



Facile synthesis of α -FeOOH/ γ -Fe₂O₃ by a pH gradient method and the role of γ -Fe₂O₃ in H₂O₂ activation under visible light irradiation

Yuan Ma¹, Beibei Wang¹, Qing Wang, Shengtao Xing*

National Demonstration Center for Experimental Chemistry Education, College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China

HIGHLIGHTS

- α -FeOOH/ γ -Fe₂O₃ was prepared by a low-cost and green method.
- It exhibited high photo-Fenton activity for tetracycline degradation at pH 3–10.
- Possible mechanism for H₂O₂ activation by α -FeOOH/ γ -Fe₂O₃ was discussed.
- Tetracycline should be degraded by \cdot OH, holes and \cdot O₂⁻.

ARTICLE INFO

Keywords:

Magnetic catalyst
Photo-Fenton
Active species
Tetracycline
Degradation

ABSTRACT

The development of an efficient and recyclable catalyst at a wide working pH range is crucial for the practical application of heterogeneous Fenton process. In this work, magnetic α -FeOOH/ γ -Fe₂O₃ nanocomposite was one-pot synthesized by a simple pH gradient method. The obtained sample was found to be an efficient Fenton catalyst for the degradation and mineralization of tetracycline hydrochloride (TC) over a wide pH range under visible light irradiation. It exhibited higher adsorption capacity towards TC at neutral pH, which facilitates the surface reactions of TC with active species. The contribution of homogeneous reactions can be ignored at neutral and alkaline pH, but increased significantly at acidic pH. The mechanism for H₂O₂ activation by α -FeOOH/ γ -Fe₂O₃ at neutral pH is quite different from that by FeOOH. In the α -FeOOH/ γ -Fe₂O₃ photo-Fenton process, γ -Fe₂O₃ could act as an electron trap and inhibit the reaction between photogenerated electrons and H₂O₂. Consequently, the production of HO \cdot was reduced, whereas more holes were separated and the production of \cdot O₂⁻ from the reaction of holes with H₂O₂ was significantly enhanced. TC should be degraded by HO \cdot , holes and \cdot O₂⁻. Finally, the intermediates were determined by liquid chromatography–mass spectrometry and a possible pathway for TC degradation was proposed.

1. Introduction

Tetracycline (TC) is a widely used antibiotic and frequently detected in surface and ground waters [1,2]. This may lead to the development of antibiotic resistant bacteria that threaten human health [3]. TC cannot be effectively degraded by the conventional water treatment technologies. Moreover, its degradation intermediates may be more toxic [4]. Hence, the development of efficient water treatment technology for removing TC is highly desired.

Advanced oxidation processes (AOPs), which can generate highly potent radicals, were found to be effective in the removal of refractory organic pollutants [5–9]. Among them, heterogeneous Fenton process seems to be more promising for practical applications due to its low cost

and easy operability. Up to now, many iron-based nanomaterials have been extensively investigated as a Fenton catalyst [10–14]. However, most of them only have high activity at low pH values, which can be due to the slow regeneration of Fe²⁺ from the reaction between Fe³⁺ and H₂O₂ at high pH values. Therefore, the improvement of the performance of heterogeneous Fenton process over a wide pH range is crucial for its practical application. Recently, visible light, the largest proportion of the solar spectrum and artificial light sources, was found to be effective to improve the efficiency of heterogeneous Fenton process [15–19]. Narrow band gap semiconductors can generate electrons and holes under visible light irradiation. The photogenerated electrons can accelerate the reduction of Fe³⁺ to Fe²⁺, thus promoting the production of hydroxyl radical (HO \cdot) from the reaction between Fe²⁺ and

* Corresponding author.

E-mail address: stxing07@sina.com (S. Xing).

¹ Yuan Ma and Beibei Wang contributed equally to this project and should be considered cofirst authors.

