



In-situ fabrication of supported iron oxides from synthetic acid mine drainage: High catalytic activities and good stabilities towards electro-Fenton reaction



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ABSTRACT

Acid mine drainage (AMD) contains a large amount of ferrous iron and the recovery of iron oxides from the AMD has been of extensive research interest. Here we report a novel air-cathode fuel cell strategy to in-situ utilize ferrous iron in the AMD for the fabrication of heterogeneous electro-Fenton catalysts. Three types of nano-structured iron oxide/graphite felt (GF) composites, including FeOOH/GF, Fe₂O₃/GF and Fe₃O₄/GF, were fabricated from a synthetic AMD and their catalytic activities towards the electro-Fenton reaction were evaluated at neutral pH with Rhodamine B (RhB) as a probe pollutant. The electro-Fenton system with GF cathode only removed 30 ± 1.4% of RhB after 120 min of reaction. In comparison, RhB removal efficiencies were significantly improved to 62.5 ± 2.0%, 95.4 ± 0.9% and 95.6 ± 0.7% when the FeOOH/GF, Fe₂O₃/GF and Fe₃O₄/GF composites were used as the cathodes, respectively. Among the three types of composites, the Fe₃O₄/GF exhibited the highest electro-Fenton catalytic activity whereas the lowest activity was observed for the FeOOH/GF. The decomposition of H₂O₂ on the iron oxides followed a completely surface-catalyzed mechanism in which the iron oxides maintained their structures without leaching of iron species. The air-cathode fuel cell technology has a potential for iron recovery from the AMD, and provides an effective way for fabricating heterogeneous electro-Fenton catalyst with high catalytic activity and good stability.

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1. Introduction

Mining industry produces a large amount of acid mine drainage (AMD) which is characterized as a high acidity effluent containing various dissolved metals and sulfate. As one of the most abundant metals in the AMD, the ferrous iron can cause pollution of natural water and should be removed from the AMD before it is discharged into the environment. The AMD is conventionally deferrized via processes involving alkaline neutralization and air oxidation, producing a chemical sludge containing a mixture of iron oxides such as hematite (Fe₂O₃), magnetite (Fe₃O₄) and goethite (FeOOH) [1,2]. The recovery of iron oxides from AMD residues has been of extensive research interest in order to limit the AMD sludge discharge and offset the cost of AMD treatment [1–3]. However, the complex operational requirements related to the separation of iron oxides make such an iron recovery behavior economically expensive and at poor efficiency.

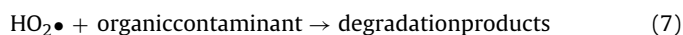
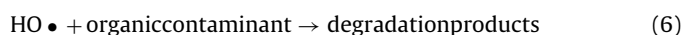
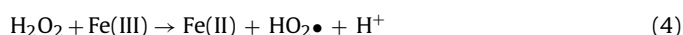
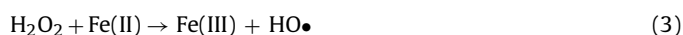
An alternative approach based on the air-cathode fuel cell has been proposed to selectively treat the ferrous iron in the AMD [4–6]. In such a device, ferrous iron is spontaneously oxidized to form ferric hydroxide at the carbon anode and oxygen in the air is reduced to water at the cathode. Electricity is concomitantly generated during the process, and the produced ferric hydroxide can be transformed to FeOOH upon drying. The primary advantage of the fuel cell approach is it realizes simultaneous recovery of FeOOH and electricity from the AMD under ambient condition [4,5]. However, this approach suffers from difficulties in the collection of iron oxides. The ferric hydroxide produced at the anode may precipitate or be absorbed on the surface of carbon electrode and form iron layers which are hard to be separated [6]. As a result, the iron recovery efficiency is significantly reduced due to the loss of iron oxides on the carbon electrode.

In order to improve the iron recovery efficiency of the fuel cell, here we propose the iron oxides attached to the carbon electrode can be recovered together with the carbon in the form of iron oxide/carbon composite. Carbon supported iron compounds have been widely used in many areas, especially as the catalysts in heterogeneous electro-Fenton processes [7]. The Fenton

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reaction is well known for its effectiveness in treating recalcitrant organic pollutants, based on the generation of highly reactive hydrogen radicals from the reaction of ferrous ion (Fe^{2+}) with hydrogen peroxide (H_2O_2) [8]. However, the homogeneous Fenton process has encountered some limitations such as the acidic pH requirement, the self-decomposition of H_2O_2 , and the loss of Fe^{2+} into iron sludge [9]. To overcome these drawbacks, heterogeneous electro-Fenton process is developed in which H_2O_2 is continuously supplied by the cathodic reduction of oxygen (O_2) and solid iron compounds (usually iron oxides) serve as the catalysts instead of Fe^{2+} [10,11]. As depicted by Eqs. (1)–(7), a typical heterogeneous electro-Fenton process involves the electro-reduction of O_2 to H_2O_2 , the production of hydrogen radicals from H_2O_2 and the oxidation of organic pollutants by hydrogen radicals. The great interest in heterogeneous electro-Fenton process arises from the satisfactory reusability of solid iron catalysts as well as the high conversion efficiency from H_2O_2 to hydrogen radicals [9,10,12].



