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# Photocatalytic degradation of bisphenol A in a visible light/$TiO_2$ system

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ABSTRACT

This study evaluates the photodegradation efficiency of bisphenol A (BPA) in a visible light/$TiO_2$ system. $TiO_2$ was generated by the sol–gel method and polyethyleneglycol (PEG) was used as a modulator. The effects of the molecular weight of PEG, the addition percentage of PEG, the pH of the solution and the $TiO_2$ dose were determined. For a given percentage of PEG added, the intensity of anatase followed the order $TiO_2$/PEG600>$TiO_2$/PEG3500>$TiO_2$/PEG200. The BPA degradation rates of visible light/$TiO_2$/PEG200 (10%), visible light/$TiO_2$/PEG600 (5%) and visible light/$TiO_2$/PEG3500 (0.5%) at pH 4 were 2.07, 3.01 and 2.90 $h^{-1}$, respectively. After 12 h of reaction, the reductions of TOC in visible light/$TiO_2$, visible light/$TiO_2$/PEG200 (10%), visible light/$TiO_2$/PEG600 (5%) and visible light/$TiO_2$/PEG3500 (0.5%) systems were 38%, 56%, 65% and 64%, respectively. The concentrations of hydroxyl radicals in visible light/$TiO_2$, visible light/$TiO_2$/PEG200 (10%), visible light/$TiO_2$/PEG600 (5%) and visible light/$TiO_2$/PEG3500 (0.5%) systems were determined to be 50.1, 88.6, 78.8 and 75.1 μM, respectively. This study finds that adding PEG during the preparation of $TiO_2$ increased the photoactivity of the generated $TiO_2$ however, the optimal PEG addition percentage varied with the molecular weight of PEG.



## 1. Introduction

Bisphenol A (BPA), a suspected endocrine disrupting compound (EDC), is widely adopted in the production of epoxy resins and polycarbonate plastics, which are used in various food and drink packaging applications, baby bottles and dental sealants [1]. The extensive use of BPA has attracted considerable attention from regulatory agencies and scientists. The removal of BPA from wastewater is regarded as important to environmental protection. BPA is an antioxidant that is non-biodegradable and highly resistant to chemical degradation, and presents a health risk to both humans and animals. Consequently, because of the wide range of applications of BPA, exposure to which is a serious concern and a health hazard, researchers must develop effective remediation procedures for destroying BPA in contaminated effluent.

Various methods for removing BPA from wastewater have been suggested. They include adsorption [2], UV [3–5], UV/$O_3$ [4], UV/$H_2O_2$ [3,5,6], Fenton [7], sono-Fenton [7], UV/Fenton [8] and UV/$TiO_2$ [9–14]. Rosenfeldt and Linden [3] studied the degradability of BPA by direct photolysis using low- and medium-pressure mercury UV lamps, finding 5% and 10–25% degradations, respectively. Moreover, the exposure of the same samples to UV/$H_2O_2$ eliminated more than 90% BPA, independently of the UV source. Katsumata et al. [8] found that the destruction of BPA was maximal at pH = 3.5–4.0 with an $H_2O_2$:Fe(II) ratio of ten under UV (λ<300 nm) irradiation, under which conditions 50% mineralization occurred in 24 h. The degradation of BPA by the Fenton process was much more rapid in the presence of ultrasound than in its absence [7]. In previous studies, $TiO_2$ was the most commonly used catalyst in the treatment of wastewater because of its non-toxicity, reasonable cost, high availability, photochemical stability and relatively high photocatalytic activity [9–14]. Coleman et al. [12] found that adding silver or platinum did not affect photocatalytic degradation or mineralization by UV/$TiO_2$ for any of the EDCs at concentrations present in water. At a high concentration of BPA, a significant increase in the reaction rate was observed over Pt/$TiO_2$. However, the reaction rate of BPA was reduced over Ag/$TiO_2$. Variations in the experimental conditions are the main cause of variations in the final outputs and conclusions of those studies. Therefore, no universal explanation of the effects of photocatalysis of organics in water is available, and several factors should be considered. UVB and UVC are commonly applied light sources in the photocatalytic degradation of BPA. Visible light/$TiO_2$ has seldom been used to degrade BPA and accordingly, further research on the photodegradation of BPA by visible light/$TiO_2$ must be performed.

