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Photocatalytic degradation of 4-*tert*-octylphenol in a spiral photoreactor system

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Abstract

A spiral photoreactor system (SPS) was developed for the degradation of 4-*tert*-octylphenol (4-t-OP) in aqueous phase. 4-t-OP was previously considered as an endocrine disrupting compound frequently present in water. The direct photodegradation reaction caused by the SPS was found to accord with the characteristic of apparent first-order reaction with reaction rate constant $k = 4.8 \times 10^{-2} \text{ min}^{-1}$. However, the direct photodegradation reaction could not make the 4-t-OP mineralized. The photodegradation efficiency increased from 88% to 91.2% in 45 min irradiation period after the internal surface of SPS was sintered with TiO_2 thin film as catalyst. Catalyst concentration, number of catalyst coating layers and initial concentration of 4-t-OP were proven to be the factors affecting the photocatalytic degradation performance of the SPS on aqueous 4-t-OP. The degradation mechanism was investigated and the byproducts were analyzed using total organic carbon analyzer (TOC) and LC-MS. The possible chemical structures of the products were suggested. SPS with single layer of TiO_2 prepared by sintering 13.6% of TiO_2 precursor was proven to be more efficient than most of previous systems for removal of 4-t-OP from aqueous phase. 28.3% of the 4-t-OP was mineralized in 45 min according to the decreased amount of TOC value.

Key words: spiral photoreactor system; UV light; 4-t-OP; photocatalytic degradation; TiO_2

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Introduction

Octylphenols (OPs), a kind of alkylphenols, are very common raw materials for industrial, household, and commercial applications. OPs are also final biodegradation products of octylphenol polyethoxylates (OPEOs) in sewage treatment systems (Kohtani et al., 2003). Recently, OPs were reported to be widely distributed in water of rivers and lakes as well as aquatic sediments (Ferguson et al., 2001), tending to bio-accumulate in the lipids of aquatic organisms (Tsuda et al., 2000). Being endocrine disrupting compounds (EDCs) as well, OPs may cause modification of sexual development and reproductive function in exposed life forms (Aydoğan and Barlas, 2006).

The main isomer of OPs, 4-*tert*-octylphenol (4-t-OP) was previously reported as the most potent xenoestrogen of OPs (Madsen et al., 2006). In recent years, a great deal of attention has been paid to the removal of 4-t-OP from aquatic environments. Several biodegradation methods were tested for 4-t-OP. For example, 4-t-OP could be biodegraded by *Tolypothrix*, however, its degradation efficiency was only 54.65% after 5 days exposure (Zhao et al., 2007). The degradation efficiency of 4-t-OP through aerobic approach reached 90%, whereas it took 15 days

(Ying and Kookana, 2005). Photodegradation method was also attempted. It was shown that the degradation efficiency reached 80% after 8 hr irradiation when 0.05 mol/L H_2O_2 was added in the initial solution and the efficiency of degradation reached > 90% after 5 hr irradiation when the 4-t-OP aqueous solution was circulated through 1.2 g of TiO_2 (Neamu et al., 2009; Yamazaki et al., 2008). Most of these efforts have proven 4-t-OP recalcitrant.

TiO_2 is photoactive in the UV region (< 400 nm) and is currently considered as the most promising catalyst in air and water decontamination research area (Linsebigler et al., 1995). TiO_2 photocatalysis has more advantages over other techniques because of its faster photocatalytic performance compared to biodegradation method and lower cost than ozonization or sonication (Yamazaki et al., 2008). Many organic compounds can be ultimately oxidized into CO_2 by TiO_2 photocatalysis (Yamazaki et al., 2008; Ike et al., 2002). In this study, we designed and built a spiral photoreactor system (SPS) and developed a method for efficient degradation of 4-t-OP in water solution with TiO_2 used as a photocatalyst. The effects of catalyst dosage, number of TiO_2 film layers and initial concentration of 4-t-OP on the photodegradation efficiency were evaluated under ultraviolet light (254 nm) irradiation followed by TOC and LC-MS analysis.

