

Optimization of solar photocatalytic degradation conditions of bisphenol A in water using titanium dioxide

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Abstract

The photocatalytic degradation conditions of 4,4'-isopropylidenediphenol (bisphenol A, BPA), a representative endocrine disruptor, in water using titanium dioxide were optimized under sunlight illumination. The effect of various factors, such as photocatalyst dosage, initial substrate concentration, temperature, pH and light intensity, on the photocatalytic degradation of bisphenol A was investigated. The final degradation product was carbon dioxide, and the stoichiometric formation of CO₂ from aqueous bisphenol A solution was observed as the complete mineralization. The solar photocatalytic degradation treatment is simple, easy handling and cheap. Therefore, since the artificial lamp devices, for example Hg–Xe lamp, are particularly expensive in the local and nonexclusive areas, the proposed technique appears to be a very suitable method for the treatment of wastewater including bisphenol A in those areas.

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1. Introduction

4,4'-Isopropylidenediphenol (bisphenol A, BPA) is manufactured in high quantities, 90% or more being used as a monomer for the production of polycarbonate (PC) and epoxy resins, unsaturated polyester-styrene resins and flame retardants. The final products are used as coatings on cans, as powder paints, as additives in thermal paper, in dental fillings and as antioxidants in plastics [1]. It is well-known that bisphenol A has an estrogenic activity, that is, it serves as an environmental endocrine disruptor [2]. The release into the natural environment as well as in surface water is possible during manufacturing processes and by leaching from final products. Hence, it is very important to develop the treatment technology for bisphenol A urgently.

A variety of treatment techniques for wastewater, which contains phenolic compounds, have been examined using chemical [3], biological [4], photochemical [5], and electrochemical [6] procedures. However, only a few reports have appeared on the treatment of wastewater which contains bisphenol A [7–13]. Recently, some researchers [10–13]

have reported the photocatalytic degradation of bisphenol A in a TiO₂ aqueous suspension using an artificial light source such as a Hg–Xe lamp. The artificial lamp device is particularly expensive in the local and nonexclusive areas. Therefore, we have investigated the photodegradation system of bisphenol A in aqueous TiO₂ suspension under sunlight illumination [7]. In the photocatalytic degradation system, bisphenol A could be degraded in aqueous TiO₂ dispersion under sunlight illumination. It was found that the primary solar photocatalytic degradation reaction follows a pseudo first-order kinetic law. However, the solar photocatalytic degradation conditions of bisphenol A in the aqueous TiO₂ suspension were not optimized in the initial experiments.

In the present work, the solar photocatalytic degradation conditions of bisphenol A in water with TiO₂ were optimized, and the final degradation product was investigated in order to evaluate the mineralization of bisphenol A. On the basis of the evidence of the intermediate formation, the photocatalytic degradation mechanism was discussed.

2. Experimental

The bisphenol A used in this study was purchased from Nacalai Tesque Inc., Kyoto, Japan (gas chromatography

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Table 1
Experimental conditions

Bisphenol A	100 $\mu\text{g/ml}$ (50 ml)
TiO ₂	0–1000 mg
Temperature	10–70 °C
pH	2–10
Light intensity	0–1.7 mW/cm ²
Illumination time	60 min

(GC) grade >99%). Bisphenol A aqueous solutions were prepared with ultrapure water, which was purified by an ultrapure water system (Advantec MFS Inc., Tokyo, Japan) resulting in a resistivity >18 M Ω cm. A 50 ml aqueous solution containing 100 $\mu\text{g/ml}$ (440 μm) bisphenol A was put into a Pyrex reaction vessel (100 ml capacity). TiO₂ powder (anatase, purity 99.9%, diameter 230 nm, surface area 8.7 m²/g, Wako Pure Chemical Industries, Ltd., Osaka) was added to the solution to produce a given concentration of TiO₂ suspension. The temperature was kept constant with a water bath. The detailed experimental conditions were shown in Table 1. The TiO₂ suspension containing bisphenol A was irradiated under sunlight illumination. In this case, the short ultraviolet radiation ($\lambda < 300$ nm) was filtered out by the vessel wall. The intensity of light was measured by a UV radio meter with a sensor of 320 to 410 nm wavelengths (UVR-400, Iuchi Co., Osaka, Japan). The variations of sunlight intensity for 60 min were less than 10%.

