



## Research article

# Photocatalytic oxidation of trace carbamazepine in aqueous solution by visible-light-driven $\text{ZnIn}_2\text{S}_4$ : Performance and mechanism



Longli Bo<sup>\*</sup>, Kebo He, Na Tan, Bo Gao, Qiqi Feng, Jiadong Liu, Lei Wang

School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Yan Ta Road No. 13, Xi'an, 710055, China

## ARTICLE INFO

## Article history:

Received 31 July 2016

Received in revised form

17 December 2016

Accepted 20 December 2016

## Keywords:

Carbamazepine

$\text{ZnIn}_2\text{S}_4$

Photocatalysis

Intermediates

Degradation pathway

## ABSTRACT

In this work, visible-light-driven  $\text{ZnIn}_2\text{S}_4$  photocatalyst (band gap 1.98 eV, absorption wavelength 300–600 nm) was synthesized by a facile hydrothermal method for photocatalytic degradation of trace pharmaceutical carbamazepine (CBZ) in aqueous solution, and characterized by UV–Vis diffusive reflectance spectroscopy, BET, SEM and XRD, respectively. It demonstrated that a complete degradation of CBZ was achieved with an optimal  $\text{ZnIn}_2\text{S}_4$  dosage of 30 mg/L under a 100 W iodine-gallium lamp irradiation of 20 min, which afforded the reaction rate constant and half-life being respectively 10.44 times higher and 1/8 less than that obtained by a direct photolysis without  $\text{ZnIn}_2\text{S}_4$  photocatalyst. A negligible influence of initial solution pH on photocatalytic degradation of CBZ was confirmed under the given pH range of 5.0–9.0. The degradation efficiency of CBZ was slightly decreased from 91% to 84% after five consecutive cycles. Hydroxy radical ( $\cdot\text{OH}$ ) plays an important role in CBZ degradation accompanying a synergistic effect of photogenerated hole ( $\text{h}^+$ ) and  $\text{O}_2^{\cdot-}$  active species during reaction. Further, 44 intermediates were detected by LCMS-IT-TOF technique and tentative degrading pathways were proposed on the basis of the experimental results.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Pharmaceuticals as emerging environmental pollutants have aroused great attention to researchers due to their potential harm resulted from easy bioaccumulation and persistence for aquatic life and human beings (Kümmerer, 2009). Among them, carbamazepine (CBZ, 5H-dibenzo [b, f] azepine-5-carboxamide) as an aromatic heterocyclic compound with symmetrical structure was frequently detected in aquatic environment and already considered to be a typical representative (Zhang et al., 2008) owing to its extensive use as medicine/medical intermediate for epilepsy, psychomotor seizure and trigeminal neuralgia diseases, and an average consumption was approximately 1014 tons per year according to Intercontinental Marketing Services (IMS) health data (Zhang et al., 2008). Generally, 78% of CBZ can be absorbed and utilized by human tissues, while the rest is excreted into water circumstance (The Internet Drug Index, 2006). Therefore, CBZ has been determined in drinking water, surface water and the effluent of sewage treatment plant at a relative low concentration (ng/L– $\mu\text{g/L}$ ) (Silvia et al., 2010).

Although relative low concentration (ng/L– $\mu\text{g/L}$ ) of CBZ was detected in aquatic environment, it might cause special physiological malfunction to impact on aquatic ecosystem through a long-term biological accumulation, such as inducing the damage to liver of aquatic life (Li et al., 2011), thus influencing the behavior of freshwater benthic species (Jarvis et al., 2014) and altering physiological function of vertebrate (Chen et al., 2014). Additionally, the spreading of CBZ residues from surface water and groundwater to drinking water may have adverse effect on human health. Previous studies have revealed that CBZ is highly resistant to biological treatment with a lower removal efficiency (~10%) (Serge et al., 2006). Therefore, it is of great importance to develop low-cost treatment technique for highly efficient removal of CBZ from aqueous environment to protect water safety.