The SPS sintered with TiO_2 thin film has an important

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application prospect for water purification. It can be used in the degradation of organic pollutants in wastewater treatment because of its high photodegradation efficiency. It is also worth mentioning that the photocatalyst can be used in an immobile phase. Thus the effluent of SPS could go to next process directly without sedimentation or filtration.

1 Materials and methods

1.1 Materials

Analytical grade 4-t-OP was purchased from Sigma-Aldrich Chemie GmbH. HPLC grade methanol was obtained from J&K Chemicals (USA). Titanium dioxide was prepared by the sol-gel method with tetra-*n*-butyl titanate as raw material (Wen et al., 2001). Tetra-*n*-butyl titanate, nitric acid, ethanol and acetylacetone were analytical grade. 4-t-OP stock solutions of 10 mg/L were prepared with purified water. The same water was used throughout this work.

1.2 Reactor preparation

Figure 1 presents the spiral photoreactor system (SPS) developed for studying the photodegradation of aqueous 4-t-OP. A 40-mL spiral reactor is made of quartz glass tube, of which the inner diameter and wall thickness are 5 and 1 mm, respectively. The diameter of spiral tube is 60 mm. A UV-lamp (length = 120 mm, power = 9 W, wavelength = 254 nm) was located at the centre of the reactor. Without flowing through the pump, the 4-t-OP solution was drawn into or driven out of the reactor by a peristaltic pump (BT100-1J, Longer Co. Ltd., China) connected to outlet or inlet of the reactor.

The TiO₂ precursor sol was prepared by dissolving 20 mL tetra-*n*-butyl titanate in 100 mL ethanol with 3 mL acetyl acetone. Nitric acid 0.8 mL was added to a mixture of 3 mL deionized water and 20 mL ethanol, which was then added to the TiO₂ precursor sol during magnetic stirring. The TiO₂ thin film was obtained using dip-coating method. To allow the UV light to irradiate directly on the interface between the solution and TiO₂ film, only half inner wall of the tube further from the UV lamp was coated with the TiO₂ thin film. Therefore, in the reactor, the maximal thickness of the solution for optical path was 5 mm. The gel film was dried at 100°C for 2 hr, and was then heated at 500°C for 1 hr in a muffle furnace,

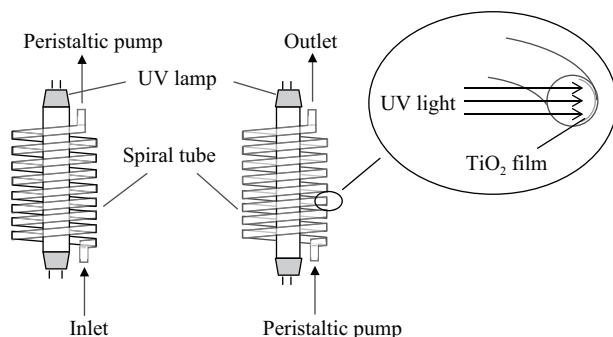


Fig. 1 A sketch of the spiral photoreactor system.

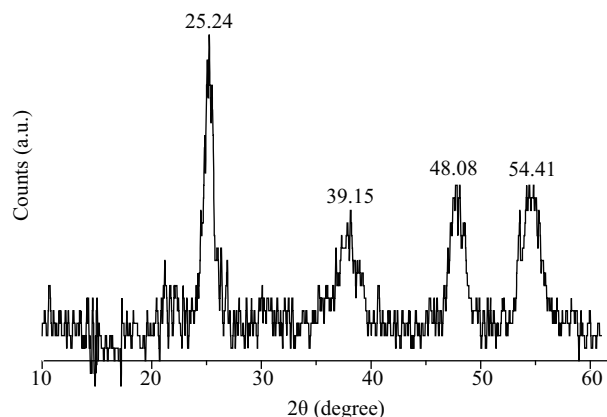


Fig. 2 XRD patterns of TiO₂ photocatalysts.