This study employs the sol–gel method to generate $TiO_2$; polyethyleneglycol (PEG) was used as the modulator. BPA was the model compound. This study attempts the following; to (i) identify the characteristics of the sol–gel-produced $TiO_2$ with the addition of different proportions of PEG; (ii) evaluate the effects of the molecular weight and addition percentage of PEG on the photocatalytic activity of the produced $TiO_2$; (iii) determine the effects of pH and the $TiO_2$

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dosage in visible light/$TiO_2$ to degrade BPA and (iv) compare the mineralization performance of BPA with the various sol–gel-produced $TiO_2$ compounds under 410 nm irradiation.

## 2. Materials and methods

### 2.1. Materials

Parent compound BPA was obtained from Aldrich (purity>99%) and used as received. Three PEGs were adopted as modulators in the preparation of $TiO_2$. The molecular weights of PEG were 200, 600 and 3500 g/mol (Merck). Titanium (IV) ethoxide ($Ti(OC_2H_5)_4$) (Merck) was used as the source of Ti. The pH of the solution was controlled by adding $HClO_4$ and NaOH using an automatic titrator. Salicylic acid, 2, 3-dihydroxybenzoic acid (2, 3-DHBA), 2, 5-dihydroxybenzoic acid (2, 5-DHBA) and catechol (Acros) were utilized to detect hydroxyl radicals in a visible light adding $TiO_2$ system. All experimental chemicals were of analytical grade.

### 2.2. Synthesis of catalyzers

The $TiO_2$/PEG powder was synthesized using the sol–gel method, which was modified from Atsunori et al. [15] and Sonawane et al. [16]. Briefly, 44 mL titanium (IV) ethoxide was added to 60 mL $C_2H_5OH$ solution then 180 mL deionized water was added, and the solution was mixed for 30 min. 10 mL PEG was added and the solution was aged for 24 h. Then, PEG and $H_2O$ were removed by heating, and the resulting precipitate was calcined at 400 °C for 2 h. The effects of PEG molecular weight were evaluated at 200, 600 and 3500 g/mol and the produced $TiO_2$ was denoted $TiO_2$/PEG200, $TiO_2$/PEG600 and $TiO_2$/PEG3500, respectively. The molar fraction of PEG added was 1–30% for $TiO_2$/PEG200, 0.5–5% for $TiO_2$/PEG600 and 0.1–1% for $TiO_2$/PEG3500.

### 2.3. Characterization

The size and morphology of generated $TiO_2$ were observed by transmission electron microscopy (TEM) using a JEM-2010 (JEOL, Japan). The specific surface areas of various $TiO_2$ were measured by the BET method, using a Model ASAP 2010 surface area analyzer (Micromeritics, USA). The crystallinity of $TiO_2$ was analyzed by X-ray diffraction (XRD) using CuKα radiation (Bruker AXS). The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. The XRD patterns were recorded at $2\theta$ values of between 20° and 80°, and a scanning speed of 3°/min. The isoelectric point ($pH_{iep}$) is that at which the zeta potential equals zero: it was measured at pH values of 2–10 using a Zeta-Meter 3.0 (Zeta-Meter Inc., USA). Electrodes placed at each end of the chamber were connected to the Zeta-Meter 3.0 unit, producing an electric field across the chamber. Charged colloids moved in the field and their velocity and direction were related to their zeta potential. Each sample was measured ten times at each pH, and the mean for each sample was taken as the zeta potential.

### 2.4. Photodegradation experiments

Photocatalytic degradation experiments were performed in a 3.5 L, hollow, cylindrical, glass reactor. The reaction system was stirred continuously at 400 rpm and aerated to keep the catalysts suspended. A 400 W visible lamp (Philips) was placed inside the quartz tube as an irradiation source. The light intensity and main emission wavelength were 2.03 mW/cm$^2$ and 410 nm, respectively. The BPA concentration was 10 mg/L in each experiment. Direct photolysis and adsorption reactions were also performed to compare the photodegradation efficiency of BPA with that associated with visible light/$TiO_2$ reactions. A 15 mL aliquot was extracted from the photoreactor at pre-specified intervals. The $TiO_2$ suspension was separated out by centrifugation at 5000 rpm for 10 min, and then filtered through a 0.22 μm filter. The concentration of hydroxyl radicals that was generated in various visible light/$TiO_2$ systems was measured using the method of Jen et al. [17].

