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Photocatalytic degradation of bisphenol A over a $ZnFe_2O_4/TiO_2$ nanocomposite under visible light

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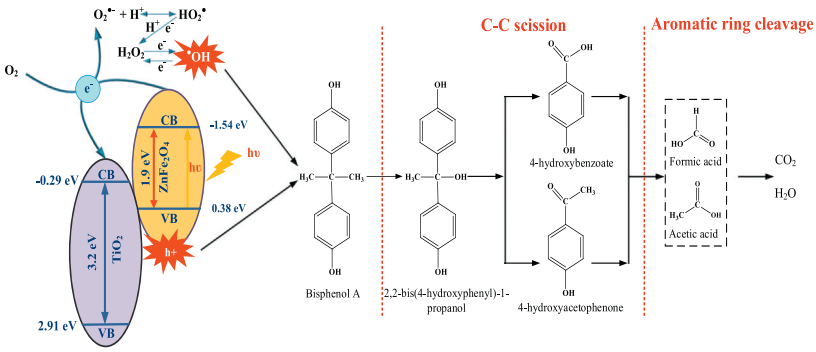
HIGHLIGHTS

- TiO_2 doped with 1.0-wt% $ZnFe_2O_4$ exhibited the highest visible-light BPA photodegradation.
- The k_{obs} of BPA photodegradation followed the order: pH 9.0 > pH 7.0 > pH 5.0 > pH 3.0 > pH 11.0.
- Cl^- and SO_4^{2-} enhance and humic acid inhibits BPA degradation over $ZnFe_2O_4$-TiO_2.
- Near complete BPA removal (>90%) in lake water was observed under visible light irradiation
- BPA degradation over $ZnFe_2O_4$-TiO_2 in lake water was high for at least five continuous cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

A $ZnFe_2O_4$-TiO_2 nanocomposite combining p-type $ZnFe_2O_4$ and n-type TiO_2 was successfully fabricated. The $ZnFe_2O_4$-TiO_2 nanocomposite greatly enhanced the bisphenol A (BPA) photodegradation under visible light irradiation at 465 ± 40 nm. Loading TiO_2 with 1 wt% of $ZnFe_2O_4$ produced high photocurrent and low charge transfer resistance. The photodegradation rate of BPA by $ZnFe_2O_4$-TiO_2, which was highly dependent on the water chemistry including pH, anions, and humic acid, was 20.8–21.4 times higher than that of commercial TiO_2 photocatalysts. Chloride and sulfate ions enhanced BPA photodegradation mostly due to the production of more radical species; whereas nitrate, dihydrogen phosphate, and bicarbonate ions decreased the photodegradation rate of BPA due to the scavenge of hydroxyl radicals. The photoactivity and recyclability of $ZnFe_2O_4$-TiO_2 in lake water was also assessed. A near complete BPA removal from lake water was observed under visible light irradiation. Furthermore, >90% of photocatalytic activity toward BPA degradation was achieved in 5 cycles of continuous addition of BPA to the lake water. The BPA degradation intermediates were identified by HPLC/MS/MS and possible reaction pathways were proposed. Results clearly demonstrate the excellent visible-light-sensitive photocatalytic degradation of BPA over $ZnFe_2O_4$-TiO_2 composite which has a great application potential for the decomposition of emerging contaminants in impaired waters.

1. Introduction

The photocatalytic degradation of emerging contaminants such as pharmaceutics and endocrine disrupting chemicals (EDCs) has recently

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attracted considerable public attention. Bisphenol A (BPA), also known as 2,2-bis (4-hydroxyphenyl) propane, is an important industrial chemical of wide usage in the manufacture of numerous epoxy resins and polycarbonate plastics as food and cold drink packaging materials (V.K. Sharma et al., 2009). The water solubility of BPA is in the range of 120–300 mg L^{-1} with pK_a values of 9.6 and 10.2. BPA, a typical EDC and plasticizer commonly found in water and wastewater effluents, may cause endocrine-disruptive effects on human beings and aquatic biota. Therefore, there is an urgent need to develop effective BPA detoxification technology. Several studies on enhancing the photocatalytic degradation of BPA by modifying the morphology of UV and/or visible light sensitive photocatalysts have been reported recently (Doong et al., 2013; Doong and Liao, 2017; Hassan et al., 2018). However, no information is available on the performance of photocatalytic nanocomposites, with capability of highly efficient and rapid decomposition of BPA under different water chemistry conditions.

