oxidized by the  $SO_4^-$  radicals [27,28]. If we assume a steady state concentration for  $SO_4^-$  radical, the degradation rate of 4-OP was expressed as the following equation.

$$\frac{-d[4\text{-OP}]}{dt} = k[SO_4^-][4\text{-OP}] = I_{\text{abs}}\varphi \quad (8)$$

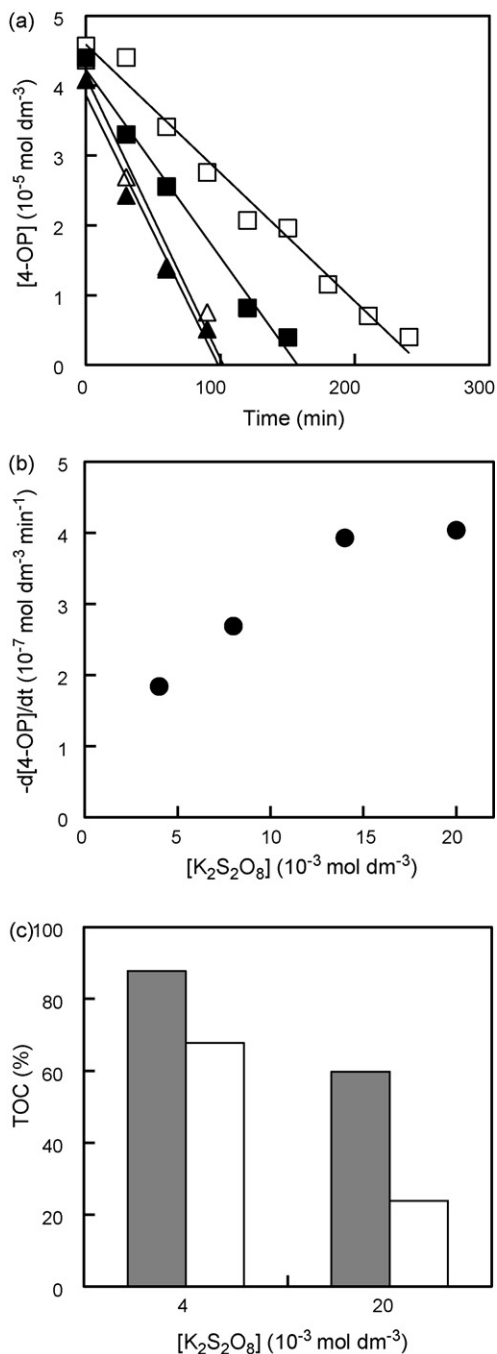
where  $k'$  is the rate constant for Eq. (7),  $I_{\text{abs}}$  denotes the light intensity absorbed by  $S_2O_8^{2-}$  and  $\varphi$  is the fraction of the formation of  $SO_4^-$  radical from the photoexcited  $S_2O_8^{2-}$ . According to Lambert–Beer's law, the  $I_{\text{abs}}$  value depends on the concentration of  $S_2O_8^{2-}$  as follows:

$$I_{\text{abs}} = I_0(1 - 10^{-\alpha c}) \quad (9)$$

where  $I_0$ ,  $\alpha$  and  $c$  denote the incident light intensity, constant comprising of molar extinction coefficient and length of light pass and concentration of  $S_2O_8^{2-}$ , respectively. Eq. (8) means that the 4-OP concentration decreases linearly against the irradiation time and the slope corresponds to  $I_{\text{abs}}\varphi$ . Eq. (9) indicates that as the  $S_2O_8^{2-}$

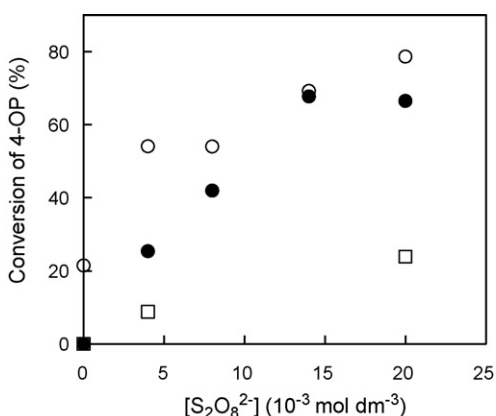
concentration increases,  $I_{\text{abs}}$  increases and approaches to a limiting value. This dependence was in good agreement with the result as shown in Fig. 7(b).

