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Photodecomposition of bisphenol A on nanometer-sized TiO_2 thin film and the associated biological toxicity to zebrafish (*Danio rerio*) during and after photocatalysis

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ABSTRACT

We investigated the relationship between the TiO_2 photocatalytic decomposition of bisphenol A and biological toxicity to zebrafish (*Danio rerio*). TiO_2 particles, which prepared using a solvothermal method, were applied to produce a nanometer-sized TiO_2 thin film. An alcoholic solution containing the TiO_2 particles and an inorganic binder was directly coated on the UV-lamp substrate. It was equipped in a photoreactor that was manufactured in our laboratory. The attachment of the thin TiO_2 film to the UV-lamp substrate resulted in a stable and transparent coating. The TiO_2 particles on the thin film were approximately 20–30 nm in size, and the resulting film thickness was approximately 200 nm after a single coat. The bisphenol A, which was eluted from epoxy resin in a drinking water tank, was completely degraded by the TiO_2 photocatalysis. We initially detected approximately 7.8 ng/ml of bisphenol A in the epoxy-resin tank, but its concentration was undetectable after a 48-h photocatalytic reaction over TiO_2. We observed a decreased survival rate in zebrafish that were reared in water exposed to the leaching process of the epoxy resin. After the photocatalysis, however, no toxic effects on the hatching rates or morphogenesis of the zebrafish were observed. In summary, toxicity during the TiO_2 photocatalysis was observed; however, toxicity was no longer observed once the bisphenol A was completely decomposed by the TiO_2 photocatalysis. On the basis of these experimental observations, we suggest that TiO_2 photocatalysis can be adopted as a treatment method to purify an epoxy-resin tank.

1. Introduction

Environmental problems are increasing on a global basis. Thus, extensive research is conducted in search of advanced chemical, biochemical, and physicochemical methods to eliminate hazardous chemical compounds from the air and water (Hermann, 1999; Tennakone and Kottegoda, 1996; Martyanov and Savinov, 1997). Many studies have been performed on the photocatalytic treatment of environmental pollutants using semiconductors such as TiO_2, $FeTiO_2$, and $ZnTiO_2$. To develop a more effective and low-cost method for volatile organic compound (VOC) decomposition, extensive research using TiO_2 photocatalytic systems has been performed; however, this research has failed to yield better photoreactivity options for industrial applications (Lee et al., 2001; Kang et al., 2002; Kang, 2002).

In recent years, several studies have investigated the application of TiO_2 to biology. The behavior of sterilization

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on a photo-excited TiO_2 surface and the sterilization effect of photo-excited TiO_2 have been described in previous studies (Legrini et al., 1993; Lee et al., 2004). The effective removal or inactivation of pathogenic organisms through disinfection is the most important process in the treatment and distribution of drinking water. The most common means of disinfecting potable water relies on the use of chlorine. However, chlorination results in the production of low molecular weight, halogenic organic compounds, collectively termed "sterilization byproducts". Although chlorinated water is generally free of pathogenic microorganisms, several of the sterilization byproducts are known to cause adverse human health effects over the course of a lifetime. Thus, an intensive search for alternative water-treatment practices, which not only maintain or improve current levels of microbiological safety but also reduce or eliminate chemical byproducts resulting from the oxidation process, is being conducted.

Bisphenol A (BPA) is manufactured in high quantities, and 90% or more are used as a monomer for the production of polycarbonate and epoxy resins, unsaturated polyester–styrene resins, and flame retardants. The final products are used as coating for cans, as powdered paints, as additives in thermal paper, in dental fillings, and as antioxidants in plastics (Staples et al., 1998). BPA shows estrogenic activity and is considered an environmental endocrine disrupter (Krishnan et al., 1993). Moreover, BPA has been reported to leach from polycarbonate baby bottles (Sun et al., 2000), reusable containers (Biles et al., 1997), and drinking water tanks (Bae et al., 2000). BPA has also been detected in plastic waste (Yamamoto and Yasuhara, 1999), in plasma stored in polycarbonate tubes (Staples et al., 1998), and in aquatic environments (Sajiki et al., 1999). High concentrations of BPA can also be contained in wastewater from BPA production factories, because it is only partially removed during wastewater treatment, and wastewater containing BPA can be a source of contamination in aquatic environments (Sajiki et al., 1999). Although BPA is readily degraded by microorganisms (Staples et al., 1998), biological methods commonly require long treatment times for wastewater containing BPA in high concentrations. Therefore, a rapid and simple wastewater treatment method for BPA is now urgently required. A variety of techniques involving chemical (Watanabe et al., 2003), biological (Jiang et al., 2005; Aguayo et al., 2004), photochemical (Horikoshi et al., 2004), and electrochemical (Tanaka et al., 1999) procedures have been studied for the treatment of wastewater that contains phenolic compounds. Recently, several researchers (Watanabe et al., 2003; Horikoshi et al., 2004; Ohko et al., 2001) have reported on the treatment of wastewater that contains BPA. They examined the degradation of BPA in the presence of TiO_2 as a photocatalyst. However, little research has been performed on the toxicology during TiO_2 photocatalysis (Kim, 2003; Sun, 2003).

