



Degradation of bezafibrate in wastewater by catalytic ozonation with cobalt doped red mud: Efficiency, intermediates and toxicity



Huanan Li^a, Bingbing Xu^b, Fei Qi^{a,*}, Dezhi Sun^a, Zhonglin Chen^{c,**}

^a Beijing Key Lab for Source Control Technology of Water Pollution, College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, PR China

^b State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, PR China

^c State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China

ARTICLE INFO

Article history:

Received 28 September 2013

Received in revised form 26 January 2014

Accepted 28 January 2014

Available online 4 February 2014

Keywords:

Bezafibrate

Catalytic ozonation

Co/red mud

Hydroxyl radical

ABSTRACT

The bezafibrate (BZF) degradation and mineralization performances of a red mud (RM) catalyst doped with cobalt (i.e. Co/RM) during the ozonation reaction have been evaluated experimentally. The purposes of this study were to study the performance reaction mechanism and intermediate. In a next stage of our study also economic evaluations for a large scale application will be considered. Results of this study showed that catalytic ozonation using Co/RM not only led to the successful degradation of BZF, but also mineralized the corresponding intermediates, in ultrapure water as well as the effluent of wastewater. Detoxification was also achieved in this reaction process. The surface and structure properties of Co/RM were characterized by several analytical methods. The leaching of toxic heavy metal from the catalyst used in this process was very low, with the heterogeneous reaction dominating the decomposition of BZF, which made the reuse of the catalyst highly feasible. The enhanced generation of hydroxyl radical was critical to the success of the catalytic activity. Furthermore, 22 of the intermediates generated during this process were identified and several degradation pathways were proposed

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

A variety of different studies have been reported in recent years regarding the occurrence of a large number of residual pharmaceutical (PhAC) agents in the aquatic environment [1], and there are concerns that the presence of these residues in secondary effluents could have an adverse impact on the aquatic organisms living in the receiving waters as well as having a long-term effect on aquatic ecosystems and human health if the reclaimed water is returned to the water supply [2]. Furthermore, it is well known that conventional wastewater treatment plants are poorly equipped to handle this particular problem [3,4].

Bezafibrate (BZF, *p*-[4-[chlorobenzoylamino-ethyl]-phenoxy]-*b*-methylpropionic acid) is a fibrinolytic drug that is currently used extensively as a lipid regulating agent [5]. Recent investigations revealed that BZF was present in a variety of different aquatic systems throughout the developed world, including the influent/effluent waters of sewage treatment plants (STPs), because of the large consumption of BZF in these countries [6]. The

bioaccumulation and bio-magnification of BZF could be potentially very harmful to the aquatic environment because of possible mixture toxicity, synergistic and additive effects [7]. Nanofiltration and reverse osmosis appear to be effective methods for the removal of BZF from water, although the BZF is invariably transferred to the concentrate and not degraded [8]. A number of advanced oxidation processes (AOPs) have also been used for the degradation of BZF, such as ozonation [9,10], UV irradiation [6], pulse radiolysis [11], UV/H₂O₂ [6], UV/TiO₂ [5] and photo-Fenton [12]. Furthermore, the intermediates and reaction mechanisms associated with the degradation of BZF via the ozonation and UV/TiO₂ pathways have been identified by gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–mass spectrometry (LC–MS) [5]. The reaction mechanism for the degradation of BZF by the UV/H₂O₂, however, remains unknown and may be different from these two processes [6].

Catalytic ozonation using a solid catalyst has been the subject of increasing levels of interest from the drinking water and wastewater treatment industries [13,14]. There are several key advantages to this technology, including its ability to (1) enhance the reaction rate of the sole ozonation process (SOP); (2) improve the mineralization process; and (3) reduce the yield of the intermediates and the toxicity of the effluent. A variety of different catalysts are commonly used for this process, including activated carbon [15,16],

* Corresponding author. Tel.: +86 10 62336615; fax: +86 10 62336596.

** Corresponding author.

E-mail addresses: qifei@bjfu.edu.cn (F. Qi), zhonglinchen@163.com (Z. Chen).

minerals [17,18], molecular sieves [19–21], transition metal oxides [13,22] and supported metal/metal oxides [23–25]. Red mud (RM) is an alkaline residue that is generated in large amounts during the extraction of aluminum from bauxite using the Bayer process [26]. The storage and maintenance of RM represents a significant environmental challenge to the aluminum industry because of the alkaline nature of this material and the risk that this possess to living organisms [26]. In general, RM is mainly composed of Fe, Al, Si and Ti oxides, as well as their oxyhydroxides and tectosilicate-like compounds [26]. Some of the main components of RM are widely used in water treatment processes, where they are used as coagulants [27,28], sorbents [29,30] and catalyst for the activation of peroxymonosulfate [31–33]. The use of RM in water treatment could provide an opportunity for turning into a valuable resource, as well as enhancing the socio-ecological-economic value of the aluminum industry. Furthermore, the Fe, Al, Si and Ti oxides and oxyhydroxides present in RM could be used in heterogeneous catalytic ozonation reactions as a catalyst or support. In addition, some other studies had found that cobalt oxides were active in heterogeneous catalytic ozonation [34,35]. Therefore, in this study, cobalt doped RM was used as a catalyst for the degradation of BZF in aqueous solution by ozonation. Main aims of this study were focused on (1) the evaluation of the catalyst in terms of its degradation performance; (2) the identification of any intermediates formed during the reaction and the elucidation of the reaction mechanism; and (3) the assessment of the toxicity of the RM in different oxidation processes.

