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Photolytic reaction mechanism and impacts of coexisting substances on photodegradation of bisphenol A by Bi_2WO_6 in water

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ABSTRACT

Bi_2WO_6 displayed great photolytic degradation efficiency to bisphenol A (BPA) under simulated solar light irradiation but its reaction mechanism and the impacts of coexisting substances on the degradation remain unclear. In present study, the reaction mechanism was investigated using DMPO spin-trapping ESR spectra and experiments with scavengers of hydroxyl radicals (•OH) and holes. The results supported that hole oxidation mainly governed the photodegradation process. As a common humic substance in natural water, humic acid accelerated the degradation of BPA when its concentration was 1 mg/L, while the photodegradation was impeded with the increase of humic acid concentration in the range of 5–20 mg/L. Almost all anions, including NO_3^-, HCO_3^-, Cl^-, SO_4^{2-} inhibited the degradation of BPA by Bi_2WO_6 and their inhibition effects followed the order of SO_4^{2-} -> Cl^- > HCO_3^- > NO_3^-. Cations of Na^+, K^+, Ca^{2+} and Mg^{2+} displayed slight suppressing effect on BPA degradation mainly due to the impact of Cl^- coexisting in the solution. However, Cu^{2+} hindered the BPA photodegradation heavily. Fe^{3+} and H_2O_2 affected the photodegradation in a complicated way: they suppressed or promoted the photodegradation depending on their concentrations. This could be the result of competition between photolyitc hole generated by Bi_2WO_6 and •OH produced by Fe^{3+} or H_2O_2.

1. Introduction

Bisphenol A [2,2-bis(4-hydroxyphenyl)propane, BPA] is a key building block material for epoxy and polycarbonate resins and has been widely used for commercial products (Staples et al., 1998). A large amount of BPA has been released into the aquatic environment. As one of the typical endocrine disrupting chemicals (Japan, 1998), BPA may cause various adverse effects on aquatic organisms even at low exposure levels (Tsai, 2006). Recently, many kinds of methods have been developed to remove or degrade BPA, and photocatalytic degradation is a promising method due to its extremely efficient degradation rate, high mineralization efficiency and low toxigenicity, ideally producing CO_2 and H_2O as end products (Belgiorno et al., 2007). Among the various photocatalysts, TiO_2 has been widely used in degradation of organic chemicals in water and could completely mineralize BPA to CO_2 under UV irradiation (Chiang et al., 2004; Ohko et al., 2001). However, the main shortcoming of TiO_2 is that it only absorbs ultraviolet light no longer than 387.5 nm, which only accounts for about 4% of sunlight (Asahi et al., 2001; Linsebigler et al., 1995; Yu et al., 2003). Bismuth tungstate (Bi_2WO_6) was reported to be capable of degrading

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chlorinated contaminants and azo dyes under visible light irradiation (Fu et al., 2005; Zhang et al., 2007; Zhao et al., 2007). In our previous research, Bi_2WO_6 prepared by hydrothermal method displayed excellent photocatalytic activity and mineralization capacity to BPA under simulated solar light irradiation (Wang et al., 2010). It was speculated that BPA molecules were attacked by the photogenerated holes by Bi_2WO_6 but not $^{\bullet}OH$ (Wang et al., 2010), which is the main oxidizing species in the photodegradation of contaminants (including BPA) by TiO_2 (Guo et al., 2009; Kaneco et al., 2004; Watanabe et al., 2003). However, no direct evidence was provided to support this assumption.

In most of the studies about photodegradation of BPA, initial concentration of BPA, dosage of photocatalyst and pH of reaction solution are usually considered as the factors which could affect photodegradation efficiency (Ahmed et al., 2011; Daskalaki et al., 2011; Tao et al., 2011; Wang et al., 2010). In real application, photodegradation could also be affected by many other factors and one of them is the coexisting substances in natural aquatic system, such as humic acid, inorganic metal cations and anions. Humic substances are one of the principal organic constituents in natural water with concentrations in the range of several mg/L to several tens of mg/L. Chen et al. reported that humic acid as a photosensitizer promoted the mineralization of dimethoate by TiO_2 under UV irradiation (Chen et al., 2010). Inorganic ions, such as cations of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+} and Fe^{3+}, and anions of NO_3^-, HCO_3^-, Cl^-, SO_4^{2-} are also very common in natural water. These inorganic ions in water would affect the degradation rate of organic pollutants and even their degradation mechanisms (Abdullah et al., 1990; Chen et al., 2001).