After illumination, TiO₂ was separated through the 0.45 μm Advantec membrane filter. The amount of bisphenol A in the aqueous solution was measured using a high-performance liquid chromatograph (HPLC, JASCO Co., Tokyo, Japan), equipped with a JASCO UVDEC-100-VI optical detector and a Chromspher 5 Poly C18 column (Chrompack, VARIAN Inc., California, USA). The elution was monitored at 276 nm. The eluent used was a mixed solvent of acetonitrile and water (1/1, v/v). The flow rate of the mobile phase was 1.5 ml/min.

The evolution of CO₂ was evaluated with a GL Science GC-353B equipped with a methanizer and a FI detector, combined with a Porapak Q column using nitrogen carrier gas. After illumination, the aqueous solution filtrated with a membrane filter was subjected to the total organic carbon (TOC) and intermediate product analyses. The TOC in water was measured using a Shimadzu TOC analyzer (TOC-V_E) based on CO₂ quantification by non-dispersive infrared analysis after high-temperature catalytic combustion [14].

The intermediate products were extracted by means of solid-phase extraction. The extraction disk (C18 disk, 3M Empore) was placed in the conventional filtration apparatus and washed with 10 ml of solvent mixture, dichloromethane and ethyl acetate (1:1), 10 ml of methanol and 10 ml of ultrapure water. Then, the sample was percolated through the disk with a flow rate of 5 ml/min under vacuum. The compounds trapped in the disk were collected by using 4 \times 5 ml of solvent mixture, dichloromethane and ethyl acetate (1:1), as eluting system. The fractions were evaporated under a

gentle stream of nitrogen to 50 μl into conical vials, and 1 μl was injected into gas chromatography and mass spectrometry (GC–MS) instrument in splitless mode. For the analysis of intermediate products, a Shimadzu Gas Chromatograph and Mass Spectrometry (GC–MS 5050A) equipped with an HP-5 capillary column (30 m \times 0.25 mm i.d.) was used at the following chromatographic conditions: injector temperature 270 °C, column temperature program 40, 40–200 °C (5 °C/min), 200–210 °C (1 °C/min), 210–270 °C (20 °C/min) and 270 °C (3 min). Helium was used as the carrier gas at 1.5 ml/min. The interface was kept at 270 °C. Qualitative analyses were performed in the electron-impact (EI) mode, at 70 eV using the full scan mode.

3. Results and discussion

In the primary experiments [7], the complete disappearance of bisphenol A was observed in <5 h, working with moderate amounts of TiO₂ under sunlight illumination. Since it was found that the solar photocatalytic purification of water in bisphenol A was possible in TiO₂ aqueous suspensions, the degradation parameters were optimized in the present study.

3.1. Effect of photocatalyst dosages

In order to optimize the TiO₂ suspension concentration, the effect of photocatalyst dosages on the degradation of bisphenol A in water was investigated under sunlight illumination. The results were shown in Fig. 1. The degradation efficiency increased with increasing the amounts up to 500 mg, and then the efficiency was nearly flat. The increase in the efficiency seems to be due to the increase in the total surface area, namely number of active sites, available for the photocatalytic reaction as the dosage of photocatalyst increased. However, when TiO₂ was overdosed, the

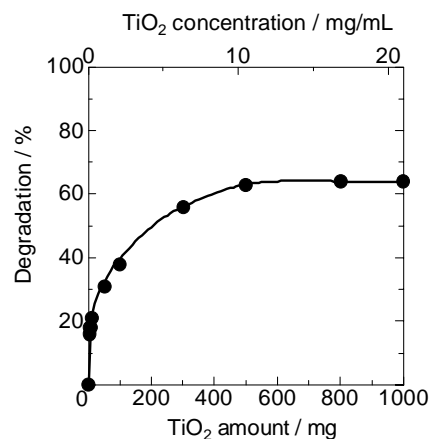


Fig. 1. Effect of TiO₂ amount on the solar photocatalytic degradation of bisphenol A in water (bisphenol A: 100 $\mu\text{g/ml}$; illumination time: 60 min; light intensity: 1.3 mW/cm²; temperature: 30 °C; pH: 6).

