Water Research 112 (2017) 167–175

Contents lists available at ScienceDirect

Water Research

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

A systematic study on photocatalysis of antipyrine: Catalyst characterization, parameter optimization, reaction mechanism a toxicity evolution to plankton

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ARTICLE INFO

Article history:
Received 13 September 2016
Received in revised form
11 January 2017
Accepted 20 January 2017
Available online 25 January 2017

Keywords:
Antipyrine
Photodegradation
Toxicity

ABSTRACT

The toxicity of antipyrine (AP) in the photodegradation using UV/$CoFe_2O_4$/TiO_2 was investigated by analyzing the characteristic of the catalyst, the effect of parameters (light source wavelength, catalyst dose, pH and initial AP concentration), the reaction mechanism (the organic intermediates, TOC reduction and inorganic ions release) and the newly proposed low-dosage-high-effective radical reaction approach. The catalyst shows the optimal removal efficiency under the conditions of wavelength at 350 nm, the catalyst dose at 0.5 g/L, and pH value at 5.5. Ten organic intermediates were identified, and five of them were newly reported in AP treatment process. Hydroxylation, demethylation and the cleavage of the pentacyclic ring were included in the decomposition pathways. The ring opening was certified by the 45% TOC reduction and 60% ammonia release during the process. The parent compound AP and its degradation products show positive effects on the growth of the algae. However, acute toxicity of AP was detected on brine shrimps *Artemia salina*. The toxicity was eliminated gradually with the decomposition of AP and the generation of the byproducts. The results indicate that the photocatalysis process is effective in AP removal, TOC reduction and toxicity elimination.

1. Introduction

Plankton, including phytoplankton and zooplankton play critical roles in aquatic ecosystem. Firstly, by taking over bottom levels of the food chain, plankton serve as food for organisms at higher trophic levels e.g., shellfish and fish. Secondly, molecular oxygen (O_2) is released during photosynthesis of phytoplankton, which not only guarantee the diluted oxygen in the water for survival of all aerobic organisms, but also help to control the atmospheric CO_2/O_2 balance. Finally, plankton play an important role in biogeochemical cycles of chemical elements as a biological pump in the carbon cycle (Herndl and Reinthaler, 2013).

However, nowadays, the life activities of the plankton are threatened by various emerging contaminants. Among them, pharmaceuticals receive extensive concern in recent studies. Due to the wide use, the casual release and the incomplete treatment in sewage treatment plants (STPs), pharmaceuticals have been detected in surface water, ground water at levels ng/L or μg/L (Gulkowska et al., 2008; Loos et al., 2013). Some pharmaceuticals such as sulfamethoxazole, ibuprofen, have been proved to be harmful for aquatic organisms including phytoplankton and zooplankton even at trace concentration (ng/L) (Isidori et al., 2005; Richards and Cole, 2006; Han et al., 2010; Gong and Chu, 2016). In terms of anti-inflammatory drugs, for example, ibuprofen was determined to be harmful for the growth of *Chlorella vulgaris* (Geiger, 2014) and aspirin was proven to have adverse effect on survival of *Artemia salina* (Calleja et al., 1994). The untreated pharmaceuticals may enter the human bodies through food chain and the concentration may be enhanced owing to biological magnification. Therefore, the efficient removal of pharmaceuticals from the environment is a hot topic in recent years.

The process UV/TiO_2 was demonstrated to be efficient in degradation of varieties of pharmaceuticals including sulfamethoxazole, ibuprofen, antipyrine (AP) and so on (Calza et al., 2011; Hu et al., 2012; Tong et al., 2012). However, one of the limitations of the wide application for TiO_2 is the difficulty in its separation from the treated water, and thus the difficulty of being reused/recycled. A recyclable catalyst was reported and shown to be efficient in

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http://dx.doi.org/10.1016/j.watres.2017.01.041
0043-1354/

sulfamethoxazole degradation (Gong and Chu, 2015), while whether it is widely applicable in degradation of other pharmaceutical molecule is unknown. Besides, the knowledge on the catalyst is limited, hence a deeper study on the catalyst based on the characterization of the obtained nanoparticles will be conducted.

AP (also known as phenazone, 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one), a powerful analgesic, antipyretic and anti-inflammatory drug (Miao et al., 2015), is selected as the target compound owing to its wide use, removal resistance, frequent detection and the insufficient toxicity information (Monteagudo et al., 2016). AP is applied extensively and largely consumed in many countries (Pieper et al., 2010). For example, about 0.35 g/capita AP was consumed in Germany every year (Sadezky et al., 2008). AP is very polar, highly environmental persistent and hardly degradable (Tan et al., 2013). According to Züehlke et al. only about 30% AP was removed in traditional sewage treatment plant (STP) (Zühlke et al., 2006). Owing to the incomplete removal, AP is frequently detected in STP effluents, rivers, ground water and even drinking water (Wiegel et al., 2004; Zühlke et al., 2004). For instance, the concentration of AP was determined to be 0.05–0.25 μg/L in drinking water from Germany (Zühlke et al., 2004). To humans, long term exposure to AP may cause lungs and mucosas damages (Cai et al., 2013), while the information on the toxicity of AP to phytoplanktons and zooplanktons is still limited.

To fill up the above knowledge gaps, a systematic study including the characteristic of the catalyst, the efficiency evaluation of the catalyst on the removal of AP, the determination of the reaction mechanism, and the toxicity assessment of AP solutions before and after the treatment were conducted.