H_2O_2 . In addition, the electrons and holes can also react directly with H_2O_2 to generate $\text{HO}\cdot$ and superoxide radical ($\cdot\text{O}_2^-$) for degrading organic pollutants. It is well known that the recombination of electrons and holes is very fast in a narrow band gap semiconductor. In order to promote the separation efficiency of electrons and holes, some nanocomposites were developed [20–24]. Unfortunately, the difficult separation and sophisticated synthetic procedure of these nanomaterials limit their practical application. Therefore, it is highly desirable to develop a low-cost and effective magnetic Fenton catalyst.

Goethite ($\alpha\text{-FeOOH}$) is an abundant iron mineral and exhibits the highest Fenton activity among iron (hydr)oxides [25,26]. However, only nano-sized $\alpha\text{-FeOOH}$ shows high activity, and its separation from water is very difficult. Compared with $\alpha\text{-FeOOH}$, magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are easily recyclable, but have a lower catalytic activity for the treatment of water and wastewater at neutral pH. The combination of $\alpha\text{-FeOOH}$ with $\gamma\text{-Fe}_2\text{O}_3$ or Fe_3O_4 should be an effective alternative for the synthesis of active magnetic catalyst. Since they have different structure and optical properties, a synergistic effect between them might be achieved. In this work, magnetic $\alpha\text{-FeOOH}/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite was one-pot synthesized by a low cost and green method. It exhibited excellent photo-Fenton performance for the degradation of TC over a wide pH range. The correlation between its structure and catalytic performance was investigated. The active species in this photo-Fenton process and the degradation intermediates of TC were analyzed. Finally, the possible catalytic mechanism for H_2O_2 activation and the pathway for TC degradation were proposed.

2. Experimental section

2.1. Catalyst preparation

$\alpha\text{-FeOOH}/\gamma\text{-Fe}_2\text{O}_3$ was one-pot synthesized by a pH gradient method. Firstly, 1 g of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ was dissolved with 60 mL of deionized water. This solution was adjusted to pH 10 with NaOH solution and placed in a water bath at 60 °C for 2 h. Then, 0.5 g of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ was added and the suspension pH was adjusted to 6. This mixture was still maintained at 60 °C for 3 h. The solid product was washed with deionized water for several times. Finally, it was separated from water by a magnet and dried at 60 °C overnight. For comparison, two samples were prepared by treating the $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ solution at 60 °C for 2 h at the initial pH of 6 and 10, respectively, and designated as Fe6 and Fe10, respectively.

2.2. Catalyst characterization

The crystal phase, morphology and structure of the prepared samples were studied using powder X-ray diffraction (XRD, Bruker D8-Advance), scanning electron microscope (SEM, Hitachi S-4800), and transmission electron microscope (TEM, Hitachi H-7500). Nitrogen adsorption–desorption experiments were performed on a surface area analyzer (Quantachrome NOVA 4000e), and the surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The saturation magnetization value was determined by a quantum design physical property measurement system at room temperature. Infrared (IR) spectra and ultraviolet–visible diffuse reflectance spectra (UV-DRS) were recorded on a Nicolet iS 50 IR spectrometer and a Hitachi UV-3600 spectrophotometer, respectively. X-ray photoelectron spectroscopy (XPS) was determined with a Thermo ESCALAB 250 spectrometer. The Mössbauer measurements were performed at room temperature using a conventional spectrometer (Germany, Wissel MS-500) in transmission geometry with constant acceleration mode. A $^{57}\text{Co}(\text{Rh})$ source with activity of 25 mCi was used. The velocity calibration was done with a room temperature $\alpha\text{-Fe}$ absorber. The surface charge property of the samples in aqueous solution was measured by a Malvern 3000 Zetasizer. Mott–Schottky analysis was performed on a VMP3 electrochemical system.