by which the TiO₂ thin film in anatase phase with high photocatalytic efficiency was obtained (Kwona et al., 2003; Hu et al., 2007). The XRD pattern of TiO₂ sample is shown in Fig. 2. The XRD measurements were carried out on an X-ray powder diffractometer (SMART APEX, Bruker, Germany). The TiO₂ was anatase phase similar to the materials described in other previous reports (Fang et al., 2006; Tayade et al., 2007; Cheng et al., 2012). This procedure was repeated to get multiple layers of film. Different amount of tetra-*n*-butyl titanate in the sol was used to get different mass concentration of TiO₂ in the film. The microstructure and crystallization of TiO₂ thin film were characterized by means of scanning electronic microscope (SEM) (XL-30, Philips, the Netherlands).

1.3 Irradiation experiments

Due to the slow and low solubility of 4-t-OP in water, solid 4-t-OP was magnetically stirred in water for three days to ensure complete dissolution, and finally a concentration 10 mg/L was obtained for this study. The initial pH of the solution was 4.5. To compare the degradation efficiency of photocatalysis with that of direct photolysis for aqueous 4-t-OP solution, irradiation experiments were carried out in the same SPS with and without TiO₂ thin films sintered on its inner wall. The prepared 4-t-OP water solution was pumped into the reactor and then stayed to be irradiated for a certain period before being driven out for sample analysis.

1.4 Sample analysis

4-t-OP and its degradation products were analyzed with HPLC (UltiMate 3000, Dionex, USA) equipped with diode array detector (DAD), of which the main detecting wavelength was set at 223 nm. A C18 column (250 mm × 4.6 mm × 5 μm, Kromasil, Sweden) was used and the mobile phase was a mixture of methanol and water (V:V = 80:20) with a flow rate of 0.8 mL/min. The temperature of the column compartment was 40°C. The function relationship of the peak area (*A*) measured by HPLC against 4-t-OP concentration (*C*, mg/L) was: $A = 0.34226C - 0.04349$ ($R = 0.9996$), and the detection limit of 4-t-OP was 0.05 mg/L. The irradiated solution was also analyzed with total organic carbon analyzer (TOC-V CPH, Shimadzu, Japan) to monitor the mineralization degree.

The degradation products were identified with liquid chromatography-mass spectrometer (LC-MS). The LC (UltiMate 3000, Dionex, USA), which was equipped with a C18 column (150 mm \times 4.6 mm \times 5 μ m, Dionex, USA) with water and methanol ($V/V = 20:80$) as mobile phases. The mass spectrometer (MicrOTOF II, Bruker, Germany) was operated through a negative mode electrospray ionization (ESI) method.

2 Results and discussion

2.1 Direct photolysis of 4-t-OP

As shown in Fig. 3, the direct photolysis rate of 4-t-OP increased as a function of irradiation time.

In Fig. 3, the significant correlation coefficient ($R = 0.9879$) indicates that direct photolysis of 4-t-OP follows first-order reaction kinetics with about 88% of the 4-t-OP degraded after 45 min irradiation. The apparent reaction rate equation can be written as:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (1)$$

The first-order reaction rate constant k is estimated to be $4.8 \times 10^{-2} \text{ min}^{-1}$ from the slope of the plots of $\ln(C/C_0)$ vs. irradiation time.

The same sample was analyzed by TOC analyzer and the result was shown in Fig. 4. Although 88% of 4-t-OP was degraded after 45 min irradiation, TOC of the solution did not decrease evidently, which indicated that the direct photolysis process could not make the 4-t-OP degrade into inorganic materials.

2.2 Photocatalysis degradation of 4-t-OP

2.2.1 Effect of catalyst concentration

In order to obtain the optimum catalyst concentration, the relationship between the concentration of catalysts and degradation reaction rate of 4-t-OP was investigated. TiO_2 precursor sol was prepared with concentrations (V/V) of 7.4%, 13.6% and 23.4% coated on the inner wall of the spiral tube to change TiO_2 amount. The initial concentration of the 4-t-OP in the solution was 10 mg/L.