When we compared Figs. 7(a) and 4, 4-OP was degraded more effectively by the UV/ $S_2O_8^{2-}$  system than the photocatalysis on  $TiO_2$ . However, more TOC was remained in the UV/ $S_2O_8^{2-}$ , suggesting that mineralization was more difficult to occur. Furthermore, it must be noted that fine white particles were formed as the reaction proceeded in the UV/ $S_2O_8^{2-}$  system. Fig. 7(c) illustrated that the TOC in the reaction solution decreased after filtration. This



**Fig. 7.** (a) Homogeneous photodegradation of 4-OP in the presence of 4 (□), 8 (■), 14 (△) or 20 (▲)  $\times 10^{-3} \text{ mol dm}^{-3} K_2S_2O_8$  without  $TiO_2$ . (b) Effect of the  $K_2S_2O_8$  concentration on the slope obtained in (a). (c) TOC (%) remained in the solution at the irradiation time of 4 h in the presence of  $4 \times 10^{-3} \text{ mol dm}^{-3} K_2S_2O_8$  and 2 h of  $2 \times 10^{-2} \text{ mol dm}^{-3} K_2S_2O_8$ . Open bars showed the values obtained after filtration.





**Fig. 8.** Comparison of photocatalysis (○), homogeneous photodegradation in UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (●) and thermal decomposition (□) at the irradiation time of 1 h.

suggested that the particles were organic compounds which were insoluble to water. The particles were collected on filter (0.45 μm) and extracted with 0.5 ml of hexane. The GC–MS analyses of the extracts showed some unidentified peaks as well as the peak which was identified to 4-OP. The fact that ionic species in water decrease the aqueous solubility of compounds has been known and is commonly referred to as “salting out”. Zhou reported that salinity has a significant impact on the solubility and sediment/water interaction of 4-OP and other similar compounds [29]. Thus, the fine white particles formed in the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system was due to the salting out of organic compounds by increasing the ionic species such as SO<sub>4</sub><sup>2-</sup>. Such white fine particles were not formed in the UV/TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system. The reason might be lower concentrations of SO<sub>4</sub><sup>2-</sup> ions since photon was mainly absorbed by TiO<sub>2</sub> rather than by S<sub>2</sub>O<sub>8</sub><sup>2-</sup> or the formation of more water-soluble byproducts in the UV/TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system.

Fig. 8 showed the 4-OP conversion at the reaction time of 1 h in the UV/TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> systems together with that in thermal decomposition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. At 30 °C, 4-OP was degraded by SO<sub>4</sub><sup>-</sup> radicals that were formed by thermal decomposition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. Conversion of 4-OP by the thermal decomposition was about one-third of that in the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system. At the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration of 4 × 10<sup>-3</sup> mol dm<sup>-3</sup>, the 4-OP conversion in the UV/TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> was much higher than that in the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. On the other hand, the 4-OP conversions in both systems were not so different at the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration more than 8 × 10<sup>-3</sup> mol dm<sup>-3</sup>. However, the decrease in TOC was smaller and fine particles precipitated in the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system as mentioned above.

#### 4. Conclusion

We developed the recirculating system of aqueous 4-OP solutions through the packed bed reactor with TiO<sub>2</sub>. The addition of

S<sub>2</sub>O<sub>8</sub><sup>2-</sup> improved the degradation rate by preventing the recombination process of the photogenerated holes and electrons and by producing SO<sub>4</sub><sup>-</sup> radicals that are capable of oxidizing 4-OP. At the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration of 2 × 10<sup>-2</sup> and 5 × 10<sup>-5</sup> mol dm<sup>-3</sup>, 4-OP was completely disappeared at the irradiation of 2 h and the TOC decreased to 34.6% at the irradiation of 4.5 h. In the presence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, 4-OP was photodegraded without TiO<sub>2</sub>. However, mineralization was difficult to occur in the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system and fine particles precipitated. Although further research is needed to clarify the difference between the byproducts in the UV/TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> systems, it is concluded that the UV/TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system was more appropriate for decontamination of 4-OP in water.

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