Chemical Engineering Journal 326 (2017) 1197–1209

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Degradation of UV-filter benzophenone-3 in aqueous solution using persulfate catalyzed by cobalt ferrite

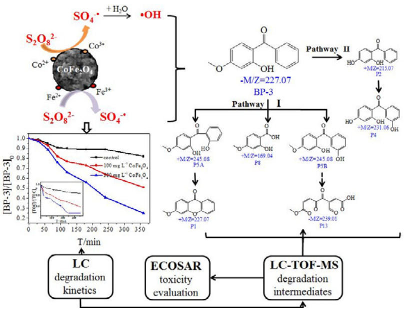
Xiaoxue Pan[a], Liqing Yan[b], Chenguang Li[a], Ruijuan Qu[a,*], Zunyao Wang[a]

[a] *State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Jiangsu, Nanjing 210023, PR China*
[b] *Environmental Engineering School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0373, USA*

HIGHLIGHTS

- $CoFe_2O_4$ is an effective catalyst to activate PS for the degradation of BP-3.
- Kinetics and mechanisms of BP-3 degradation by PS/$CoFe_2O_4$ were studied.
- $SO_4^{-\cdot}$ was the dominant radical for BP-3 decomposition.
- 15 transformation products were identified by LC-TOF-MS.
- Hydroxylation, demethylation, direct oxidation, benzene ring opening were observed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 April 2017
Received in revised form 13 June 2017
Accepted 14 June 2017
Available online 15 June 2017

Keywords:
Benzophenone-3
Cobalt ferrite
Persulfate
Catalytic degradation
Reaction mechanisms

ABSTRACT

The occurrence of benzophenone-3 (BP-3) in aquatic environments constitutes a potential risk to the environment and human health due to its phytotoxicity, carcinogenicity and endocrine disrupting effects. In this work, cobalt ferrite ($CoFe_2O_4$) prepared by chemical co-precipitation method was used as a catalyst for the degradation of BP-3. The catalyst was characterized by SEM, TEM, XRD, XPS, BET and FT-IR spectroscopy, and its catalytic activity on BP-3 removal by persulfate (PS) was then evaluated at different operating parameters (catalyst loading, reaction temperature, solution pH and PS dose). The removal of BP-3 (1.31 μM) in 6 h reached 91% under the condition of $[BP\text{-}3]_0$: $[PS]_0 = 1$: 1000, initial pH = 7.0, T = 25 °C and catalyst load = 500 mg L^{-1}. In addition to the satisfactory catalytic performance, the $CoFe_2O_4$ also showed high stability and excellent recyclability. Electron paramagnetic resonance and radical quenching tests showed that sulfate radicals predominated in the decomposition of BP-3 by PS/$CoFe_2O_4$, while hydroxyl radicals also contributed to the catalytic oxidation process. Fifteen degradation products were identified by liquid chromatography-mass spectrometry (LC-MS), and two reaction pathways involving hydroxylation, demethylation, direct oxidation and benzene ring opening were proposed. This study could provide useful information for the potential application of $CoFe_2O_4$ activated PS technology to treat water and wastewaters containing BP-3.

1. Introduction

Benzophenone-3 (BP-3), a typical hydroxylated derivative of benzophenone, can absorb sunlight in the UVA and UVB regions with limited phototransformation. This property leads to its widely application as sunlight filter in personal care products (PCPs) and

---

* Corresponding author.
E-mail address: quruijuan0404@nju.edu.cn (R. Qu).

http://dx.doi.org/10.1016/j.cej.2017.06.068
1385-8947/

as photostabiliser in polymeric materials to protect humans and materials against harmful exposure to UV irradiation. Due to the use in recreational water activities or the incomplete elimination in wastewater treatment plants (WWTP) [1], BP-3 has been widely detected in WWTP effluents [2], lakes [3], rivers [4], tap waters [5], and sediments [6] at the concentrations ranging from several ng L^{-1} to μg L^{-1}. As a persistent and bio-accumulative compound ($\mathrm{Log}K_{ow} = 3.79$) [3], BP-3 constitutes a potential risk to the environment and human health. Considering that BP-3 has potential endocrine disrupting effect [7–9] and high phytotoxicity and carcinogenicity [10], it is necessary to effectively remove BP-3 in aquatic environment.

In the past few years, sulfate radicals-based advanced oxidation processes (SR-AOPs) have received wide attention in water treatment. Sulfate radicals ($SO_4^{-}\cdot$), which are strong oxidants with a redox potential of 2.5–3.1 V, could achieve a higher mineralization degree of organic pollutants in the oxidation process [11,12]. Because they are more selective and stable than hydroxyl radicals, $SO_4^{-}\cdot$ are promising alternatives to $\cdot OH$ for advanced oxidation treatment of compounds in aqueous solutions. Recent studies have demonstrated the efficiency of SR-AOPs in removing a broad spectrum of organic pollutants, such as cylindrospermopsin [13], flumequine [14], tetrabromobisphenol A [15] and PCBs [16]. However, the information about the $SO_4^{-}\cdot$-based degradation process of BP-3 is still limited.