$\text{TiO}_2$ -based photocatalysis as a favourable technology has been widely utilized to effectively eradicate CBZ (Doll and Frimmel, 2005). Irene et al. (2014) reported that 96% of CBZ with an initial concentration of 10 mg/L can be removed by 100 mg/L  $\text{TiO}_2$  under UV irradiation of 30 min. Rao et al. (2013) confirmed that 35% of CBZ can be photocatalytically decomposed by  $\text{WO}_3$  photocatalyst within 1 h under visible light illumination with a main wavelength of 420 nm. Xu et al. (2013) demonstrated that the removal of CBZ can be up to 72.4% through a  $\text{BiPO}_4/\text{UV}$  system. To date, most of

<sup>\*</sup> Corresponding author.

E-mail address: [bolongli@xauat.edu.cn](mailto:bolongli@xauat.edu.cn) (L. Bo).

photocatalysts reported in literatures have wide band gaps, enabling them to be commonly applied in UV region. It is well-known that UV energy occupies only less than 5% of solar energy, and 45% of solar energy belongs to visible light. Therefore, development of visible light active photocatalysts is critically important to effectively remove CBZ from aqueous solution. Compared with metallic oxides, the band gaps of metallic sulfides are narrower and more suitable to absorb visible light. Ternary metallic sulfides with visible light activity become a research hotspot currently due to their strong resistance to photochemical corrosion, especially for those containing transition metal (Lei et al., 2003). As a representative,  $ZnIn_2S_4$  has unique structure and excellent photocatalytic activity under visible light, and have been already employed in hydrogen production (Chai et al., 2011), dye decolorizing (Chen et al., 2009) and tribromophenol degradation (Gao et al., 2014), while the degradation of trace pharmaceuticals in aqueous solution was rarely reported.

Herein, visible light active  $ZnIn_2S_4$  was synthesized and applied to catalyze CBZ in aqueous solution through an experimental photoreactor. The aim of the study is to investigate the photocatalytic removal of CBZ under visible light so as to develop a low-cost and high efficiency technology for eliminating the adverse effect of trace pharmaceuticals in aquatic environment.

## 2. Material and methods

### 2.1. Chemicals

CBZ was analytical grade (AR, 99%) and supplied by Beijing J&K scientific Ltd., China. Indium nitrate ( $In(NO_3)_3 \cdot 4.5H_2O$ , AR) and terephthalic acid (TPA, 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. and Shanghai Crystal Pure Reagent Co. Ltd., respectively. Thioacetamide (TAA), zinc nitrate, hydrochloric acid and sodium hydroxide were all of analytical grade and obtained from Tianjin Kermel Chemical Reagent Co. Ltd., China. Acetonitrile and methanol, HPLC grade, were from Fisher Scientific Co., USA. All chemicals were used directly without further purification. The deionized water used was obtained from PURELGA Ultra Genetic water purification system.

### 2.2. Preparation and characterization of $ZnIn_2S_4$

$ZnIn_2S_4$  was synthesized via a hydrothermal method. Firstly, a mixed solution was prepared by dissolving 0.4 mmol zinc nitrate, 1.0 mmol indium nitrate and a slight excess of 8.0 mmol TAA in 80 mL of deionized water. Then, the mixture was transferred to a 100 mL of Teflon-lined autoclave and kept at 80 °C for 6 h before cooled naturally to ambient temperature. And then, yellow  $ZnIn_2S_4$  sample was washed five times with deionized water to remove the impure ions and dried at 60 °C for 10 h. Finally, the as-prepared  $ZnIn_2S_4$  sample was ground and sieved through a 325 mesh screen, and stored in a desiccator for further use (Gao et al., 2014).

The optical property of  $ZnIn_2S_4$  was recorded by a diffuse-reflectance UV–vis spectrometer (Babcock Hitachi U4100) using  $BaSO_4$  as a reference. The crystal structure was determined by X-ray diffractometer (XRD) with  $Cu K\alpha$  ( $\lambda = 0.15405$  nm) radiation at a scanning speed of 5°/min ranging from 5° to 90° and its accelerating voltage and current were 40 kV and 40 mA, respectively. The surface morphology of sample was characterized by scanning electron microscopy (SEM) (JEOL JSM-6510LV), and the surface area was calculated according to  $N_2$  adsorption–desorption isotherms that measured by a specific surface area and pore size analyzer (BET V-sorb2800P).