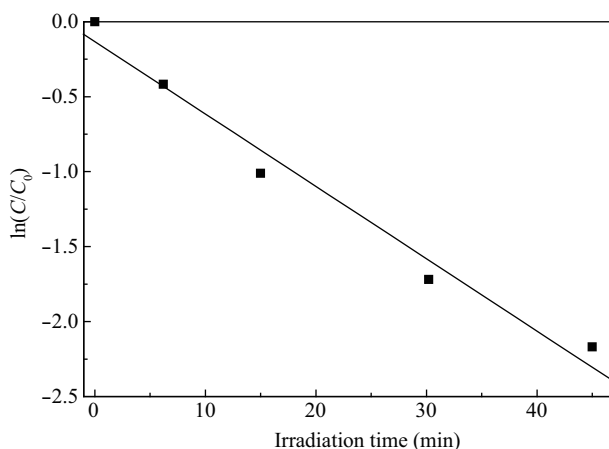


Fig. 3 Photolysis kinetics of 4-t-OP in water.

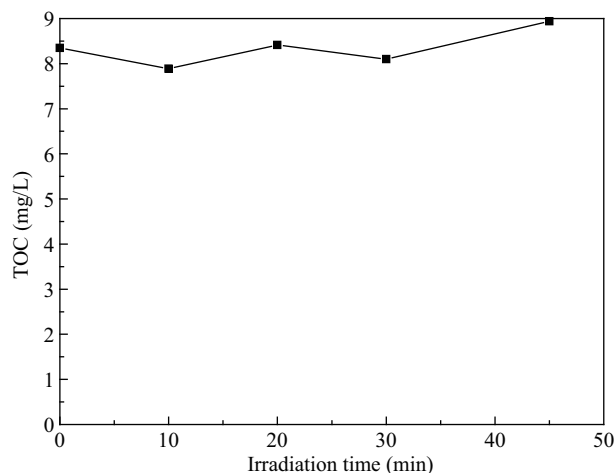


Fig. 4 Relationship between TOC and irradiation time.

Figure 5 shows the time dependence of 4-t-OP degradation on concentration of TiO_2 precursor sol.

The highest photocatalytic degradation efficiency of 4-t-OP was achieved when the concentration of TiO_2 precursor sol was 13.6%, where 90% of the 4-t-OP was degraded after 30 min irradiation. This result indicated that the method we used for the degradation of 4-t-OP was more effective than the previous studies which took 8 hr (Neamtu et al., 2009) and 300 min (Yamazaki et al., 2008) to obtain a similar degradation efficiency. In the meanwhile, it only took about 40 min for the other two concentrations of TiO_2 precursor sol to achieve the same degradation efficiency in the present study.

The photocatalytic degradation efficiency increased and then decreased when the concentration of TiO_2 precursor sol increased from 7.4% to 13.6%, and to 23.4%. Similar results were reported in previous studies (Chen and Ray, 1998; Terzian and Serpone, 1995). The reason for this observation was probably due to the following two factors: (1) the dosage of TiO_2 was not enough to provide active radicals for the degradation of 4-t-OP when the concentration of TiO_2 precursor sol was 7.4%; and (2) the aggregation of TiO_2 at higher concentration resulted in the decreased number of surface active sites (Chen and Ray, 1998).

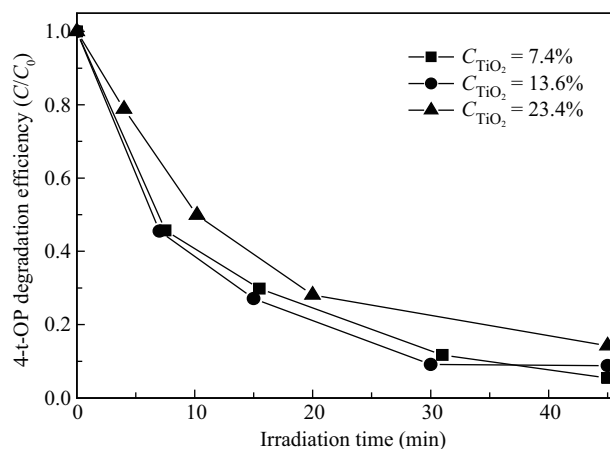


Fig. 5 Effect of catalyst concentrations on the photocatalytic performance.