Since it is stable, soluble, cheap (<\$2.65/kg for $Na_2S_2O_8$ [17]) and owns high redox potential (2.01 V), persulfate (PS, $S_2O_8^{2-}$) is widely used in laboratory researches as a source of $SO_4^{-}\cdot$ [18]. Various methods such as heat [19], UV [20,21], transition metal ions (Fe^{2+}, Co^{2+}, Cu^{2+}) [22] or metal oxides [23], and quinones [16] can activate PS to produce $SO_4^{-}\cdot$. Currently, the key to improve the efficiency of SR-AOPs is to develop highly effective activation methods for PS. Metaloxide nanoparticles have been widely used in AOPs for decades [24,25]. The fine physicochemical characteristics of cobalt ferrite ($CoFe_2O_4$) nanoparticles make it suitable to be used as magnetic material in electric films and as photocatalyst in pollutants removal [26,27]. However, at present, there is little information on cobalt ferrite activated PS oxidation, which limits the application of this technology to degrade persistent organic pollutants.

In this study, we investigated the degradation kinetics and reaction mechanisms of BP-3 by PS activated with $CoFe_2O_4$ catalyst in aqueous solution. The catalyst was synthesized and characterized, and its catalytic performance was then assessed under different conditions. Two different radical scavengers were adopted to clarify the contributions of radical species in the reaction system. Based on the identified degradation products of BP-3, the reaction pathways were proposed. Additionally, the mineralization degree of reaction solutions was evaluated by total organic carbon (TOC) measurement, and the ecotoxicity of BP-3 and its degradation products was estimated using Ecological Structure Activity Relationships (ECOSAR) program. To the best of our knowledge, this is the first attempt to employ $CoFe_2O_4$ as a catalyst of PS for the degradation of BP-3.

2. Materials and methods

2.1. Chemicals

BP-3 (CAS NO. 131-57-7, purity 98%) and the spin-trapping agent 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) were obtained from J&K and Aladdin Chemistry, respectively. Potassium persulfate ($K_2S_2O_8$, purity $\geq 99.5\%$) was provided by Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). The chromatographic grade formic acid and methanol were acquired from Merck (Darmstadt, Germany). The rest of reagents used in the present work were of analytical grade or higher. Ultrapure water (18.2 MΩ cm) was prepared with a Milli-Q water purification system (Millipore, Bedford, USA).

2.2. Synthesis and characterization of $CoFe_2O_4$

The $CoFe_2O_4$ catalyst was synthesized using the chemical co-precipitation method, according to Gao et al. [28]. First, 3.00 g $Co(NO_3)_2{\cdot}6H_2O$ and 5.50 g $FeCl_3{\cdot}6H_2O$ were dissolved into 100 mL ultrapure water (Co^{2+}: Fe^{3+} = 1: 2 at a molar concentration ratio) with continuous mechanical and ultrasonic stirring at 62 °C. Second, 8 M NaOH solution was added dropwise into the mixture solution until the pH value of the solution was approximately 10. Then, stop stirring and keep the mixture solution at 75 °C for 30 min. After cooling down to room temperature, the suspension was filtered and washed with ultrapure water at least three times. Finally, the material was calcined at different temperatures (100, 200, 300, 400, 500 and 600 °C) for 4 h in the muffle furnace and then ground to powders for further use.

The morphology and internal structure of $CoFe_2O_4$ were observed by scanning electron microscope (SEM, Quanta FEG 250, FEI, the Netherlands) and transmission electron microscopy (TEM, JEM-200CX, JEOL, Japan), respectively. Meanwhile, energy dispersive spectroscopy (EDS) analysis was carried out during SEM characterization to identify the chemical component. X-ray powder diffraction (XRD) spectrum was analyzed by an X'TRA X-ray diffractometer (ARL, Switzerland). The metal valance state was identified by X-ray photo-electron spectroscopy (XPS, Al K-Alpha, Thermo Fisher Scientific, USA). The specific surface area and pore size of $CoFe_2O_4$ were measured by a Brunauer-Emmett-Teller (BET) analyzer (ASAP 2020, USA). The Fourier-transform infrared (FT-IR) spectrum was recorded on a Bruker Vertex 70 FT-IR spectrometer (Bruker Optics Inc., Billerica, MA, USA). The leaching of Co^{2+} and Fe^{3+} were determined by an atomic absorption spectrophotometer (AAS, Solar M6, Thermo Fisher Scientific, USA).

2.3. Oxidation procedure

In a typical run, conical flasks containing 50 mL reaction solution were kept at a controlled temperature in a water bath shaker (SHA-B, Jintan, China) to conduct the experiments. The initial concentration of BP-3 was 1.31 μM. After 30 min of adsorption equilibrium between BP-3 and $CoFe_2O_4$, the oxidation reaction was initiated by adding a desired amount of PS. The pH in the solution was adjusted by H_2SO_4 or NaOH solution using a Mettler-Toledo S20 SevenEasy pH Meter. The reason for selecting H_2SO_4 was that SO_4^{2-} can be also generated in PS oxidation process so that no other anions such as Cl^-, NO_3^-, $H_2PO_4^-$ and HPO_4^- were introduced into the reaction. After 0, 30, 60, 90, 120, 180, 240 and 360 min, 800 μL of reaction solution was withdrawn and filtered through 0.22 μm organic filters into 1.5 mL brown sample vials, and 200 μL of 100 mM $NaNO_2$ solution was immediately added to terminate the reaction. To evaluate the stability and reusability, the catalyst after reaction was collected by a magnet, washed and dried, and then reused five times under the same reaction conditions.

To ensure the accuracy of data in this study, the tests were performed in triplicate and the average values were presented in the figures.

2.4. Analytical methods

The concentration of BP-3 was analyzed at 239 nm by an Agilent 1200 high performance liquid chromatography (HPLC) system (Agilent Technologies, Palo Alto, CA, USA) equipped with a quaternary pump and a UV detector. A Zorbax 300SB-C18 column (4.6 × 150 mm, 5 μm) was used for the separation of analytes,