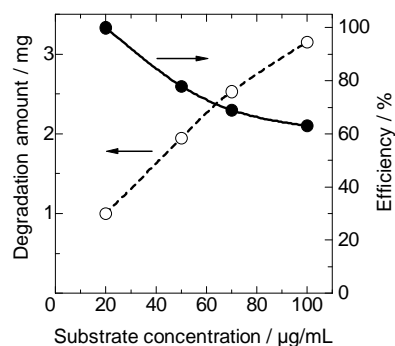


Fig. 2. Effect of initial substrate concentration on the solar photocatalytic degradation of bisphenol A in water using TiO_2 (TiO_2 : 500 mg; illumination time: 60 min; light intensity: 1.3 mW/cm^2 ; temperature: 30°C ; pH: 6).

number of active sites on the TiO_2 surface may become almost constant because of the decreased light penetration, the increased light scattering and the loss in surface area occasioned by agglomeration (particle–particle interactions) at high solid concentration [15]. Therefore, 500 mg of TiO_2 was selected as the optimal amounts of photocatalyst for the sequential experiment. The TiO_2 amounts corresponded the suspension concentration of 10 mg/ml.

3.2. Effect of initial substrate concentration

It is very important, from the application point of view, to study the dependence of the photocatalytic degradation on the substrate concentration. Therefore, the effect of initial substrate concentration on the solar photocatalytic decomposition using TiO_2 was investigated, as illustrated in Fig. 2. With increasing the initial substrate concentration the degradation amounts of bisphenol A almost linearly increased, although the degradation efficiency decreased gradually. Therefore, 100 $\mu\text{g/ml}$ bisphenol A solution was used for evaluating the solar photocatalytic degradation, in view of the practical wastewater with high concentration of bisphenol A.

3.3. Effect of temperature

Little information on the temperature effect on the photocatalytic degradation of pollutants in water with TiO_2 has been presented. Therefore, the effect of temperature on the solar photocatalytic degradation of bisphenol A in water using TiO_2 was investigated in the range of 10– 70°C . The results were illustrated in Fig. 3. Although the degradation efficiency of bisphenol A gradually increased as the temperature increased, the appreciable change was not observed in the temperature range. Since the photonic activation seems to occur at considerably high speed, the photocatalytic system may be not so sensible to the temperature [16]. Hence, all subsequent illuminations were performed at 30°C because of the operating cost for the photodegradation system.

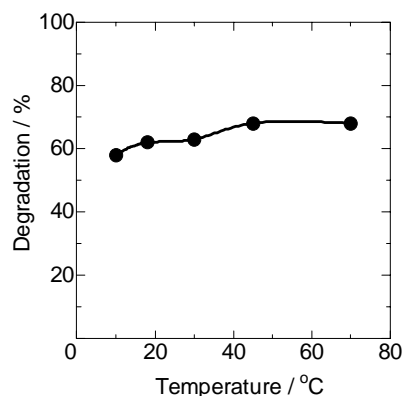


Fig. 3. Effect of temperature on the solar photocatalytic degradation of bisphenol A in water using TiO_2 (TiO_2 : 500 mg; bisphenol A: 100 $\mu\text{g/ml}$; illumination time: 60 min; light intensity: 1.3 mW/cm^2 ; pH: 6).

3.4. Effect of initial pH

The amphoteric behavior of most semiconductor oxides influences the surface charge of the photocatalyst. Therefore, the role of initial pH on the degradation efficiency of bisphenol A was investigated in the pH range 2–10, as shown in Fig. 4. The degradation efficiency increased with increase in pH. The zero point charge (zpc) pH_{zpc} of TiO_2 particles is around 6 [17]. TiO_2 surface is positively charged in acidic media ($\text{pH} < 6$) whereas it is negatively charged under alkaline condition ($\text{pH} > 6$). Generally, the pH changes can have a non-insignificant result not only on the mode of adsorption of the bisphenol A substrate on TiO_2 surface, but also on the selectivity of the photodegradative reaction occurring on the particle surface since redox reactions are very sensitive to changes in the surface potential [18]. On the other hand, at high initial pH, more hydroxide ions (OH^-) in the solution induced the generation of hydroxyl free radicals (HO^\bullet), which came from the photooxidation of OH^- by holes forming on the titanium dioxide surface. Since

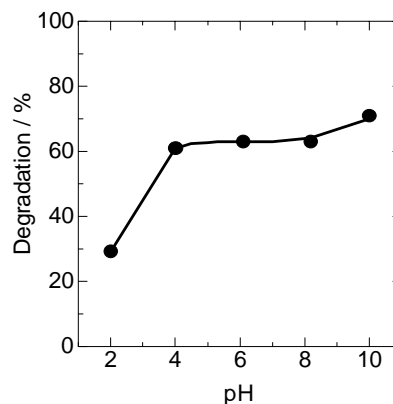


Fig. 4. Effect of initial pH concentration on the solar photocatalytic degradation of bisphenol A in water using TiO_2 (TiO_2 : 500 mg; bisphenol A: 100 $\mu\text{g/ml}$; illumination time: 60 min; light intensity: 1.3 mW/cm^2 ; temperature: 30°C).