### 2.5. Analysis

The BPA concentration was measured using a high-performance liquid chromatograph (HPLC) with a UV detector (Agilent Technologies). The UV detector was set to a wavelength of 197 nm. Separations were performed using a Supelcosil C18 column (Supelco). The mobile phase was MilliQ-water and $CH_3CN$ (40:60 v/v) at a flow rate of 0.5 mL/min. The injection volume was 20 μL. The equation of the calibration curve for BPA is peak area = 539.42 $C_{BPA}$ + 11.267 ($r^2$ = 0.9999), where $C_{BPA}$ is the concentration of BPA in the range 0–10.0 mg/L. The detection limit of the approach for BPA was determined to be 0.02 mg/L herein. The decrease in total organic carbon (TOC), as measured using an O.I. 1010 TOC analyzer, revealed the mineralization of BPA. Kato and Niihara [18] determined that PEG decomposes completely at a relatively low temperature. Since the generated $TiO_2$ was herein calcined at 400 °C, adding PEG did not affect the TOC analyses. HPLC was also applied indirectly to detect hydroxyl radicals following a trapping reaction with salicylic acid (250 mg/L) in visible light/$TiO_2$ systems. The flow rate of the mobile phase was set to a flow rate of 0.8 mL/min. The wavelengths of salicylic acid, 2, 3-DHBA, 2, 5-DHBA and catechol were set to 296, 308, 320 and 275 nm in the UV detector, respectively.

## 3. Results and discussion

### 3.1. Characteristics of produced $TiO_2$

Fig. 1 presents the TEM images of $TiO_2$ with different PEG ratios. The diameter of $TiO_2$/PEG600 ranged from 10 to 30 nm, independently of the PEG600 addition ratio. In PEG/catalyst systems, PEG acts as a surfactant stabilizer, suppresses coagulation and increases the homogeneity of the final product. The $TiO_2$ powder that is prepared without adding PEG is non-uniform, while that prepared by adding PEG to the sol is uniform and has a granular texture (Fig. 1). Notably, increasing the PEG addition ratio reduced the coagulation of the particles. This observation resembles that made by Sonawane et al. [16]. Stengl et al. [19] noted that adding PEG to the reaction mixture narrowed the size distribution of the prepared particles.

Fig. 2 displays the XRD diagrams of the generated $TiO_2$. The $2\theta$ peaks at 25.4°, 37.8° and 48.1° reveal the anatase-type $TiO_2$ structure and those at 27.6° and 36.1° reveal rutile-type $TiO_2$ (Fig. 2). The temperature affects the distribution of these two phases, and 400 °C appears to yield more of the active anatase phase than the other temperatures considered [20]. Accordingly, all catalysts were calcined at 400 °C. For a given PEG mol percentage addition (1%), the intensity of anatase followed the order $TiO_2$/PEG600>$TiO_2$/PEG3500>$TiO_2$/PEG200 (Fig. 2 and Table 1). Therefore, PEG molecular weight at 600 g/mol was associated with a larger anatase type of the produced $TiO_2$. The effects of PEG molecular weight showed that the suitable molecular weight was at 600 g/mol because higher or lower PEG molecular weight could lag or increase to decompose PEG during forming $TiO_2$ process. In addition, 400 °C not only yielded more of the active anatase phase but decomposed PEG just right during forming $TiO_2$ process. Anatase is generally considered to be the photoactive form, whereas rutile is considered to exhibit low photocatalytic activity. However, the source of the difference in activity is unknown. Table 1 displays the surface areas of the various produced $TiO_2$ particle and adding PEG increased the surface area of $TiO_2$. When 1% PEG was added, the