Cobalt modified red mud catalytic ozonation for the degradation of bezafibrate in water: Catalyst surface properties characterization and reaction mechanism

Bingbing Xu [a], Fei Qi [b,*], Jizhou Zhang [c], Huanan Li [b], Dezhi Sun [b], Didier Robert [d], Zhonglin Chen [e,1]

[a] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, PR China
[b] Beijing Key Lab for Source Control Technology of Water Pollution, College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, PR China
[c] Institute of Natural Resources and Ecology, Heilongjiang Academy of Sciences, Harbin 150040, PR China
[d] Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), CNRS-UMR 7515-University of Strasbourg, Saint-Avold Antenna, Université de Lorraine, 12 rue Victor Demange, 57500 Saint-Avold, France
[e] State Key Lab of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China

HIGHLIGHTS

- Identification the roles of ROS and surface adsorption for bezafibrate degradation.
- Identification the role of the solution/ interface reaction in catalytic ozonation.
- Cobalt loading changed the texture and chemical property of catalyst.
- Establishment the relationship between surface property and catalytic activity.

GRAPHICAL ABSTRACT
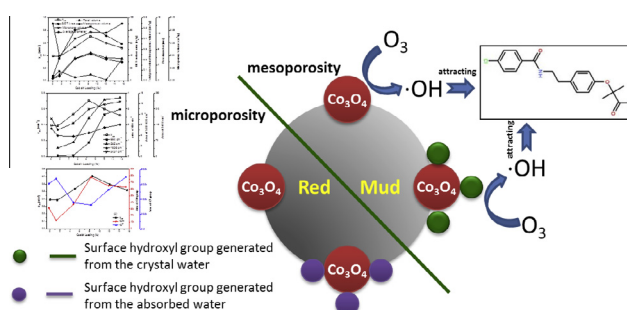
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ABSTRACT

A systematic investigation of the catalytic reaction mechanism of surface cobalt-loaded red mud (RM) was carried out using the reaction kinetics analysis and catalyst surface property characterization. First, multiple characterization methods (XRD, FT-IR and XPS) were used to investigate the variation of surface texture and chemical properties of the catalyst after surface cobalt loading. Second, the contributions of molecular ozone (39.22%), hydroxyl radicals (45.20%), and surface adsorption (15.57%) for bezafibrate (BZF) degradation by Co/RM were identified by the reaction kinetic analysis using the tertiary butanol used as an organic quencher, confirming that surface cobalt loading promoted the role of the hydroxyl radical reaction. The phosphate was used as an inorganic probe to study the role of the solution and surface reactions in catalytic ozonation. The presence of phosphate inhibited 17.5%, 25.1%, and 27.2% efficient when phosphate concentration was 0.0104, 0.0208, and 0.0416 mM, respectively. The kinetics analysis showed that the inhibiting effect of phosphate on BZF degradation was due to quenching of HO· in solution, and not the surface chelation reaction. However, surface cobalt loading enhanced this surface interface reaction. Finally, the relationship between surface texture/chemical properties and

* Corresponding author. Tel.: +86 10 62336615; fax: +86 10 62336596.
  E-mail addresses: qifei@bjfu.edu.cn, qifei_hit@163.com (F. Qi), zhonglinchen@163.com (Z. Chen).
[1] Co-corresponding author.

catalytic activity was established, confirming that surface cobalt loading developed mesopores leading to an increase of the specific surface area. This was favorable for the catalytic activity. Co_3O_4 covered over the mesopore surface of RM and developed the surface hydroxyl group by the chemical water deduced from the cobalt surface loading. This is the main catalytic reaction site.

1. Introduction

Much increasing attention has been paid to pharmaceutical residues in aquatic environments, including their occurrence [1], analytical methods [2], degradation technology [3], and toxicity evaluation [4]. Many studies showed that the presence of pharmaceutical residues in effluents has a negative effect on the aquatic organisms living in the receiving water and a biological effect on human beings in an unpredictable way [5]. However, the conventional wastewater treatment with active sludge is poorly to handle these particular concerns [6].