Therefore, in the present work we report a facile and controllable air-cathode fuel cell strategy to in-situ fabricate heterogeneous electro-Fenton catalyst from a synthetic AMD. Graphite felt (GF) was selected as the supporting material of iron oxides due to its high surface area, good electrochemical stability and high electroconductivity. GF supported iron oxides, including FeOOH/GF , $\text{Fe}_2\text{O}_3/\text{GF}$ and $\text{Fe}_3\text{O}_4/\text{GF}$, were obtained from the synthetic AMD by using the fuel cell strategy. The catalytic activities of these iron oxide/GF composites towards electro-Fenton reaction were evaluated at neutral pH with Rhodamine B (RhB) as a probe pollutant. The catalytic mechanisms involved in the heterogeneous electro-Fenton process were investigated by characterizing the surface structures of iron oxides and clarifying the roles of free radicals in such a process.

2. Experimental

2.1. Preparation of the iron oxide/GF composites

The iron oxide/GF composites were prepared by loading iron oxides on the GF in an air-cathode fuel cell. The single-chamber glass-made fuel cell architecture was employed with an anodic volume of 175 mL (Fig. 1) [6]. A $3 \times 3 \text{ cm}^2$ GF (2 mm in thickness) was located in the chamber as the anode. The cathode was a $2 \times 2 \text{ cm}^2$ carbon paper (090S, wet-proofed, Toray Industries Inc., Japan) with a 0.05 mg cm^{-2} platinum catalyst coating on one side. The coated side of the cathode was positioned facing the cation exchange membrane (GEFC-10 N, GEFC Co., China), and the uncoated side was directly exposed to air. Titanium wires (1 mm in diameter) were used to connect the anode and cathode.

A synthetic AMD composed of 40 mM FeSO_4 , 200 mM NaCl and 50 mM NaHCO_3 was used as the anode electrolyte. The anodic chamber was firstly filled with 150 mL of solution that contained NaCl and NaHCO_3 and sparged with a mixture of nitrogen (N_2) and carbon dioxide (CO_2) for 30 min to remove dissolved O_2 . The $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was then added to the anodic chamber in an anaerobic glove box and the pH was adjusted to 7.0 with HCl under continuous

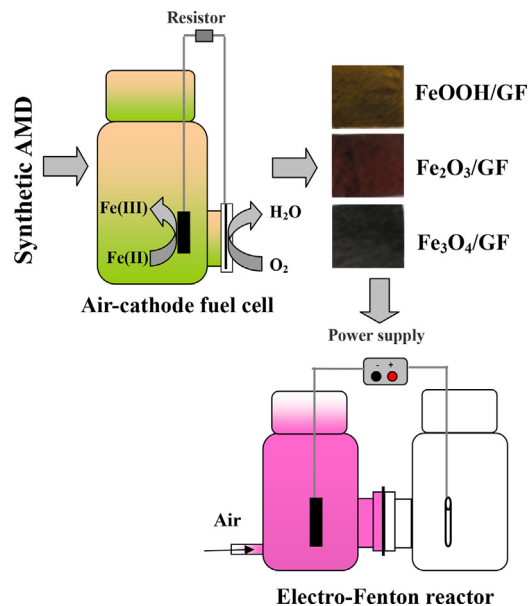


Fig. 1. Schematic diagram for the fabrication of iron oxide/GF composites and their applications in electro-Fenton reaction.

CO_2 sparging. The circuit of fuel cell was left open until a constant open circuit voltage was obtained, and then was connected with a 1000Ω resistor. A data acquisition system (USB2801, ATD Co., China) was used to monitor the voltage across the 1000Ω resistor. When the voltage dropped below 1 mV the anode electrode was removed and rinsed with distilled water. The FeOOH/GF composite was prepared by drying the electrode at 40°C for 24 h. Next, the FeOOH/GF was thermally treated at 300°C for 1 h in air to obtain the $\text{Fe}_2\text{O}_3/\text{GF}$ composite, or was calcined at 700°C for 1 h in N_2 to obtain the $\text{Fe}_3\text{O}_4/\text{GF}$ composite.

2.2. Characterization of the iron oxide/GF composites

Iron contents in the iron oxide/GF composites were determined by thermogravimetry (TG) on a TGA DT-50 apparatus (Sahimadzu Corporation, Japan). The TG was performed from room temperature to 1000°C at a heating rate of $10^\circ\text{C min}^{-1}$ under air atmosphere. The microscopic images of the composites were obtained using a Sirion 200 scanning electron microscope (SEM) (FEI Co., Netherlands). The crystalline phases of composites were identified by X-ray diffractogram (XRD) using a Bruker D8 advance-X-ray diffractometer equipped with graphite-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Valence states of iron in the composites were determined using X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 spectrometer (Thermo, USA) equipped with a monochromatic $\text{Mg K}\alpha$ X-ray source (1253.6 eV). The C1s electron binding energy corresponding to graphitic carbon was set at 284.6 eV and used as a reference to position the other peaks in the XPS spectrum. A nonlinear, Shirley-type baseline and an iterative least-squares fitting algorithm with a Gaussian-Lorentzian sum function were used to deconvolve the XPS peaks. Functional groups in the iron oxides were analyzed by infrared spectrum (IR) on a KBr dist with a VERTEX 70 Fourier transform infrared spectroscopy (Bruker Co., Germany). The composites were cut into $5 \times 5 \text{ mm}^2$ pieces for the SEM and XRD analyses, and were ground into powders for the TG, XPS and IR analyses.

Redox activities of the iron oxide/GF composites were evaluated by cyclic voltammetry (CV) on a CHI 660D electrochemical workstation (CH Instruments Inc., USA). The composites ($3 \times 3 \text{ cm}^2$) were

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