Chemosphere 150 (2016) 139–144

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Photocatalytic degradation and removal mechanism of ibuprofen via monoclinic $BiVO_4$ under simulated solar light

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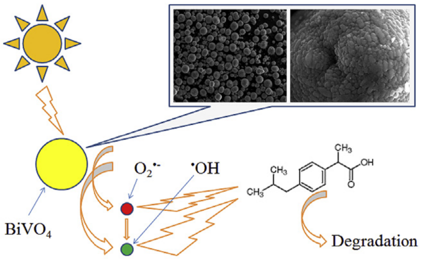
HIGHLIGHTS

- Synthesis and characterization of monoclinic $BiVO_4$.
- Photocatalytic activity for degradation of ibuprofen under simulated solar light.
- Effect of operational parameters on the photocatalytic degradation of ibuprofen.
- Removal mechanism of ibuprofen via monoclinic $BiVO_4$ under simulated solar light.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 December 2015
Received in revised form
7 February 2016
Accepted 9 February 2016
Available online xxx

Handling Editor: Klaus Kümmerer

Keywords:
$BiVO_4$
Photocatalytic degradation
Ibuprofen
Kinetics
Mechanism

ABSTRACT

Characterized as by X-ray diffraction, scanning electron microscopy and UV–vis diffuse reflectance spectra techniques, $BiVO_4$ photocatalyst was hydrothermally synthesized. The photocatalytic degradation mechanisms of ibuprofen (IBP) were evaluated in aqueous media via $BiVO_4$. Results demonstrated that the prepared photocatalyst corresponded to phase-pure monoclinic scheelite $BiVO_4$. The synthesized $BiVO_4$ showed superior photocatalytic properties under the irradiation of visible-light. The photocatalytic degradation rate of IBP decreased with an increase in the initial IBP concentration. The degradation process followed first-order kinetics model. At an IBP concentration of 10 mg L^{-1}, while a $BiVO_4$ concentration of 5.0 g L^{-1} with pH value of 4.5, the rate of IBP degradation was obtained as 90% after 25 min. The photocatalytic degradation of IBP was primarily accomplished via the generation of superoxide radical ($O_2^{•-}$) and hydroxyl radicals (•OH). During the process of degradation, part of the •OH was converted from the $O_2^{•-}$. The direct oxidation of holes (h^+) made a minimal contribution to the degradation of IBP.

1. Introduction

The compound 2-[3-(2-methylpropyl)phenyl] propanoic acid is commercially available as ibuprofen (IBP). Relative to other anti-inflammatory and antipyretic drugs like aspirin and acetaminophen, the IBP appears excellent properties of low toxicity, high efficacy and minimal side effects (Buser et al., 1999). Thus, IBP is more widely used at present. Due to its widespread application, IBP brought the formation of pseudo persistent phenomena. IBP inflicted damage on species of flora and fauna in aquatic ecosystems (Mendez-Arriaga et al., 2009; Ternes et al., 2004). Hence, IBP emerged as a new form of organic micropollutant.

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http://dx.doi.org/10.1016/j.chemosphere.2016.02.045
0045-6535/

Photocatalytic technology is a potential way in the treatment of organic pollutants. As a regularly studied semiconductor photocatalyst, TiO_2 is widely adopted in environmental modification and water treatment (Anandan and Ashokkumar, 2009; Hu et al., 2007; Im et al., 2012). However, TiO_2 has a wide band gap of 3.20 eV. The band gap is selective for the absorption of ultraviolet light and it accounts for only ~5% of the ambient sunlight spectrum (Asahi et al., 2001; Wang et al., 2010; Yu et al., 2003). So it is difficult to develop TiO_2 as commercially acceptable products for photocatalyst candidate. New visible-light-driven photocatalytic materials is indispensable to develop to efficiently utilize a greater portion of the solar spectrum. The materials must possess robust activity. Recently, $BiVO_4$ come into the focus of researchers for its such unique properties as ferroelasticity (Nepochatenko and Dudnik, 2005), ionic conductivity (Rullens et al., 2006), photocatalytic activity for water splitting (Sayama et al., 2006; Su et al., 2010; Tokunaga et al., 2001) and capacity for the degradation of harmful pollutants (Jiang et al., 2008; Yin et al., 2010; Zhang et al., 2006). The photocatalytic activity of $BiVO_4$ depends strongly on its crystalline form (Kohtani et al., 2003; Li et al., 2009; Zhang et al., 2007) and morphology (Liu et al., 2010; Wang et al., 2009). $BiVO_4$ possesses such three primary crystalline forms, as tetragonal zircon, monoclinic scheelite and tetragonal scheelite structures. Monoclinic scheelite $BiVO_4$ owns a moderate band gap (2.40 eV) and exhibits a best photocatalytic activity under visible-light irradiation (Tokunaga et al., 2001).

The photocatalytic degradation of ibuprofen was not reported via monoclinic $BiVO_4$ under solar light. Hence, the aim of this study was to investigate the photocatalytic activity of monoclinic $BiVO_4$ in the degradation of IBP, and to illustrate the effects of operational parameters. The photocatalytic degradation mechanism was studied by quenching analysis as well.