2.3. Catalytic activity evaluation

Photo-Fenton degradation of TC solution was carried out in a 200 mL glass vessel (internal diameter 5.3 cm) covered with foil, and a 300 W Xe lamp (PLS-SXE300c, $\lambda \geq 420$ nm, Perfectlight) was placed above it. This reaction was maintained at room temperature by circulating water. In a typical experiment, the suspension containing 0.5 g L^{-1} catalyst and 10 mg L^{-1} TC was magnetically stirred in dark for 30 min to reach the adsorption/desorption equilibrium, and then the concentration of TC was determined to calculate the adsorption efficiency. The solution pH during the adsorption experiment was maintained constant using dilute H_2SO_4 or NaOH solution. The photo-Fenton reaction was started by adding a certain amount of H_2O_2 (10 mM) and turning on the lamp. The samples at different reaction times were withdrawn and filtered through a Millipore filter (0.25 μm) for analysis. The concentration of TC was determined by high performance liquid chromatography (HPLC, Agilent 1200) equipped with a ZORBAX Eclipse XDB-C18 column at the wavelength of 280 nm. Acetonitrile and ammonium acetate aqueous solution (0.1 M) with the ratio of 35:65 were used as the mobile phase. The total organic carbon (TOC) of the solution was analyzed using a TOC analyzer (Phoenix 8000). The concentration of leached Fe was determined by an atomic absorption spectrometer (Hitachi 180-70). The degradation intermediates were identified by liquid chromatography-mass spectrometry (LC–MS, 3200 Q-TRAP, AB SCIEX) using acetonitrile and ammonium acetate solution (0.01 M) as the mobile phase (1 mL min^{-1}). The ratio of acetonitrile ranged from 90% to 65%. MS analysis was performed in the positive and negative ion modes from 20 to 500 m/z . The formed $\text{HO}\cdot$ and $\cdot\text{O}_2^-$ in different systems were determined by a MS-5000 electron paramagnetic resonance (EPR) spectrometer (Magnetech, Germany) using DMPO (5,5-dimethyl-1-pyrroline-N-oxide) as a probe.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the as-synthesized samples are shown in Fig. 1. The diffraction peaks of the sample prepared at pH 10 can be indexed to $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS 39-1346), while that of the sample prepared at pH 6 can be assigned to a mixture of $\alpha\text{-FeOOH}$ (JCPDS No. 29-0713) and $\gamma\text{-FeOOH}$ (JCPDS 08-0098). As for the sample prepared by the pH gradient method, three weak peaks assigned to $\alpha\text{-FeOOH}$ were observed, besides the peaks assigned to $\gamma\text{-Fe}_2\text{O}_3$, indicating the coexistence of $\alpha\text{-FeOOH}$ and $\gamma\text{-Fe}_2\text{O}_3$. The weak peak intensity of $\alpha\text{-FeOOH}$ can be ascribed to its low content or less ordered structure. The saturation magnetization value of $\alpha\text{-FeOOH}/\gamma\text{-Fe}_2\text{O}_3$ was determined to be

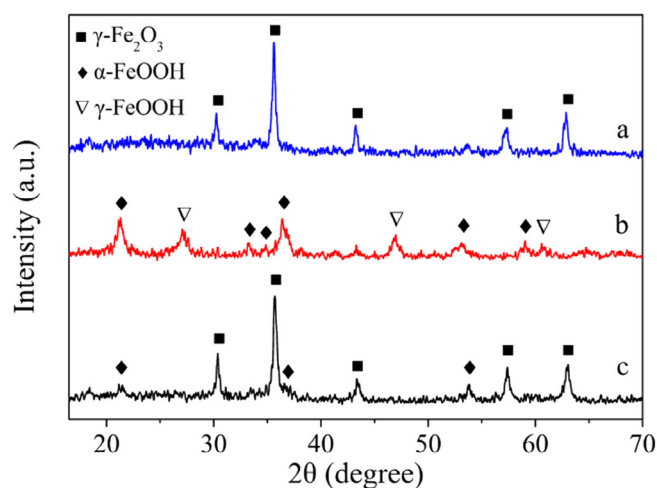


Fig. 1. XRD patterns of (a) Fe10, (b) Fe6 and (c) $\alpha\text{-FeOOH}/\gamma\text{-Fe}_2\text{O}_3$.

Download English Version:

<https://daneshyari.com/en/article/6577885>

Download Persian Version:

<https://daneshyari.com/article/6577885>

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