2. Materials and methods

2.1. Chemicals and reagents

The RM samples used in the present study were obtained from China Shandong Hongqiao Aluminum Co., Ltd. (Shandong province, China) and were composed of particles in the range of 0.15–0.30 mm in size. The samples were washed with ultrapure water and air-dried prior to their use. BZF (>98% purity) was obtained from Sigma–Aldrich (USA). Ultrapure water (18.2 M Ω cm) was used throughout the current study and was obtained from a CLASSIC UVF pure water treatment system (ELGA Inc., UK). Acetonitrile and methanol (J.T. Baker Inc., USA) were degassed prior to being used for the high-performance liquid chromatography (HPLC) analyses performed as part of this study. All of the other reagents used in the current study were purchased as the analytical grade or higher, and were used without further purification. All of the glassware used in the current study was soaked in a H₂SO₄/K₂Cr₂O₇ solution overnight, before being washed sequentially several times with tap water and distilled water prior to its use.

2.2. Synthesis and characterization of cobalt doped RM

The cobalt doped RM catalyst, which shall be referred to as Co/RM hereafter, was prepared in our laboratory using a wetness impregnation method. Cobalt nitrate was used as the cobalt precursor because it underwent a better interaction with the supports than other cobalt precursors available for this process [31]. The fresh RM powder samples were washed with ultrapure water at least three times to remove any surface dust before being crushed and sieved to obtain particles of 0.15–0.3 mm in size. A portion of the resulting RM material (5.0 g) was then added to a solution of Co(NO₃)₂·6H₂O (1.022 g) in ultrapure water (100 mL), and the resulting suspension was stirred continuously at 333 K until all of the water had completely evaporated. The resulting residues were then collected and dried at 353 K overnight before being calcined

at 673 K for 4 h in air. After the calcinations process, the samples were crushed and sieved to give particles of 0.15–0.3 mm in size before being stored in a desiccator prior to their use.

X-ray diffraction (XRD) patterns of the RM or Co/RM were collected on a Japan Rigaku D/max 12KW X-ray diffractometer using a filtered Cu K α radiation source, with an accelerating voltage of 40 kV and a current of 30 mA, and scanned at 2θ from 5° to 80° at a rate of 4° min⁻¹. UV–visible diffuse reflectance spectra (UV–vis DRS) were recorded on a UV-365 (Shimadzu, Japan) equipped with an integrating sphere. BaSO₄ was used as a reference material and the wave was scanned from 300 to 800 nm.

The specific surface area and pore volume properties of the catalysts, including RM and Co/RM, were analyzed using an ASAP 2020M Surface Area and Porosity Analyzer (Micromeritics, USA). The level of N₂ gas adsorption–desorption was measured during this process at 77 K to obtain specific surface area information using the Brunauer–Emmett–Teller (BET) method, whereas the pore size distributions of the catalysts were determined by the Barrett–Joyner–Halenda (BJH) desorption $dV/d\log(D)$ pore volume method. The total pore volume and the micropore were also calculated by this method. The mesopore was the total pore volume minus the micropore volume. The point of zero charges (pH_{PZC}) were determined using the method described previously by Altener et al. [36]. Further details of this procedure are provided in the Supporting Information (SI, Text S1).

2.3. Catalytic ozonation procedure

A batch mode experiment was conducted at ambient temperature in a glass cylinder reactor with an effective solution volume of 250 mL to evaluate the degradation performances of the catalysts. Ozone was produced using a standard laboratory ozonizer (3S-A5, Beijing Tonglin Gaoke Technology, Beijing, China) supplied with the dry pure oxygen. After the generator had reached a steady state, ozone gas was bubbled into the ultrapure water in the reactor through a silica dispenser to give the desired dissolved ozone concentration under 297 K. This solution was used as a stock solution of dissolved ozone. A calculated volume of the dissolved ozone stock solution and the catalyst powder were then added to the BZF solution, with the magnetic stirrer being turned on at the same time. In this way, the ozone was introduced to the reaction system at once. Samples were collected from the reactor at specific time points and immediately quenched into an excess of a sodium sulfite solution (1.0 mM). Prior to their analysis, the samples were filtered with cellulose acetate filters (0.45 μ m) to remove any catalyst particles. The cellulose acetate filters did not remove any of the BZF. To identify any of the intermediates formed during the different processes, a higher concentration of BZF (0.2 mM) was used in a continuous ozone gas purging mode experiment. In this mode, a constant dissolved ozone concentration of 0.38 mg/L was achieved with the diffuser at a flow rate of 1.0 mL/min, in the same glass cylinder reactor that was used in for the batch mode experiments. All of the experiments in the current study were conducted in triplicate and the standard deviations have been shown as error bars.

The dissolved BZF was analyzed by HPLC using a Waters2695 HPLC system (Waters, USA) equipped with a Waters2998 UV detector at a wavelength of 200 nm. The HPLC analyses were performed with an Agilent C18 column (150 mm \times 4.6 mm, 5 μ m, Agilent, USA) using an isocratic elution of 50% buffered solution (H₂O/CH₃OH/H₃PO₄ = 1000/25/0.002) and 50% CH₃CN at a flow rate of 1.0 mL/min. The intermediates were identified using a Finnigan SpectraSYSTEM[®] LC (Finnigan, USA) coupled with a Thermo Quest Finnigan LCQ Duo mass spectrometer system (Finnigan) equipped with an electrospray ionization interface operating in the electrospray ionization mode (LC–ESI/MS). The effluent (0.8 mL/min) was

Download English Version:

<https://daneshyari.com/en/article/6501479>

Download Persian Version:

<https://daneshyari.com/article/6501479>

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