2. Materials and methods

2.1. Reagents

$Bi(NO_3)_3 \cdot 5H_2O$ and NH_4VO_3 were purchased from Aladdin Industrial Corporation (Shanghai). Ibuprofen was purchased from TCI Development Co. Ltd. (Shanghai). Sulfuric acid, nitric acid, sodium hydroxide, acetic acid, ethanol, benzoquinone, isopropanol were purchased from Chengdu Kelong Chemical Reagent Co. Ltd. All of the reagents above were of analytical grade and required no further purification. The methanol and acetonitrile purchased from Anaqua Chemicals Supply Co. Ltd. (USA) were of HPLC grade. Ultrapure water from a TKA Smart 2 Pure system (Germany) was used in the preparation of all aqueous solutions.

2.2. Synthesis of $BiVO_4$ photocatalysts

The $BiVO_4$ photocatalyst was prepared by a hydrothermal process. In a typical procedure, $Bi(NO_3)_3 \cdot 5H_2O$ (5 mM) and NH_4VO_3 (5 mM) were dissolved in 40 mL of HNO_3 (4 M) and 40 mL of NaOH (4 M) respectively. To obtain a stable homogeneous mixture, these two solutions were combined under ultrasonication for 10 min. The pH value of the final mixture was adjusted to 7 with the addition of NaOH. After standing for 24 h, the suspension was transferred into a 100 mL Teflon autoclave. The autoclave was filled up to 80% of the total volume. The hydrothermal treatment was performed at 180 °C for 3 h. Subsequently, the product was collected by filtration and rinsed several times with ultrapure water and ethanol. Finally, the products were dried at 80 °C for 6 h in ambient air (Ge, 2008; Zhang et al., 2006).

2.3. Characterization of $BiVO_4$ photocatalysts

The samples were characterized by means of X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and ultraviolet–visible (UV–Vis) diffuse reflectance spectroscopy. The XRD patterns were acquired through X-ray diffractometer (ULTIMA-III, Rigaku, Japan). The SEM images were obtained with a field emission scanning electron microscope (SXL-30ESM, Philips, Netherlands). The absorption spectrum was measured with a UV–vis spectrophotometer (UV-2450, Shimadzu, Japan).

2.4. Ibuprofen solution

The 1 g L^{-1} IBP stock solution was prepared with acetonitrile and reserves were stored in a refrigerator at 4 °C. Experimental solutions were prepared by the addition of an appropriate volume of stock solution into a brown volumetric flask. Nitrogen was supplied to evaporate the acetonitrile completely. Ultrapure water was then added. Next, agitation was introduced to promote the process. Dissolution was facilitated using sonication. The pH value was subsequently adjusted through the addition of 1% sulfuric acid or sodium hydroxide solution. Finally, the required volumes were achieved.

2.5. Photocatalytic degradation of ibuprofen

All experiments were performed within an XPA-7 photochemical reactor. Pyrex test tubes were adopted to contain the solutions. The irradiation was provided by a 350 W long-arc Xe lamp ($\lambda > 290$ nm). Prior to illumination, the suspension was magnetically stirred in the dark for 1 h. The aim was to ensure the adsorption/desorption equilibrium of IBP with the photocatalyst powders. The samples were removed at different time intervals for analysis. Three parallel experiments were conducted for each group. The results of each group were averaged in the analysis.

2.6. Analytical method

Ibuprofen concentrations were determined with a HPLC system (Shimadzu, Japan). The chromatographic conditions were as follows. Column: Zorbax Eclipse XDB-C18 (2.1 mm × 150 mm, 5 μm); Temperature: 30 °C; Mobile phase: acetonitrile/acetic acid buffer solution (containing 0.3% acetic acid, 50:50, v/v); Flow rate: 0.2 mL min^{-1}; Injection volume: 4 μL; Photodiode array detector: 263 nm wavelength.

3. Results and discussion

3.1. Morphology and structure

The diffraction pattern (Fig. 1) shows that all of the peaks could be indexed as the standard card (JCPDS Card No. 14-0688) of monoclinic $BiVO_4$ (Yu and Kudo, 2005; Zhou et al., 2006) and no other peaks from possible impurities were detected. The XRD analysis results indicated that the prepared photocatalyst corresponded to phase-pure monoclinic scheelite $BiVO_4$. The SEM micrographs (Fig. 2) of the $BiVO_4$ sample indicates that the prepared $BiVO_4$ was in the form of microspheres. The surfaces of the sample were formed by many small particle agglomerations. These surfaces were uneven, and part of which were comprised of hollow structures.

The UV–Vis DRS of the $BiVO_4$ sample is illustrated in this work (Fig. 3). Based on the equation of $Eg = 1240/\lambda g$, the Eg value of the $BiVO_4$ sample was obtained as 2.32 eV. The Eg value is slightly lower than, or similar to, those of the $BiVO_4$ materials reported in