2.2.2 Effect of multiple layers of TiO₂ film

Layers of the TiO₂ film layers in the reactor is another important parameter for the photocatalytic reaction. The optimal catalyst concentration of 13.6% was used to test the effect of multiple layers of TiO₂ film on the degradation efficiency of aqueous 4-t-OP. The corresponding ratio of TiO₂ precursor sol was: $V_{(\text{tetra-}n\text{-butyl titanate})}:V_{(\text{ethanol})}:V_{(\text{acetyl acetone})}:V_{(\text{nitric acid})}:V_{(\text{deionized water})} = 20:120:3:0.8:3$. The inner wall of the reactor were re-coated with TiO₂ thin films following the same method mentioned above to obtain multiple layers of TiO₂ film. The initial concentration of the 4-t-OP solution was 10 mg/L. Figure 6 indicates that 4-t-OP degradation efficiency decreased when the number of TiO₂ film layers increased. As shown in the SEM picture (Fig. 7), for single layer of TiO₂ film, TiO₂ particles were about 20–60 μm in size and some space existed in between particles. Compared to that in other study (Wen et al., 2001), current TiO₂ particles were smaller and had much more even film surface. Due to relatively larger specific surface area of TiO₂ particles, more reactive sites were exposed to the solution then photo-induced holes and electrons were easier to be trapped by the water or pollutants (Zheng et al., 2001). When double or triple layers of TiO₂ film were introduced, most of the space in between TiO₂ particles was filled and the specific surface area decreased, which in return reduced the efficiency of

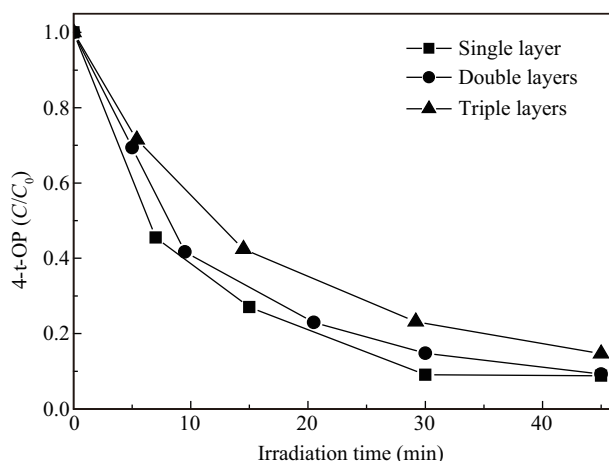


Fig. 6 Efficiency of 4-t-OP photocatalytic degradation by different layer of TiO₂ film.

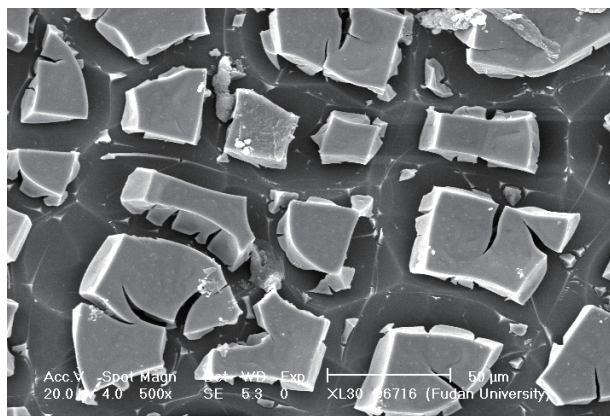


Fig. 7 SEM of single layer TiO₂ film sintered on the inner wall of the spiral photoreactor.

photocatalytic degradation (Chen and Ray, 1999).