Fibrates are a group of concerned pharmaceutical compounds that have been marketed since 1963 [7]. They are included in the 2002 list of the most used pharmaceuticals in the world [7]. These pharmaceuticals are most often given to patients with mixed or combined hyperlipidemia when high cholesterol levels are associated with high levels of triglycerides. In the fibrate group, bezafibrate (BZF, 2-(4-(2-[(4-chlorobenzoyl)amino]ethyl)phe noxy)-2-methylpropanoic acid) is commonly used as a lipid regulating agent. Many studies revealed that BZF was released into the aquatic environment in the effluents from wastewater treatment plants because of its large consumption and inefficient removal [8]. The presence of BZF in aquatic environments could be potentially harmful because of its mixture toxicity, synergistic, and additives effects [9]. In addition, bioaccumulation and biomagnification of BZF could occur through food chains [10].

Many methods have been developed in an attempt to enhance the removal of BZF from water, such as ozonation [9] and UV-based advanced oxidation processes (AOPs) [11]. Catalytic ozonation with solid catalysts has attracted increasing interest in drinking water and wastewater treatment for many years [12,13]. In a previous study, we used catalytic ozonation with cobalt-doped red mud (Co/RM) to degrade BZF in water, which resulted in better performance and detoxification than un-doped RM [14]. In the above AOP, RM, the alumina industry waste, was used as the catalyst supporter. The presence of Fe, Al, Si, and Ti oxides and oxyhydroxides in RM are potential reaction sites, and the surface modification by cobalt oxide is another reason for the higher catalytic activity in Co/RM than RM. The utilization of RM as waste is a bi-functional effect being different with other common catalyst, as (1) utilization alumina industry waste to support a new disposal method; (2) decreasing the cost of catalyst preparation in wastewater treatment. Both molecular ozone and the hydroxyl radical (HO·) oxidation intermediates were identified in the previous publication. However, the surface cobalt loading on the structure and surface chemistry property were not discussed deeply; furthermore, the reaction activity site and reaction mechanism should be clarified. More importantly, the identification of the solution or surface reaction in catalytic ozonation was the key to study the reaction mechanism, but few publications discussed this [15], which will be explain in this study. Therefore, a series of cobalt loading RM catalysts were prepared in this study, to determine (1) the reaction kinetics of catalytic ozonation, (2) the change of the surface structure and properties after cobalt doping, and (3) the relationship between the surface structure/properties and the catalytic activity. The above content is an important development for our previous study and catalytic ozonation technology.

2. Materials and methods

2.1. Chemicals and reagents

The RM samples were purchased from China Shandong Hongqiao Aluminum Co., Ltd. (Shandong province, China). Prior to use, samples were washed with ultrapure water until the supernatant pH did not change, and air-dried to reduce the amount of alkali metals adsorbed on the RM surface. After being crushed and sieved, RM samples were composed of particles with size 0.15–0.30 mm. BZF (>98% purity) was obtained from Sigma Aldrich (USA). Ultrapure water (18.2 MΩ cm) was used throughout the current study and was obtained with a Classic UVF pure water treatment system (Elga Inc., UK). Acetonitrile and methanol (J.T. Baker Inc., USA) were degassed prior to being used in the high-performance liquid chromatography (HPLC) analyses. All of the other reagents were of analytical grade or higher, and used without further purification. All of the glassware was soaked in a $H_2SO_4/K_2Cr_2O_7$ solution overnight, before being washed sequentially several times with tap water and distilled water prior to use.

2.2. Synthesis of Co/RM catalyst and characterization

The Co/RM catalyst was prepared using a wet impregnation method, as described in our previous study [14], however, the cobalt loading was changed according to the required weight in this study. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy, and N_2 gas adsorption–desorption measurements were carried out to investigate the surface properties of the catalyst, and the detailed information is shown in Text S1 of the Supporting information (SI).

2.3. Catalytic ozonation procedure and analysis methodology

To investigate the degradation performance of the catalysts, batch mode experiments were conducted at ambient temperature in a glass cylinder reactor with an effective solution volume of 250 mL. Ozone was produced using a standard laboratory ozonizer (3S-A5, Beijing Tonglin Gaoke Technology, Beijing, China) supplied with the dry pure oxygen. The full reaction procedure is the same as our previous publication [14] with only the catalyst changed in this study. 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. If there was not specific instruction, the initial concentration of BZF was 2.76 μM. The ozone was introduced into the solution only once and the dissolved ozone concentration decreased during all reaction process. The ultrapure water was used in all experiment as the matrix. The initial solution pH was adjusted by with NaOH or $HClO_4$ to maintain that each experiment was conducted at the same initial pH (6.68, expect special instruction in this study) to avoid pH influence. Because the initial concentration of BZF was