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Enhanced catalytic activity of α-FeOOH-rGO supported on active carbon fiber (ACF) for degradation of phenol and quinolone in the solar-Fenton system

Ying Wang [a,*], Hailong Tian [a], Yange Yu [a], Chengzhi Hu [b,**]

[a] *The Key Laboratory of Water and Sediment Sciences, Ministry of Education, School of Environment, Beijing Normal University, Beijing, 100875, PR China*
[b] *Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, PR China*

HIGHLIGHTS

- A new catalyst, α-FeOOH-rGO/ACF was prepared by electrophoretic deposition in situ self-assembly process.
- The role of every component on catalytic capacity was investigated.
- α-FeOOH-rGO/ACF exhibited excellent activity at a wide pH.
- The possible degradation pathways of phenol and quinoline were proposed.

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ABSTRACT

A new heterogeneous solar-Fenton catalyst, α-FeOOH-reduced graphene oxide (rGO) supported on active carbon fiber (ACF), was synthesized via in situ electrophoretic deposition in a self-assembly process. Optimization of the components (electrophoretic deposition time of GO and Fe, GO dosages), the effect of pH and the catalysts stability were investigated systematically. The results indicated that rGO-α-FeOOH composite is formed during the ferrous-ion-induced self-assembly process on ACF. FeOOH-rGO/ACF displayed excellent catalytic activity for degrading phenol and quinoline under the solar-driven photo-Fenton process in a wide range of pH values (4.5–9.5) and possess good stability in neutral condition. The phenol oxidation process on this catalyst was described by a pseudo-first-order kinetics model. Both the ACF support and solar irradiation promoted greater H_2O_2 decomposition and produced more $^{\bullet}OH$ radicals, thus, significantly improving the catalytic capacity. The introduction of graphene improved the catalytic capacity of the catalyst under solar irradiation. The optimal electrophoretic deposition time of GO and the optimal Fe and initial GO content in deposition were 10 min, 9.8 wt% and 15.0 wt%, respectively. The degradation pathways of phenol and quinoline in the solar-driven photo-Fenton process were also elucidated.

1. Introduction

As is well known, coking wastewater is one of the most refractory wastewaters (Zhu et al., 2009) and contains large quantities of phenol, cyanide, benzene, ammonia and other toxic and hazardous substances (Zhou et al., 2015). Once these contaminants enter the human body through the food chain and are concentrated there, they pose a danger to health (Chu et al., 2012). Unfortunately, many of the widely used biological methods for wastewater treatment are largely inefficient against removing them. Thus, it is necessary to develop advanced treatment methods to remove toxic and hazardous substances from wastewater.

At present, treating coking wastewater include advanced oxidation processes (AOPS) (Chu et al., 2012), an adsorption method (Zhang et al., 2010), a membrane separation technique (Kumar and Pal, 2015), coagulation (Lai et al., 2007), or combinations of processes. Advanced oxidation technologies are environmentally friendly methods due to the in situ production of hydroxyl radicals as main oxidants. The produced hydroxyl

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* Corresponding author.
** Corresponding author.
E-mail addresses: yingwang@bnu.edu.cn, 10490554@qq.com (Y. Wang), czhu@rcees.ac.cn (C. Hu).

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radicals mineralize some of the refractory organics or increase the biodegradable property of the pollutants. As a promising advanced oxidation technology, the heterogeneous photo-Fenton process (HPFP) has attracted much attention because of its rapid reaction, little iron loss, lack of iron sludge production and activity in wide pH values (Liu et al., 2017). Most importantly, the HPFP provides a better way to overcome the low pH requirement of the traditional Fenton reaction system. However, the reaction is still affected by pH to some extent (López et al., 2017; Ma et al., 2017). Compared to the traditional Fenton system, the unique feature of the HPFP is that iron ions are immobilized onto a solid catalyst and a stable light source is applied. Currently, ultraviolet (UV) light-driven processes such as UV/H_2O_2 are used, but these processes require large energy consumption. Unlike UV-Fenton, solar-light-driven Fenton is an effective way of using solar energy to degrade organic pollutants.