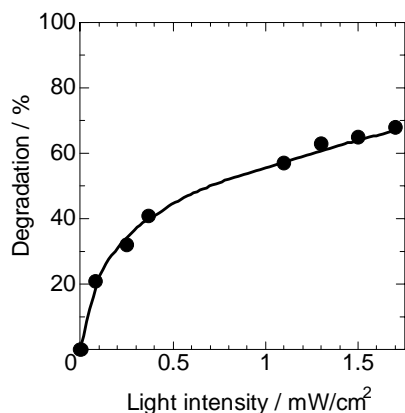


Fig. 5. Effect of light intensity on the solar photocatalytic degradation of bisphenol A in water using TiO₂ (TiO₂: 500 mg; bisphenol A: 100 μg/ml; illumination time: 60 min; temperature: 30 °C; pH: 6).

hydroxyl free radical is the dominant oxidizing species in the photocatalytic process, the photocatalytic decay of bisphenol A may be accelerated in an alkaline medium. Similar reaction has been suggested by a number of researchers [15,19–21]. Consequently, pH 6 was selected for the optimal experimental conditions, because of the unnecessary of chemical treatment including neutralization process.

3.5. Effect of light intensity

The influence of light intensity on the solar photocatalytic destruction of bisphenol A in water with TiO₂ was studied. The degradation experiments were performed during different periods of time with various light intensities on sunny and cloudy days. The results were illustrated in Fig. 5. The degradation efficiency increased rapidly with increase in the light intensity up to 0.35 mW/cm², and then the efficiency increased gradually. Since the catalyst powders are suspended in a stirred solution, the light intensity will affect the degree of absorption of light by the catalyst surface. Ollis [22] reviewed the effect of light intensity on the kinetics of photocatalysis and stated that (i) at low light intensities, the rate would increase linearly with increasing light intensity; (ii) at intermediate light intensities, the rate would depend on the square root of the light intensity; and (iii) at high light intensities, the rate is independent of light intensity. Therefore, the results obtained in the solar photocatalytic degradation of bisphenol A in aqueous TiO₂ suspension were reasonable. In the previous study, when the photocatalytic degradation of bisphenol A in aqueous solutions with TiO₂ semiconductors was carried out under sunlight intensity of 1.3 mW/cm², 100 μg/ml of bisphenol A could be almost degraded for 300 min [7].

3.6. Mineralization

Watanabe et al. [11] has described the release of CO₂ during the photocatalytic degradation of bisphenol A using

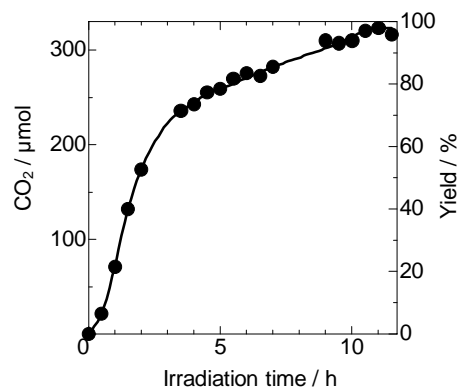
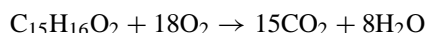


Fig. 6. Carbon dioxide formation from the solar photocatalytic degradation of bisphenol A in water using TiO₂ (TiO₂: 500 mg; bisphenol A: 10 μg/ml; temperature: 30 °C; pH: 6).

mercury lamp. For the photocatalytic degradation of bisphenol A with TiO₂ semiconductors, the total mineralization reaction can be estimated as follows:

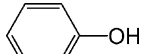
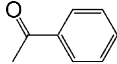
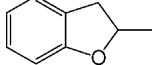
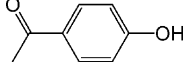