### 2.3. Photocatalysis measurements

The photocatalytic degradation experiments of CBZ were carried out in a photochemical reactor ( $L \times W \times H = 480 \times 420 \times 1200$  mm, BL-GHX-II, Shanghai BILON Instrument Co. Ltd.), as shown in Fig. 1. Firstly, 400 mL of solution containing CBZ and  $ZnIn_2S_4$  was added to a cylindrical flask, and a quartz cold trap ( $\Phi 60 \times 390$  mm) was inserted to keep reaction temperature constantly. Then a 100 W iodine-gallium lamp with the wavelength of 350–450 nm was settled in the centre of quartz cold trap and a magnetic stirrer was equipped at the bottom of the flask and aerated simultaneously for thorough mixing and suspension. Prior to irradiation, the mixture was firstly stirred in darkness for 60 min to achieve adsorption–desorption equilibrium for eliminating the adsorption influence. With the light on, the experiment was beginning and an aliquot of 5 mL of reactant was sampled at a given interval, then the sample was filtered through a 0.22  $\mu m$  membrane to remove the catalyst and then analyzed by high performance liquid chromatography (HPLC) quantitatively.

To investigate the photocatalytic degradation behavior of CBZ, two important factors, pH of solution and  $ZnIn_2S_4$  dosage were both investigated, and the pH was adjusted to 5, 7 and 9 by sodium hydroxide or hydrochloric acid, respectively. The stability test of the catalyst was studied by the reuse of used catalyst. In order to detect hydroxyl radical ( $\cdot OH$ ), terephthalic acid (PTA) was added to capture  $\cdot OH$  and then the fluorescence of PTA-OH was determined immediately after reaction (Hirakawa and Nosaka, 2002). The effects of  $\cdot OH$ , photo-generated hole ( $h^+$ ) and  $O_2^{\cdot -}$  on CBZ degradation were verified by the additions of isopropanol (IPA,  $\cdot OH$  quencher), potassium iodide (KI,  $h^+$  scavenger) and no aeration, respectively.

The stock solution of CBZ (10 mg/L) was prepared and stored at 0–4 °C firstly, and the desirable experimental concentration of CBZ (100  $\mu g/L$ ) was diluted gradually with deionized water before experiment. All experiments were carried out at room temperature ( $20 \pm 2$  °C) in triplicate to reduce experimental error and ensure the reproducibility.

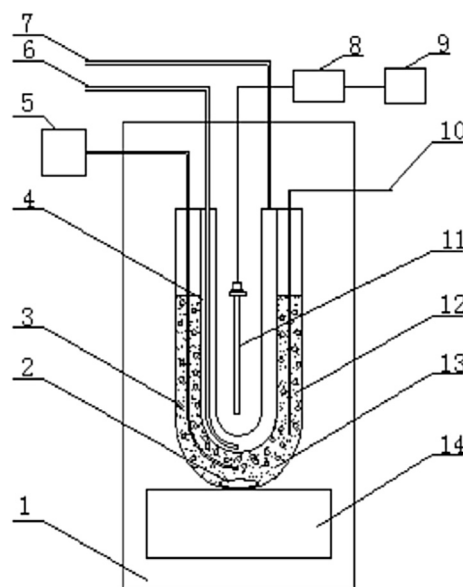


Fig. 1. Schematic diagram of the photocatalytic reactor. 1, reaction chamber; 2, magnetic rotor; 3, bubbles; 4, quartz cold trap; 5, air pump; 6, water inlet; 7, water outlet; 8, rectifier; 9, power; 10, sampling port; 11, iodine-gallium lamp; 12, mixed solution; 13, catalyst; 14, magnetic stirrer.

Download English Version:

<https://daneshyari.com/en/article/5116904>

Download Persian Version:

<https://daneshyari.com/article/5116904>

[Daneshyari.com](https://daneshyari.com)