2.3 Effect of initial 4-t-OP concentration

Figure 8 shows the effect of initial 4-t-OP concentration on the photocatalytic performance of single layer of TiO₂ film sintered on the inner wall of the spiral photoreactor. The calculated first-order rate constants (k) were $6.9 \times 10^{-2} \text{ min}^{-1}$, $7.1 \times 10^{-2} \text{ min}^{-1}$, $8.3 \times 10^{-2} \text{ min}^{-1}$ and $9.3 \times 10^{-2} \text{ min}^{-1}$ for the initial 4-t-OP concentrations of 10 mg/L, 8 mg/L, 5 mg/L and 2 mg/L, respectively, with Eq. (1). The optimal initial concentration of 4-t-OP was 2 mg/L.

It was indicated that 4-t-OP molecules were mainly reacted with the active radicals (mainly $\cdot\text{OH}$) for the photocatalytic degradation (Barakat et al., 2005). As a result of constant irradiation, the active radicals could be continuously generated while the decay rate kept growing with the concentration. After a short period when the decay rate was equal to the generation rate, the number of the active radicals could attain a steady value. Therefore, the degradation of 4-t-OP in this study was shown as an apparent first-order reaction.

Figure 8 shows the apparent reaction rate constant k (min^{-1}) of 4-t-OP degradation slightly decreases when the initial concentration of 4-t-OP increases from 2 to 8 mg/L. The reason was that solution with higher initial concentration generated more byproducts, which might absorbed some photons or consumed additional active radicals. The similar results were observed by other researchers (Doll and Frimmel, 2003; Fu et al., 2005; Neamtu and Frimmel, 2006; Chang et al., 2010).

2.4 Characterization of the degradation products

The degradation products of catalytic reaction under the optimum condition were investigated employing a total organic carbon analyzer and a LC-MS. Figure 9 shows the time dependence of 4-t-OP concentration and TOC concentration during irradiation when the initial concentration of the 4-t-OP solution was 10 mg/L. After 45 min irradiation, 91.2% of 4-t-OP was degraded but only 28.3% of the initial reagent was mineralized according to the decreased amount of TOC value.

To characterize the degradation products of 4-t-OP, the

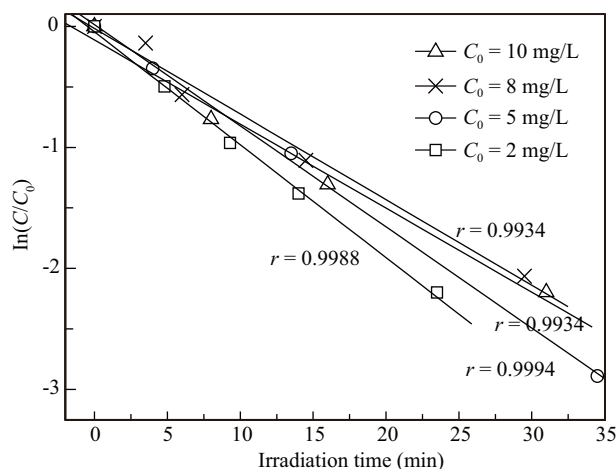


Fig. 8 Effect of initial 4-t-OP concentration on the photocatalytic performance.

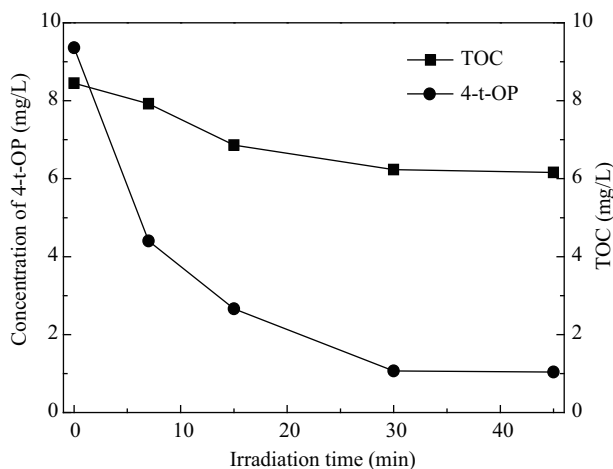


Fig. 9 Variations of the concentrations of 4-t-OP and TOC against irradiation time.

