



Improving heterogeneous photo-Fenton catalytic degradation of toluene under visible light irradiation through Ba-doping in BiFeO₃ nanoparticles



Tayyebeh Soltani, Byeong-Kyu Lee*

Department of Civil and Environmental Engineering, University of Ulsan, Nam-gu, Daehak-ro 93, Ulsan 680-749, Republic of Korea

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ABSTRACT

In this study, we prepared Bi_{1-x}Ba_xFeO₃ MNPs (x = 0.03, 0.08, 0.12) via a rapid sol gel procedure to improve heterogeneous photo-Fenton catalytic degradation of toluene under visible light irradiation. We found that Ba-substitution in BiFeO₃ magnetic nanoparticles (BFO MNPs) can play an important role in improving the photo-Fenton catalytic degradation of toluene from aqueous solution. Increasing the Ba doping level up to 12%, greatly affect in iron redox cycling and oxygens vacancies as compared to pure BFO MNPs. The iron redox cycling and existence of oxygen on the surface of Ba doped BFO had been affected by the photo-Fenton process. The scavenger effect evident from the study results confirmed that the photo-Fenton catalytic degradation of toluene from aqueous solution was mainly controlled by the formation characteristics of hydroxyl radical (*OH) and also partially by the formation of other active species such singlet oxygen (¹O₂). The proposed radical reaction mechanism was also discussed. The degradation of toluene was partial in the dark but almost complete under visible light irradiation by the photo-Fenton catalytic degradation reaction. Bi_{1-x}Ba_xFeO₃ (x = 0.12) showed the highest photo-Fenton catalytic degradation efficiency with a toluene removal of 98%, total organic carbon (TOC) and chemical oxygen demand (COD) reduction of 85% and 94%, respectively, after 40 min of visible light irradiation.

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1. Introduction

Volatile and flammable aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene have commonly been used in solvents and exist in fossil fuels such as gasoline and petroleum [1,2]. Long-term exposure to volatile organic compound (VOCs) may cause serious problems such as a wide range of sensory irritation and acute or chronic diseases.

Various methods have been developed for eliminating VOCs [3–5]. Among advanced oxidation processes, Fenton (Fe(II)/H₂O₂) and photo-Fenton (Fe(II)/H₂O₂/UV) reagents have been used in a lot of wastewater purification processes due to their favorable organic treatment efficiency [6]. However, homogeneously catalyzed Fenton reactions require higher concentrations of aqueous iron ions than the 2 ppm permitted by the European Community Directives [7]. Thus, it has essential requirements for precipitation, re-dissolution, separation and recovery of the iron species especially in industrial wastewater treatment due to a large amount

of iron salts that are presented in the effluents. In heterogeneous catalysis, iron is perched within the interlayer space of the catalyst's structure and can effectively generate hydroxyl radicals (*OH) from the oxidation of hydrogen peroxide (H₂O₂), without iron hydroxide precipitation under non-controlled pH conditions [8,9].

BiFeO₃ magnetic nanoparticles (BFO MNPs) belong to the ABO₃ type of compounds with a rhombohedral distorted perovskite structure, which is a new visible-light photocatalyst for the photo degradation of organic pollutants because of its narrowing band gap energy (2.2 eV), magnetic property and excellent chemical stability [10–12]. Multi-ferroic BFO MNPs were used as a catalyst for ultrasensitive fluorometric determination of hydrogen peroxide and glucose [13]. BFO MNPs are able to catalytically activate H₂O₂ for the decomposition of organic pollutants in the dark, but their catalytic ability for more resistant organic pollutants is rather weak [14]. Thus, visible light irradiation can be utilized to improve the catalytic ability of BFO MNPs [9,15]. However, the catalytic ability of BFO MNPs was not enough to degrade more stable organic pollutants, such as bisphenol A and methyl violet, from aqueous solution. Therefore, it was necessary to improve the catalytic ability of BFO MNPs by an in-situ surface modification using chelating agents such as ethylenediaminetetraacetic acid (EDTA) [16,17]. Recently, it was

* Corresponding author.

E-mail address: bklee@ulsan.ac.kr (B.-K. Lee).

reported that the BFO lattice undergoes a large structural distortion even at a low concentration of Li doping [18]. It has been reported that the substitution of Ca and Sr for Bi induced oxygen vacancies and mixed Fe valences, which can play an important role in the photocatalytic property of BFO MNPs [19,20].

In this study, we prepared $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ MNPs with different Ba^{2+} ion-dopant levels ($x=0.03, 0.08, 0.12$) via a rapid sol gel procedure to improve heterogeneous photo-Fenton catalytic degradation of toluene under visible light irradiation. For the first time, we found that Ba substitution in BFO MNPs greatly improved the photo-Fenton catalytic degradation of toluene at a very weak acidic medium, $\text{pH}=5.5$, due to greatly affect in iron redox cycling and oxygens vacancies as compared to pure BFO MNPs. The iron redox cycling and existence of oxygen on the surface of Ba doped BFO had been affected after photo Fenton process. Finally, we found that, singlet oxygen was partly exhibited roles in the photo-Fenton catalysis process of toluene in addition to $\cdot\text{OH}$, and relevant radical reaction mechanism was also proposed.

