Visible-light photo-Fenton oxidation of phenol with rGO-α-FeOOH supported on Al-doped mesoporous silica (MCM-41) at neutral pH: Performance and optimization of the catalyst

Ying Wang [a], *, Mingxing Liang [a], Jiasheng Fang [b], Jun Fu [c], Xiaochun Chen [b]

[a] The Key Laboratory of Water and Sediment Sciences, Ministry of Education, School of Environment, Beijing Normal University, Beijing 100875, PR China
[b] College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China
[c] Sino-Japan Friendship Centre for Environmental Protection, Beijing 100029, PR China

HIGHLIGHTS

- The catalyst RFAM displayed excellent catalytic activity for the VLD photo-Fenton process at neutral pH.
- Excellent capacity of RFAM ascribed to synergistic effects of α-FeOOH, rGO and the Al-MCM-41 support.
- The effects of the contents of loading and bubbling gas were studied.
- The energy utilization factor at different parameters and the degradation intermediates were studied.

ARTICLE INFO

ABSTRACT

In this study, α-FeOOH on reduced graphene oxide (rGO-α-FeOOH) supported on an Al-doped MCM-41 catalyst (RFAM) was optimized for the visible-light photo-Fenton oxidation of phenol at neutral pH. The stability of the catalysts, effect of bubbling aeration, and degradation intermediates were investigated. Results indicated that RFAM with a large Brunauer-Emmett-Teller (BET) area and mesoporous structure displayed excellent catalytic activity for the visible-light-driven (VLD) photo-Fenton process. Phenol degradation was well described by a pseudo-first-order reaction kinetics model. Raman analysis demonstrated that an rGO-α-FeOOH (RF) composite is formed during the ferrous-ion-induced self-assembly process. Al-MCM-41 could uniformly disperse RF nanosheets and promote the mobility and diffusion of matter. The activity of the main catalyst α-FeOOH was enhanced after the incorporation of rGO nanosheets. The α-FeOOH crystal in RFAM showed catalytic activity superior to those of Fe_3O_4 and Fe_2O_3. The RFAM catalyst, with an optimal GO-Fe^{2+} mass ratio of 2.33, exhibited a larger BET area, pore size, and pore volume, and thus exhibited high performance and energy utilization efficiency in the VLD photo-Fenton reaction with remarkable stability. Bubbling N_2 inhibited catalytic performance, while bubbling O_2 or air only slightly accelerated the phenol degradation. Visible light played an important role in accelerating the formation of reactive oxygen species (·OH) for the highly efficient phenol degradation. Analysis of degradation intermediates indicated a high phenol mineralization level and the formation of low-molecular-weight organic acids. This work would be helpful in providing an insight into a new type of catalyst assembly and a possible route to a promising heterogeneous catalyst applicable in the visible light photo-Fenton process for effective wastewater remediation at neutral pH.

© 2017 Published by Elsevier Ltd.

1. Introduction

Advanced oxidation processes (AOPs) are cost-effective options for water purification and wastewater treatment (Guimarães et al., 2012). Among AOPs, the photo-Fenton process has garnered significant interest as a promising technology for the treatment of aqueous contaminations, as it accelerates the regeneration or reduction of Fe^{3+} into Fe^{2+} and restarts a typical cycle of the Fenton reaction to boost an abundant generation of ·OH radicals with its powerful oxidizing ability (Sun and Lemley, 2011; Kim and Kan,

2014; Guo et al., 2015). Nevertheless, the main drawbacks of a homogeneous Fenton-based process involve the subsequent removal of iron oxyhydroxide sludge and requirement of acidic pH for the reaction; hence, attention has been focused on the application of a heterogeneous photo-Fenton process for the photodegradation of various contaminants in wastewater under ultraviolet (UV) irradiation (Yuan et al., 2013). Although assisted UV light can provide the possibility of a wide workable pH range and considerably enhance catalytic performance, it is difficult to utilize sunlight as an irradiation source since the UV band (200–400 nm) comprises only 3–5% of the solar light energy that reaches the earth (Lee et al., 2013; Pradhan et al., 2013). Hence, it is imperative to develop photocatalysts that can efficiently use sunlight or visible light in the heterogeneous photo-Fenton process (Hassan et al., 2016). Recent studies reported some new visible light responding catalysts, such as Fe_2O_3/TiO_2 (Hassan et al., 2016), $BaFe_{12}O_{19}$ (Valero-Luna et al., 2016), $ZnFe_2O_4$ (Cai et al., 2016), Ni_3Fe/Fe_3O_4 (Laipan et al., 2016) was developed. Heterogeneous photo-Fenton oxidation using catalysts under visible lights led to significant enhancement of ·OH production and degradation of synthetic dyes, phenol and pesticides due to synergistic effects of photocatalysis and Fenton oxidation (Pimentel et al., 2008).

Previously, we developed reduced graphene oxide (rGO)-α-FeOOH-supported Al-CMC-41 (RFAM) using *in situ* ferrous-ion-induced self-assembly (Ying et al., 2017). The catalyst has been proved to be efficient in the degradation and mineralization of phenol under visible light irradiation in a wide pH range (4.0–8.0). To further increase catalytic activity, catalyst optimization should be systematically investigated.