The combination of n-type TiO_2 with p-type photocatalysts such as CuO, Cu_2O, and $CuFe_2O_4$ is known to be photosensitive toward the decomposition of contaminants in aqueous solutions under visible light irradiation (Song et al., 2018; Lee et al., 2018; Li et al., 2017; Casbeer et al., 2012). Specifically, the spinel ferrite of zinc ferrite ($ZnFe_2O_4$), a magnetic p-type photocatalyst with a narrow bandgap of 1.9 eV, offers extra catalytic reactivity by virtue of its crystal lattice and band gap capable of absorbing visible light that significantly enhances the photodegradation efficiency of a wide variety of contaminants (Y.C. Sharma et al., 2009; Sathishkumar et al., 2013) as well as solar energy harvesting, water splitting, and manufacture of dye-sensitized solar cells (Kulkarni et al., 2016; McDonald and Choi, 2011; Sheikh et al., 2013). However, low valence band potential and poor photoelectric conversion efficiency make $ZnFe_2O_4$ an inferior photocatalyst for pollutant degradation (Hankarea et al., 2011). Several studies have reported that incorporating $ZnFe_2O_4$ to TiO_2 and graphene forms a new type of nanocomposite, which exhibits significant improvement on photocatalytic activity (Nada et al., 2017; Yao et al., 2015; Rani and Rajan, 2017; Mady et al., 2017). Nada et al. (2017) have fabricated $ZnFe_2O_4$@TiO_2 nanofibers and reported that the deposition of TiO_2 onto $ZnFe_2O_4$ increases the electron–hole separation and improves the photodegradation efficiency of methylene blue under visible light. Yao et al. (2015) have synthesized N-doped TiO_2/$ZnFe_2O_4$ hybrid and reported that the photocatalyst is effective in the degradation of various organic dyes and recyclable for reuse. We have previously reported that the addition of a small amount of $ZnFe_2O_4$ to TiO_2 can enhance the visible-light photoactivity of the photocatalyst in rapid photodegradation of organic dyes (Nguyen and Doong, 2016) and BPA (Nguyen and Doong, 2017) using synthetic water solutions. However, we did not evaluate the optimal loading of $ZnFe_2O_4$ on TiO_2 for the best BPA degradation under visible light irradiation in our previous studies.

The water chemistry of aqueous solutions such as anionic species, pH, and dissolved organic matters (DOMs) can affect the photocatalytic activity of photocatalysts. Several studies have shown that pH plays a crucial role in controlling the surface charge of photocatalysts, the aggregation of nanoparticles, and the position of conduction and valence bands (Doong et al., 2001; L. Li et al., 2016; Hisatomi et al., 2014). Moreover, it has been demonstrated that the adsorption of some ions such as Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^- can scavenge holes and hydroxyl radicals during photocatalysis and inhibit the photocatalytic degradation of contaminants in water (Carbajo et al., 2016; Rioja et al., 2016). Dissolved organic matters (DOMs) have multiple effects on the degradation of contaminants. For example, humic acids, upon adsorption onto photocatalysts, bring about light attenuation, scavenge holes, occupy active sites of photocatalysts, and ultimately affect the photocatalytic activity (Chládková et al., 2015; Maeng et al., 2015; Chiang and Doong, 2014). On the other hand, Doong et al. (2014) and R. Li et al. (2016) have reported that the quinone moiety of humic acid can be electron mediator or photosensitizer that accelerates the degradation efficiency of contaminants. It must be noted that the above studies were conducted mainly in synthetic water medium and only a few have attempted to investigate the effect of water matrix on the photocatalytic degradation of organic contaminants in natural water (Sturini et al., 2013; Rimoldi et al., 2017; Uyguner-Demirel et al., 2017). Moreover, the reaction kinetics and mechanism for BPA photodegradation over $ZnFe_2O_4$-TiO_2 nanocomposites under various water chemistry conditions remain unclear. The feasibility of $ZnFe_2O_4$-TiO_2 nanocomposites for the visible-light photodegradation of BPA in contaminated water has also not been assessed.