final solution of the photocatalytic reaction was subjected to LC-MS analysis. According to the total ion current (TIC) chromatogram, three main peaks were detected (Fig. 10a) and the mass spectra of the three corresponding

species were also showed in Fig. 10b, c, d, respectively. The third peak was identified to be 4-t-OP determined from its mass spectrometry (Fig. 10d) to that of pure 4-t-OP solution. For the other two peaks, their m/z values were both determined to be 221. The actual m/z for these two components was 222 because the MS was operated in negative mode (Shao et al., 2005). It was assumed that these two components were isomerides. The possible chemical structures for the photoproducts of 4-t-OP are listed in Fig. 11. All of them were considered to be the effects of the adding of hydroxyl to 4-t-OP (Mazellier and Leverd, 2003; Ning et al., 2007; Yamazaki et al., 2008).

The possible reaction mechanism was deduced as follows. It is well known that TiO_2 will produce electrons and holes in conduction band and valence band respectively when it is irradiated with UV light ($\lambda < 380 \text{ nm}$) (Ning et al., 2007). The reaction can be described as Eq. (2) (Eshaghi et al., 2010). Then the $\cdot\text{OH}$ radicals can be produced by reaction of photoholes with water molecule (Eq. (3)) (Barakat et al., 2005).

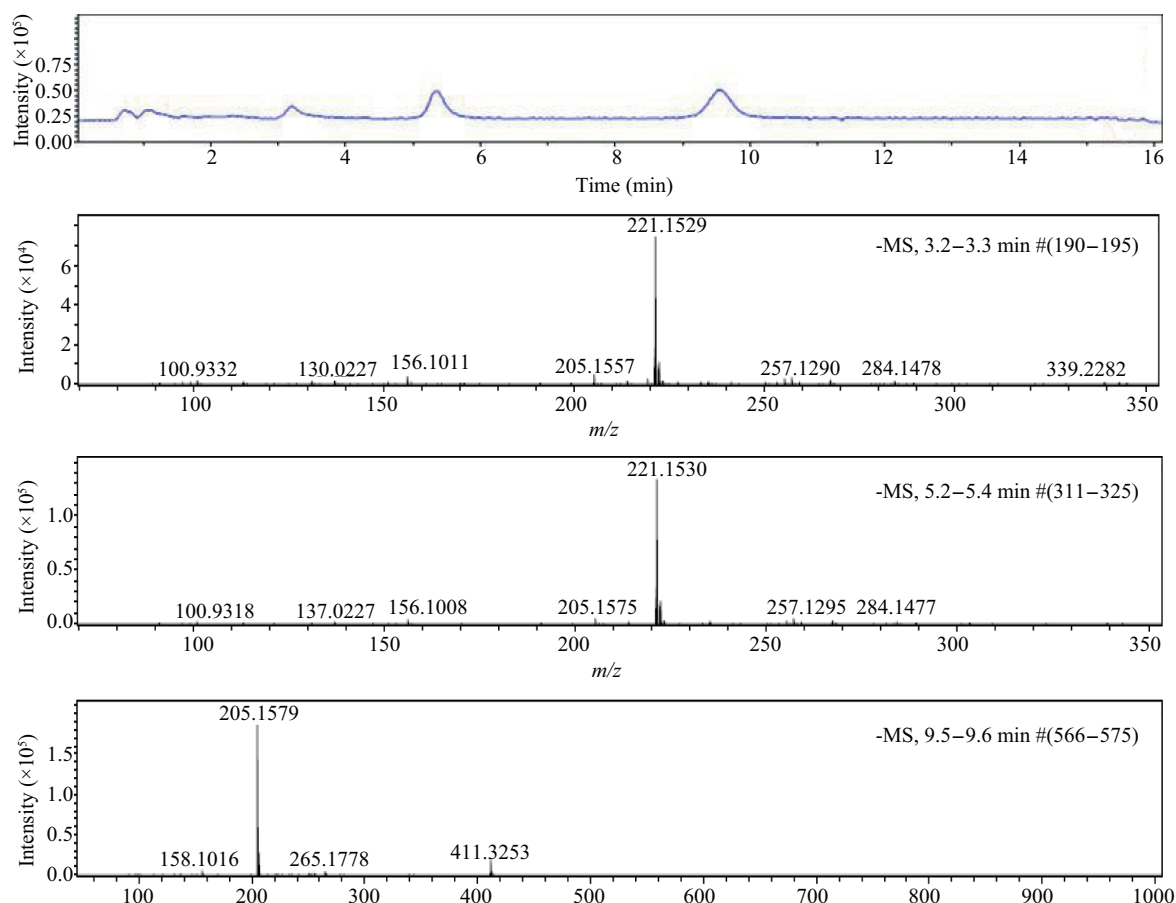
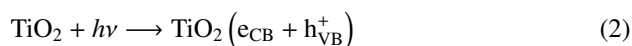