As reported, the crystal phase of iron is a crucial factor for catalytic activity (Guo et al., 2015; Ruales-Lonfat et al., 2015). In terms of degrading organic pollutants, goethite (α-FeOOH) has been found to show a stronger catalytic ability to degrade azo dyes (e.g., Mordant Yellow 10) than those of hematite (α-Fe_2O_3) and akaganeite (β-FeOOH) in aqueous dispersions of H_2O_2 at neutral pH under UV-light irradiation (He et al., 2002). However, some other studies reported that Fe(II) minerals (e.g., magnetite and pyrite) were more effective than ferric oxides (goethite, ferrihydrite, lepidocrocite, and hematite) for the transformation of 2,4,6-trinitrotoluene (TNT) at acidic and neutral pH (Matta et al., 2007). With respect to sterilization, iron oxides and Fe(III) hydroxides are effective for the catalytic oxidation of waterborne viruses at near neutral pH under solar-light illumination (Nietojuarez and Kohn, 2013). Catalytic efficiency decreased in the order $Fe(OH)_3$>Fe_3O_4>α-Fe_2O_3>α-FeOOH. Besides, active composition content and ratio are also key factors affecting the catalytic activity (Yu et al., 2016). Extremely low content of catalysts possibly leads to insufficient active sites, while excess doping causes overlapped active sites. Hence, it is imperative to investigate the optimal content and ratio. Dissolved oxygen (DO) is another significant factor affecting the photo-Fenton reaction. Compared with N_2-saturated conditions, air-saturated conditions strongly improve the reduction of the total organic carbon (TOC) (Kribéche et al., 2016). According to their study, oxygen can possibly reduce the quenching of ·OH in the Fenton reaction. Simultaneously, aeration can enhance the interaction between ·OH and substrate molecules (Hong et al., 2011).

The objective of this study was the optimization of a heterogeneous catalyst, RFAM, in the visible-light-driven (VLD) photo-Fenton process for the oxidative removal of phenol from synthetic wastewater. In addition, the effects of active components with different iron oxide crystal phases, doping amounts of Fe^{2+} and rGO, and GO-Fe^{2+} ratios were systematically investigated. In addition to the brief analysis of degradation intermediates, t-butanol (TBA) scavenging and bubbling aeration methods were also employed to investigate the role of visible light in the VLD photo-Fenton process using RFAM.

2. Experimental

2.1. Materials

Expandable graphite powders (>99%) were purchased from Qingdao Yijiu Graphite Co., Ltd (Qingdao, China). Goethite (α-FeOOH, A.R.) was purchased from Sigma-Aldrich Co., LLC (China). Titanium potassium oxalate (A.R.) was purchased from Aladdin Reagent Co., Ltd (Shanghai, China). Chromatographic grade methanol was purchased from Mreda Technology Co., Ltd (Beijing, China). Analytical-grade chemicals and reagents used as received were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and Xilong Chemical Co., Inc (Beijing, China). All solutions were prepared with deionized water, except that the mobile phase solution for HPLC analysis was prepared from ultrapure water.

2.2. Catalyst preparation

First, a GO solution (7.75 mg mL^{-1}) was obtained by the modified Hummers' method (Hummers et al., 1958). The Al-doped MCM-41 (Al-MCM-41) support was easily prepared according to the study by Pradhan and Parida (2012). According to a previous study (Ying et al., 2017), RFAM was fabricated with Al-MCM-41, GO, and ferrous sulfate via ferrous-ion-induced self-assembly. For comparison, rGO-α-FeOOH (RF) was prepared without the addition of Al-MCM-41, while rGO/Al-MCM-41 (rGO/AM) was prepared by replacing ferrous sulfate with hydrazine hydrate as the reducing reagent. Besides, Fe_2O_3-rGO/AM was prepared by the impregnation of rGO/AM with ferric nitrate and calcination for 5 h at 823 K in a tubular furnace under N_2. Fe_3O_4-rGO/AM was obtained by calcination for 5 h at 773 K using RFAM.

2.3. Experimental procedures

VLD photo-Fenton experiments were conducted in a glass beaker. A long-arc xenon lamp of approximately 50 cm (35 × 1 cm) was positioned (Shanghai Jiguang Special Lighting Appliance Factory, China) above the beaker to provide solar light irradiation in the visible light region (λ = 400–700 nm). Prior to the start of reaction with the addition of 10 mmol L^{-1} H_2O_2, 0.1 g of catalyst was dispersed in a 200 mL of a 100 mg L^{-1} phenol solution (pH = 6.0) irradiated by visible light under magnetic stirring for 30 min to reach adsorption equilibrium. As a calorigenic lamp was used, cooling water was circulated to maintain ambient reaction temperature. Aqueous samples were removed at fixed time intervals and filtered through 0.22 μm cellulose acetate membrane filters (Membrana, Germany) for analysis.

For investigating the visible light irradiation during the RFAM-catalyzed Fenton reaction, 6 mmol L^{-1} TBA was used to scavenge ·OH radicals so as to compare the catalytic efficiencies of the VLD photo-Fenton process and the Fenton process. Experiments under dark conditions were conducted in a glass beaker covered with an aluminum foil. Besides, to investigate the effect of dissolved oxygen on catalytic performance, aeration conditions (air, N_2, and O_2) were created using a gas purging tube to sustain insufflation during the experiments.

2.4. Analytical methods

Phenol was analyzed by high-performance liquid chromatography (HPLC,U3000, DIONEX) with UV absorbance detection at 270 nm. TOC was determined using a TOC analyzer (TOC-L,