Herein, we have fabricated visible-light-sensitive $ZnFe_2O_4$-TiO_2 nanocomposites for enhancing the photocatalytic degradation of BPA under various water chemistry conditions. Specifically, water chemistry parameters such as pH, dissolved organic matters (DOMs), and major anions that may affect the visible-light photodegradation of BPA by $ZnFe_2O_4$-TiO_2 were investigated. The photocatalytic reaction kinetics as well as the pathways for BPA degradation over $ZnFe_2O_4$-TiO_2 nanocomposites were studied under visible light irradiation. The feasibility of $ZnFe_2O_4$-TiO_2 as a visible-light-sensitive photocatalyst for the degradation of BPA in lake waters was evaluated in terms of its stability and reusability and the efficacy of eco-toxicity reduction of the treated water.

2. Materials and methods

2.1. Fabrication of $ZnFe_2O_4$-TiO_2 nanocomposite

Zinc ferrite ($ZnFe_2O_4$) was prepared by non-aqueous phase synthesis method according to our previous work (Nguyen and Doong, 2016). In brief, 14 mL of deionized water containing 297 mg of Zn $(NO_3)_2{\cdot}6H_2O$ (CAS-10196-18-6, ≥98%) and 808 mg of $Fe(NO_3)_3{\cdot}9H_2O$ (CAS-7782-61-8, ≥98%) were added into 10 mL of 1-pentanol (CAS-71-41-0, ≥99%) solution with 2 mL of 0.5 mmol of oleic acid (CAS-112-80-1, ≥99%) and oleylamine (CAS-112-90-3, ≥98%) under stirring. After the successful synthesis of $ZnFe_2O_4$ nanoparticles, various amounts of $ZnFe_2O_4$ at weight ratios of 0.2–2 wt% were mixed with 80 mg of ST01 TiO_2 (Ishihara Sangyo Ltd., Tokyo, Japan) in 20 mL of octanol (CAS-111-87-5, ≥99%) and then dispersed in an ultrasonic bath for 1 h. The mixture was heated and refluxed at 140 °C for 2 h under well-mixing condition to cross-link $ZnFe_2O_4$ on the surface of TiO_2 nanoparticles. After cooling to room temperature, the $ZnFe_2O_4$-TiO_2 nanocomposite was harvested by centrifugation and washed with *n*-hexane/ethanol mixture several times. The purified solid was dried in a vacuum oven at 60 °C for 6 h and then stored in a desiccator for future use.

2.2. Photocatalytic degradation of BPA over $ZnFe_2O_4$-TiO_2

The photocatalytic activity of $ZnFe_2O_4$-TiO_2 nanocomposite toward BPA (CAS-80-05-7, ≥99%) degradation was investigated in a quartz reactor surrounded by eight 8 W-visible-light lamps (BLB lamp, -8T5, Winstar Lighting Co., Taipei, Taiwan) at the major peak wavelength of 465 ± 40 nm. The light intensity distribution of the lamp is shown in Fig. S1 (Supplementary data) and all experiments were carried out under the irradiation at the same light intensity of 150 mW cm^{-2}. 20 mg of photocatalysts including $ZnFe_2O_4$-TiO_2, pure $ZnFe_2O_4$, and commercial TiO_2 nanoparticle were added to 20 mL of solutions containing 10 mg L^{-1} of BPA at pH 3–11. The initial solution pH was adjusted by adding 0.1 N HCl and NaOH to the desired value. The effect of DOMs, major cations and anions on BPA photodegradation over $ZnFe_2O_4$-TiO_2 was examined by the addition of an appropriate amount of stock humic acid solution and ion species such as sodium salts of Cl^-, SO_4^{2-}, $H_2PO_4^-$, and HCO_3^- and chloride salts of Na^+, K^+, Ca^+, Mg^{2+}, and Fe^{3+} to 20 mL of mixture to yield a final concentration of 1–20 mg L^{-1} of humic acid and 0.1 mM of each ion, respectively.

To minimize the influence of adsorption on the photodegradation efficiency and rate, BPA and photocatalyst were pre-mixed for 60 min