Hydrogen peroxide (H_2O_2) is a strong oxidative reagent and commonly used to enhance the rates of photocatalytic oxidation reactions (Chan, 2001). It was reported that H_2O_2 enhanced the oxidation by TiO_2. It remains unclear if H_2O_2 presents any impacts on the photocatalytical reaction by Bi_2WO_6 given that it has different photocatalytic reaction mechanism from TiO_2.

The main objectives of this paper are in two aspects: firstly, to disclose the degradation mechanism of BPA by Bi_2WO_6 under simulated solar irradiation using $^{\bullet}OH$ or hole trapping reagents, such as methanol, isopropanol, KI, and electron spin resonance (ESR) analysis. Secondly, to investigate the impacts of the following coexisting substances on the photocatalytic degradation of BPA by Bi_2WO_6: humic acid, inorganic anions (NO_3^-, HCO_3^-, Cl^-, SO_4^{2-}), inorganic cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{3+}) and H_2O_2. The results would provide useful guidance when Bi_2WO_6 is used in real applications.

2. Materials and methods

2.1. Reagents

Bi_2WO_6 catalyst was prepared by hydrothermal method using bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) and sodium tungstate dehydrate ($Na_2WO_4{\cdot}2H_2O$). The detailed synthesized process refers to our previous study (Wang et al., 2010). The nitrone spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and humic acid were purchased from Sigma–Aldrich (Shanghai) Trading Co., Ltd. P25 TiO_2 particles were purchased from Degussa Co., Ltd. Cations of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+} and Fe^{3+} were used in their chloride salts, and anions of NO_3^-, HCO_3^-, Cl^-, SO_4^{2-} were used in their sodium salts. All these salts, H_2O_2 (30 wt %) and KI were analytical grade and purchased from Chemical Technology Co., Ltd., Tianjin, China. Methanol and isopropanol were from Concord Technology Co., Ltd, Tianjin, China.

2.2. Photocatalytic reaction

The photocatalytic reaction was carried out in a XPA-7 photocatalytic reactor (Xujiang Electromechanical Plant, Nanjing, China) equipped with 10 mL quartz test tubes. Simulated sunlight irradiation was provided by an 800 W xenon lamp (Institute of Electric Light Source, Beijing), and the intensity of the lamp was 13.2 mW/cm^2. The reaction system was cooled by circulating water and maintained at room temperature. The initial concentration of BPA was 20 mg/L (0.088 mmol/L), and the dosage of Bi_2WO_6 was 1.0 g/L. The pH of the solution was 6.2. The target substances, including humic acid, inorganic anions, inorganic cations and H_2O_2 were added at predetermined concentrations. Before irradiation, the suspension was magnetically stirred in dark for 30 min to ensure adsorption equilibrium of BPA on the catalysts. The lamp was then turned on and the photodegradation was initiated. Approximately 0.5 mL of reaction solution was taken at given time intervals and filtered through 13 mm × 0.45 μm membrane for BPA analysis by high performance liquid chromatography (HPLC). The removal efficiency (R) of BPA under various conditions was calculated as follows:

$$R = (C_0 - C)/C_0 \times 100\% \quad (1)$$

where C_0 and C represent the initial and residual concentrations in the photocatalytic reaction solution. All the experiments were preformed in triplicate and the mean values were reported. All the data with standard deviation were listed in Table S1 in Supplementary data.

The settings for the ESR spectrometer (Bruker EMX-6/1, Germany) were as follows: center field, 3514.82 G; sweep width, 120.00 G; microwave frequency, 20.02 mW; modulation frequency, 100 kHz; power, 1.25 G. In the catalyst/DMPO solution, DMPO concentration was 10 mmol/L and the catalyst amount was 1.0 g/L.

The pH of the point of zero charge (pH_{PZC}) was measured by pH drift method (Lopez-Ramon et al., 1999): 20 mL of a 0.01 mol/L NaCl solution was placed in a jacketed titration vessel, thermostatted at 298 K, and N_2 was bubbled through the solution to stabilize the pH by preventing the dissolution of CO_2. The pH was then adjusted to successive initial values between 2 and 12, by adding either HCl or NaOH and 0.1 g Bi_2WO_6 catalyst was added to solution. The final pH, reached stable after 48 h, was measured and plotted against the initial pH. The pH at which the curve crossed the line pH (final) = pH (initial) was taken as the pH_{PZC} of Bi_2WO_6.

3. Results and discussion

3.1. Photodegradation mechanism of Bi_2WO_6

ESR spin-trap with DMPO is a useful technique employed to monitor reactive oxygen species generated in the reaction system. The ESR spectra of the reaction solutions using P25