In this study, we used TiO_2 photocatalysis to decompose BPA, which leached from epoxy resin in a water tank, and investigated the biological toxicity to zebrafish (*Danio rerio*) during and after the photoreaction. In addition, to diminish the effect of the TiO_2 powder on the biological toxicity, we used a solvothermal treatment method to obtain a nanometer-sized TiO_2 powder that was then fixed onto a Pyrex substrate by an inorganic (silane) binder, which was made by our laboratory, to produce a nanometer-sized TiO_2 film that was highly photoreactive.

2. Experimental

2.1. *Catalyst preparation*

The preparation of the nano-sized TiO_2 photocatalyst used a solvothermal method (Kang, 2003) as shown in Fig. 1(a). The reagents used for the preparation of the TiO_2 solution were as follows: titanium tetra-isopropoxide (99.95%, TTIP, Junsei Chemical, Japan) was used as a titanium dioxide precursor. Ethanol (99.9%, Wako Pure Chem. Ltd.) was used as a solvent

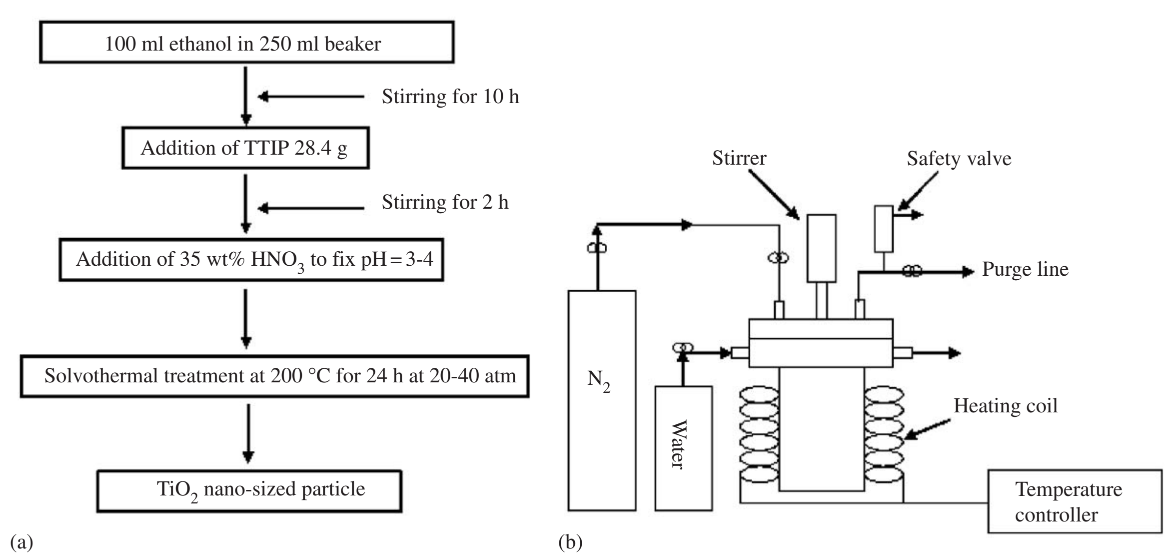

Fig. 1 – Preparation of the nanometer sized TiO_2 photocatalyst using a solvothermal method. (a) Preparation of nanometer sized TiO_2 particle and (b) autoclave for solvothermal treatment.