2. Methodology

2.1. Materials

$CoFe_2O_4$ (30 nm with purity of 99.9%) was purchased from US RESEARCH NANOMATERIALS INC.. TiO_2 (P25) was purchased from DEGUSSA. TiO_2 (bare one, mixture of anatase and rutile), AP, titanium tetrachloride ($TiCl_4$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and formic acid (CH_2O_2, >95%) were obtained from SIGMA-ALDRICH INC., USA and are at least of analytical grade. Acetonitrile (C_2H_3N), methanol (CH_4O), and isopropyl alcohol (C_3H_8O) is of LCMS grade and purchased from TEDIA COMPANY, USA. All solutions were prepared in ultrapure water from a Barnstead NANO pure water system (THERMO FISHER SCIENTIFIC INC., USA).

The green algae *Chlorella vulgaris* and the brine shrimps *Artemia salina* were selected as the test organism for phytoplankton and zooplankton, respectively, because of their wide distribution, cheap/easy culture and high sensitivity to toxicants (Barhoumi and Dewez, 2013; Rajabi et al., 2015). The algae *Isochrysis galbana* was used as the diets for *A. salina*. The algae *C. vulgaris*, *I. galbana* and dehydrated cysts of the brine shrimp *A. salina* were purchased from BIOTECH COMPANY OF JIANGMEN, CHINA. The algae were cultured in f/2 medium at temperature 22 ± 1 °C, with a 12 h light/12 h dark photoperiod. The water used in the culture of *C. vulgaris* and *I. galbana* was sterile ultrapure water and artificial seawater, respectively. The cysts of the brine shrimp were suspended in sterile seawater at 28 °C with continuous aeration and illumination. Instar I stage larvae i.e. nauplii hatched in 24 h were separated and used for the toxicity test.

2.2. Method

All experiments were conducted at 22 ± 1 °C unless stated otherwise.

2.2.1. Catalyst synthesis and characterization

The catalyst $CoFe_2O_4/TiO_2$ was synthesized by heterojuncting commercial $CoFe_2O_4$ and P25 with coprecipitation method (Gong and Chu, 2015).

The SEM (scanning electron microscopy) images with EDX (Energy Dispersive X-ray spectroscopy) analysis were obtained from a field-emission scanning electron microscopy (FE-SEM; JEOL Model JSM-6700F, Tokyo, Japan). The TEM (transmission electron microscopy) images were obtained with a JEOL JEM-2100HR electron microscopy instrument (JEOL Model JEM-2100HR).

The diffuse reflectance spectra (DRS) of the catalysts was obtained using a Varian Cary 100 Scan Ultraviolet–visible (UV–vis) spectrophotometer equipped with a labsphere diffuse reflectance accessory over a range of 200–800 nm. Labsphere USRS-99-010 was used as the reflectance standard. Kubelka–Munk method was employed for the conversion from reflection to absorbance (He et al., 2008).

The Brunauer-Emmett-Teller (BET) surface area of the catalyst was obtained from N_2 adsorption/desorption isotherms at 77 K with an ASAP 2020 automatic analyzer (MICROMERITICS INSTRUMENT CORP., NORCROSS, GA, USA).

The zero point of charge (ZPC) was determined by batch equilibrium technique (Ibrahim et al., 2016). A certain amount (0.1 g in this study) of the catalyst were introduced into 100 mL of 0.1 mol/L NaCl solution. Initial pH values (pH_0) of NaCl solutions were adjusted from 5 to 9 by the addition of 0.1 mol/L HCl or NaOH solutions. The solutions suspended with the catalysts were mixed with mechanical stirrer for 24 h. After filtration, the pH values of the suspensions were measured again and marked as pH_t. The pH levels were monitored by a digital pH meter (model: HANNA instrument, B417).

2.2.2. Photodegradation of AP

Twelve monochromatic lamps at various wavelengths were used as the light source for the photoreaction. The reaction solution was stirred mechanically before (to achieve adsorption equilibrium) and during the illumination to ensure a thorough mixing. Samples were extracted and filtered through a 0.22 μm membrane filter (ADVANTEC HP020AN, Japan, with a recovery rate of 100%) at preset intervals.

A High-Performance Liquid Chromatograph (HPLC) system, equipped with a Waters 515 HPLC pump, a Waters 717 plus autosampler, a Restek C18 column (5 μm, 4.6 × 250 mm) and a Waters 2489 Dual absorbance detector was performed for the measurement of AP concentration. The detection wavelength was 261 nm with the flow rate of 1 mL/min and the injection volume of 10 μL. The mobile phase was a mixture of 25% acetonitrile and 75% of ultrapure water. Methanol (50%) was used as the wash solvent.

2.2.3. Intermediates detection

An UPLC/ESI-MS system was employed for the intermediates determination. The system is controlled by the LC/MSD ChemStation software version A.09.03 and consists of a quaternary pump, a vacuum degasser, an autosampler, a diode array detector (DAD), an ion trap mass spectrometer detector (MSD), and a thermostated column compartment with a Thermo Hypersil GOLD column (1.9 μm, 50 × 2.1 mm). Chromatography was conducted with a Dionex UltiMate 3000 Ultra-high Performance Liquid Chromatography (UPLC). Mass analysis was performed with a Bruker amaZon SL ion trap mass analyzer in positive ion mode with a mass range of 50–400 *m/z*. Acetonitrile and 0.1% formic acid were used as A and B mobile phases, respectively. A linear gradient progressed from 5% A (0–2 min) to 30% A in 2–20 min, maintained