Therefore, the evolution of CO₂ during the solar photocatalytic degradation of bisphenol A in water using TiO₂ was investigated. The results were illustrated in Fig. 6. In order to evaluate the mineralization in the short term experiment (1 day), the concentration of bisphenol A was lowered to 10 μg/ml. The yield of CO₂ evolution increased sharply until 4 h illumination time, and after 4 h the yield increased gradually. Finally, according to mass balance analysis, it was observed that all carbon atoms were transformed to CO₂ after 11 h treatment. The quantity of total organic carbon in the aqueous solution after TiO₂ separation was negligible level. Hence, it was found from the mineralization experiment that two benzene rings of bisphenol A were cleaved by the solar photocatalytic degradation using TiO₂. Taking into account the fact that complete disappearance of the bisphenol A in the irradiated cells occurred after relatively short illumination time in the photocatalytic degradation, whereas the stoichiometric formation of CO₂ was observed after the long time, it could be deduced that transient organic intermediate products are likely to be present in the reaction system after the complete destruction of bisphenol A. In consequence, in the solar photocatalytic degradation of bisphenol A in the aqueous TiO₂ suspension, the mineralization reaction to CO₂ could proceed with the reduction in estrogenic activity.

3.7. Intermediate products and photodegradation mechanism

The intermediate products formed in the solar photocatalytic degradation of bisphenol A in the aqueous TiO₂ suspension for 30 min were investigated by GC–MS analysis. Four products were identified by the molecular ion and mass fragment peak and also through comparison with GC/MS NIST library data. Table 2 lists main

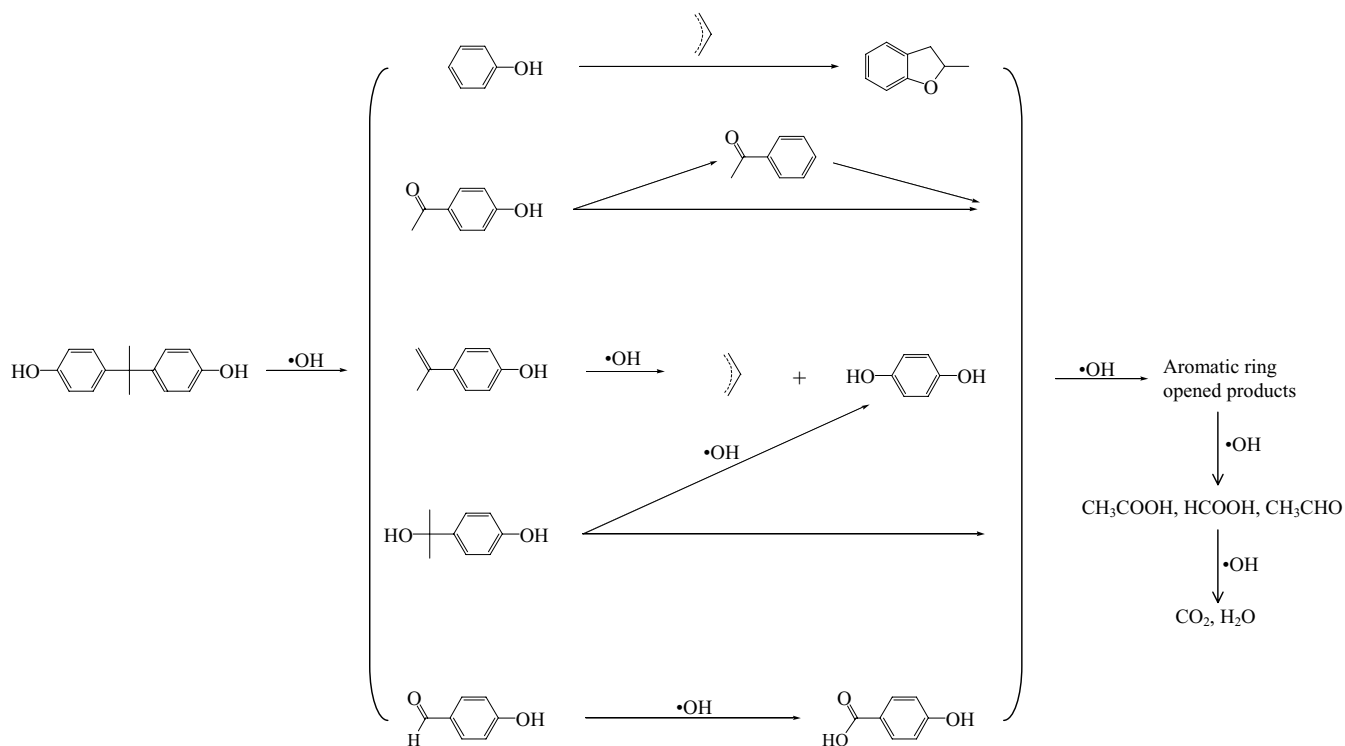
Table 2
GC–MS–EI retention time, mass fragment ions (m/z) and relative abundance (%) of intermediate products and BPA