Fig. 10 TIC (a) and corresponding mass spectra of the three peaks (retention time: (b) 3.2 min, (c) 5.3 min, (d) 9.5 min) determined by LC-MS.

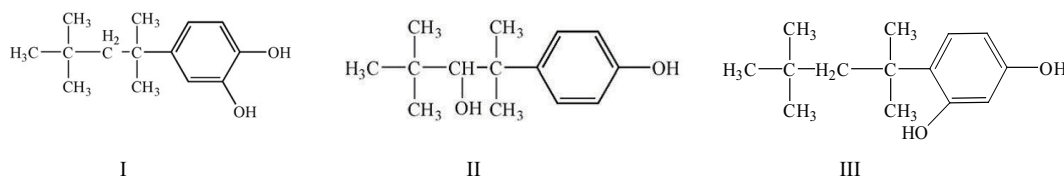
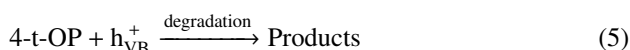


Fig. 11 Possible chemical structure of the degradation products of 4-t-OP.



It is believed that the degradation of 4-t-OP is initiated through its oxidation either by $\cdot\text{OH}$ radicals (Eq. (4)) or by photoholes (Eq. (5)).



The successive attacks of photo-generated holes or hydroxyl radicals result in the photocatalytic removal of this compound. Based on these deductions, the photoproducts of 4-t-OP degradation were supposed to be a kind of hydroxyl group containing substances as illustrated in Fig. 11.

After 45 min irradiation in the photoreactor, the reaction solution was analyzed by HPLC, and no quantifiable peaks were detected. It is believable that the degradation byproducts described above were further degraded.

3 Conclusions

A spiral photoreactor system (SPS) has been successfully developed and evaluated for its potential to function as an appropriate device for the degradation of 4-t-OP in liquid phase. The direct photodegradation of 4-t-OP followed a first-order reaction with a reaction rate constant of $4.8 \times 10^{-2} \text{ min}^{-1}$, with about 88% of the 4-t-OP degraded after 45 min irradiation. The photodegradation of 4-t-OP was proven to be more efficient when thin layer of TiO_2 film sintered on the inner wall of the photoreactor was applied as the catalyst. The catalyst concentration, number of catalyst film layers and initial concentration of 4-t-OP affected the degradation kinetics of 4-t-OP. Single layer TiO_2 film prepared with 13.6% of TiO_2 precursor was proven to be the optimal photocatalytic reaction condition, under which 90% of 4-t-OP could be degraded in 30 min when the initial concentration of it was 10 mg/L. The intermediate products of 4-t-OP degradation were probably some hydroxyl group containing substances which can be decomposed further in the reaction sequences.

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