2. Materials and methods

2.1. Chemicals

Bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), barium nitrate ($\text{Ba}(\text{NO}_3)_2$), and H_2O_2 from Fluka, ethylene glycol (EG), isopropanol (IP), sodium azide (NaN_3) and 1–4 benzoquinone (BQ) from Merck, and toluene and ethanol from Aldrich were used as received.

2.2. Catalyst preparation

To synthesize pure BFO MNPs, 25 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 65 mL EG. The mixture was stirred for 40 min at 30°C to obtain a dark red sol. For the preparation of $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.03, 0.08, 0.12$), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$ were added to the EG at a molar ratio of 1-x: 1: x; where $x=0.03, 0.08$ and 0.12 for 3%, 8%, and 12% Ba doped samples, respectively. Then, samples irradiated for 40 min at 30°C to obtain other brownish red sols. Then, all samples were incubated at 80°C to 20 h to remove the organic pollutants and to form xerogels. Finally, the powders were calcined at 500°C for 1 h at a heating rate of $6^\circ\text{C}/\text{min}$ to afford pure BFO and Ba doped BFO MNPs, respectively.

2.3. Degradation experiments

This study focuses on the application of the photo-Fenton catalytic degradation of toluene from aqueous solutions using undoped and Ba doped BFO MNPs. Before irradiation, the suspension was magnetically stirred for 45 min in a dark place and then irradiated for different time intervals at a fixed temperature of 25°C by using a water bath. The photo-Fenton catalytic degradation of toluene was carried out under the irradiation of a 55 W fluorescent lamp at a distance of 15 cm with an emission peak at 550 nm under continuous magnetic stirring. For photo-Fenton catalytic degradation of toluene under visible light irradiation, photocatalyst powder (40- mg) and 0.6–65 mM H_2O_2 were added into 100 mL of toluene solution (100 mg L^{-1}) in a 250 mL Erlenmeyer flask with an appropriate cap to stop evaporation of toluene solution during photodegradation process. After reaction completion, the photocatalyst was easily separated from the solution by using an external magnetic field. The concentration of the toluene solution was evaluated by measuring the intensity of the absorption

peak at 205 nm using a UV–vis spectrophotometer. The conversion of toluene was defined as the following Eq. (1):

$$\text{Conversion} = \left[\frac{C_0 - C}{C_0} \right] \times 100 \quad (1)$$

Where C_0 is the initial concentration of the toluene solution and C is the concentration of toluene remaining in the solution after the photocatalytic reaction.

Furthermore, a blank solution (without the photocatalyst) was used in all experiments to evaluate the amount of toluene evaporation. Toluene evaporation during the photo degradation process was negligible when a cap was used

2.4. Characterization equipment

The crystalline structure was identified by using X-ray diffraction (XRD) (BrukerD8Advance) with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda=1.5406\text{ \AA}$). The samples' morphology and size were examined by transmission electron microscopy [(TEM, JEOL TEM Model 2100)]. To analyze the chemical states of the constituents, X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo Scientific Sigma Probe spectrometer with a monochromatic $\text{AlK}\alpha$ source (photon energy 1486.6 eV), spot size $400\text{ }\mu\text{m}$, pass energy 200 eV and energy step size 1.0 eV. A Genesis 10S UV–vis spectrophotometer was used to obtain the absorbance of toluene at λ_{max} of 205 nm. The chemical oxygen demand (COD) test was used to express the COD of toluene solution. The total organic carbon (TOC) of the toluene solution was determined by TOC 500A (Shimadzu, Japan).

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. XRD results

XRD patterns of as-prepared pure BFO and Ba doped BFO samples with varying content of Ba are shown in Fig. 1. All XRD peaks corresponding to BFO perovskite structure with R3c space group (JCPDS No. 86-1518), demonstrating that single crystalline BFO MNPs phase. The rhombohedral structure of BFO MNPs does not change appreciably with Ba doping, except increase in $\text{Bi}_{25}\text{FeO}_{39}$ impurity phases. From a small magnified section of XRD patterns in the 2θ range of $31\text{--}33^\circ$, it is clear that the (104) and (110) peaks split for pure BFO MNPs and it was merged into a single (110) peak, arising from the substitution of larger ionic radius of Ba^{2+} (1.36 \AA) than that of Bi^{3+} (1.17 \AA). The calculated crystalline sizes using Scherer's formula were found to be 33.23 nm, 31.7 nm and 30.1 nm for pure BFO, Ba 8% -BFO and Ba 12%-BFO, respectively. Compared with the pure BFO MNPs, with increasing the Ba doping content, the crystalline size of Ba doped BFO slightly decreased, revealing the structural distortion of BFO induced by the Ba doping.

3.1.2. XPS results

Further evidence for the quality and composition of the BFO and Ba doped BFO MNPs was obtained from XPS studies. The survey spectra from 0 to 1000 eV for pure and Ba doped BFO MNPs as shown in Fig. 2 confirm the presence of Bi, Fe, O and minor quantities of Ba for $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.03, 0.08$ and 0.12), without traces of any other impurities and with the exception of a small amount of adsorbed carbon peak C 1s at 285 eV to calibrate the system. Furthermore, in the pure BFO MNPs, the molar ratio of bismuth, iron and oxygen is almost 1:1:3. However, in the Ba doped BFO MNPs samples, the amounts of Ba identified by the XPS analysis were a little less than those actually added in the synthesis. The detected atomic fractions of Ba in Ba doped BFO MNPs were 2.8, 7.5 and 11.6

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