Peak no.	Retention time (min)	Detected ions m/z (% abundance)	Molecular weight m/z	Molecular structure
1	7.5	94(100), 66(39)	94	
2	9.9	120(30), 105(100), 77(83)	120	
3	16.9	134(100), 119(53)	134	
4	20.7	136(29), 121(100) 93(40), 65(40)	136	
5	37.4	228(22), 213(100) 119(31)	228	

fragments (m/z) and relative abundances (%) obtained for four intermediate products. The similarities of these four products to the NIST library data were more than 85%. Ohko et al. [10] reported that in the photocatalytic degradation of bisphenol A using TiO_2 *p*-hydroxyacetophenone (peak 4 in Table 2) was detected as one of intermediate products by LC–MS. In the photocatalytic degradation of bisphenol A with TiO_2 , various intermediate products such as phenol, *p*-hydroquinone, *p*-isopropenylphenol, *p*-hydroxybenzaldehyde and 4-hydroxyphenyl-2-propanol were confirmed by several researchers [11–13]. Therefore, the present experimental data and literature reports [10–13]

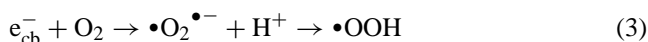
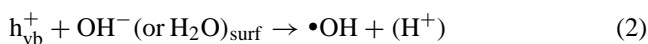
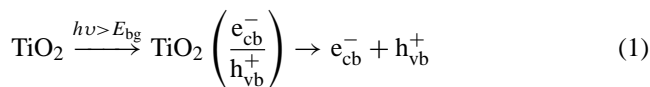
suggest the solar photocatalytic degradation pathway of bisphenol A in water with titanium dioxide, as illustrated in Scheme 1.

In the photodegradative process implicating TiO_2 particulates, the absorption of light with an energy greater than 3.2 eV (wavelengths below 387 nm) generates electron/hole pairs that upon separation yield conduction band electrons and valence band holes (Eq. (1)) [23]. Migration of these carriers to the surface in competition with a variety of other decay channels leads to trapping of the holes by OH^- groups or by H_2O to produce $\bullet\text{OH}$ radicals (Eq. (2)) and trapping of the electrons by Ti^{IV} and/or by the ubiquitous



Scheme 1. Proposed solar photocatalytic degradation pathway of bisphenol A.

oxygen molecules at the particle surface to yield the superoxide radical anion, $\bullet\text{O}_2^{\bullet-}$, which on protonation forms the hydroperoxide radical $\bullet\text{OOH}$ (Eq. (3)). In addition to the main reactions shown, other processes can also occur [24]. However, the important reaction process is that involving an oxidizing species which can attack and transform the organic molecules through the formation of intermediates having progressively higher oxygen to carbon ratios.



In the primary photocatalytic degradation of bisphenol A, the attack of $\bullet\text{OH}$ radicals may produce phenol, *p*-hydroxyacetophenone, *p*-isopropenylphenol, *p*-hydroxybenzaldehyde and 4-hydroxyphenyl-2-propanol. *p*-Isopropenylphenol seems to be converted to *p*-hydroquinone and propenyl radicals by the $\bullet\text{OH}$ radicals. The attack of propenyl radicals to phenol would yield methylbenzofuran. Since slight amounts of *p*-hydroxybenzoic acid were also detected by GC–MS analysis during the photocatalytic treatment of bisphenol A [13], *p*-hydroxybenzaldehyde possibly may be decomposed to *p*-hydroxybenzoic acid. These single aromatic intermediates are presumably further oxidized through ring-rupturing reactions into aliphatic compounds containing formic acid, acetic acid and acetaldehyde [11,12]. Finally, the mineralization reaction to carbon dioxide may occur since the stoichiometric formation of CO_2 was observed in the present study.

4. Conclusion

The optimization of solar photocatalytic degradation conditions of bisphenol A in water using titanium dioxide was investigated. The final degradation product was carbon dioxide, and all carbon atoms of bisphenol A were transformed to CO_2 . Since the artificial lamp device for photocatalytic degradation is particularly expensive in the nonexclusive areas, the solar photocatalytic degradation technology developed may be available in those areas.

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