

Optimization of Solar Photocatalytic Degradation
Conditions of Bisphenol A in Water Using TiO₂ and ZnO

Satoshi Kaneco,^{1,*} Mohammad Arifur Rahman,¹ Tohru
Suzuki,² Hideyuki Katsumata¹ and Kiyohisa Ohta¹

¹ Department of Chemistry for Materials, Faculty of
Engineering, Mie University, Tsu, Mie 514-8507, Japan
² Environmental Preservation Center, Mie University, Tsu,
Mie 514-8507, Japan

1. Introduction

Bisphenol A (BPA, 4,4'-isopropylidenediphenol) 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. 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, biological, photochemical, and electrochemical procedures. However, only a few reports have appeared on the treatment of wastewater which contains bisphenol A [2-4]. Recently, some researchers [4] 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 and ZnO suspensions under sunlight illumination [2,3]. In the photocatalytic degradation system, bisphenol A could be degraded in aqueous TiO₂ and ZnO dispersions 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 and ZnO suspensions were not optimized in the initial experiments.

In the present work, the solar photocatalytic degradation conditions of bisphenol A in water with TiO₂ and ZnO 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 (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 MΩ cm. A 50 mL aqueous solution containing 100 μg/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, Nacalai Tesque, Inc., Kyoto, Japan) or ZnO powder (purity 99.9%, diameter <5 μm, Wako Pure Chemical

Industries, Ltd., Osaka, Japan) was added to the solution to produce a given concentration of photocatalyst suspension. The temperature was kept constant with a water bath. The photocatalyst 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, the photocatalyst 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 UVIDEC-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 Porapack Q using nitrogen carrier gas. After illumination, the aqueous solution filtrated with a membrane filter was subjected to the total organic carbon (TOC) and GC-MS intermediate product analyses.

3. Results and discussion

In the primary experiments [2,3], the complete disappearance of bisphenol A was observed in < 5 hours, working with moderate amounts of photocatalyst under sunlight illumination. Since it was found that the solar photocatalytic purification of water in bisphenol A was possible in the photocatalyst aqueous suspensions, the degradation parameters, containing photocatalyst dosages, initial substrate concentration, temperature, initial pH and light intensity were optimized in the present study.

The yield of CO₂ evolution increased sharply until 4 hours illumination time, and after 4 hours the yield increased gradually. Finally, according to mass balance analysis, it was observed that all carbon atoms were transformed to CO₂ after 11 hours treatment. The quantity of total organic carbon (TOC) 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. In consequence, in the solar photocatalytic degradation of bisphenol A in the aqueous photocatalyst suspension, the mineralization reaction to CO₂ could proceed with the reduction in estrogenic activity.

References

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