As is well known, the catalyst is the key to the HPFP. Much attention has been paid to the development of solar light-driven catalysts, such as α-Fe_2O_3/SnO_2 (Pradhan et al., 2013), α-Fe_2O_3@GO (Kim and Kan, 2015), and Fe(III)-tartrate/TiO_2. Thus, the active metal components of the HPFP catalyst are mainly iron, iron oxides, mixed double metals, goethite and other metals (Molina et al., 2012; Yu et al., 2016; Zeng et al., 2016). Many scholars have focused on the α-FeOOH/H_2O_2 Fenton system because α-FeOOH exhibits very good catalytic activity (Tiya-Djowe et al., 2015; Xu et al., 2015). As previously reported, the introduction of reduced graphene oxide (rGO) can improve the electron transfer efficiency, promote the generation of hydroxyl radicals, and improve the efficiency of the catalyst in the process of the Fenton reaction. Additionally, based on recent studies, the α-FeOOH/rGO hybrid composites synthesized using simple methods exhibited a higher catalytic capacity than α-FeOOH (Huang et al., 2013). Another important factor that affects catalytic activity is the catalyst carrier. The commonly used catalyst carriers include alumina, silica gel, activated carbon, natural clay, and graphene (Molina et al., 2012; Yu et al., 2016; Zeng et al., 2016). Activated carbon fiber (ACF) has been widely used due to its low price and higher surface area, which provides a high dispersion of the active component. Good fluid permeability contributes to mass transport to and from the catalyst surface. The effects of ACF as a catalyst carrier have been demonstrated in many studies (Tiya-Djowe et al., 2015; Xu et al., 2015).

In this study, an α-FeOOH-rGO/ACF catalyst for HPFP was developed and characterized using scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectrum and N2 adsorption-desorption isotherms. The preparation methods were investigated and optimized. Phenol and quinoline were chosen to simulate coking wastewater. The effects of catalyst composition and pH changes on pollutant removal with/without irradiation were investigated. The degradation mechanisms of phenol and quinoline in the solar-driven photo-Fenton process were also elucidated.

2. Materials and methods

2.1. Preparation of catalysts

2.1.1. Pretreatment of ACF

The activated carbon fiber (ACF) was cut into pieces of 3*5 cm. The pieces were washed 3–4 times with deionized water and placed into deionized boiling water for 1 h. Then, the pieces were soaked in 0.5 mol/L NaOH for 2 h and 0.5 mol/L HCl for 12 h to successively remove impurities and production residues. The pieces were then soaked in deionized water for 2 h and washed 6–8 times to remove residual acid. Finally, the pieces were heated in an oven for 12 h at 65 °C and placed in a plastic bag.

2.1.2. Preparation of α-FeOOH-rGO/ACF catalysts

α-FeOOH-rGO/ACF was prepared using the electrophoretic deposition-in situ self-assembly process. The fabrication procedure was as follows: a 7.8 mg mL^{-1} graphene oxide (GO) aqueous solution was synthesized using the modified Hummers' method (Klamerth et al., 2010). The GO solution (0.1, 0.5, 1, 1.5 mg/mL, 40 mL) was dispersed by ultrasonication for 30 min. The pretreated ACF piece was fixed onto a titanium anode (3*5 cm). After both sides of the ACF piece were covered by GO using electrophoretic deposition (Voltage 15 V, Plate spacing 2 cm, deposition time = 5, 8, 10, 15, 20 min), the ACF was removed with tweezers and placed into a $FeSO_4 \cdot 7H_2O$ solution (Fe/ACF mass ratio = 3%, 5%, 10%, 15%). The mixed solution was heated at 90 °C for 2 h. Next, GO was reduced to rGO. α-FeOOH-rGO was formed via the in situ ferrous-ion induced self-assembly process (Wang et al., 2017). The ACF was removed with tweezers, washed several times with deionized water and then heated at 65 °C for 12 h in an oven. The catalyst obtained was α-FeOOH-rGO/ACF.

The goethite (α-FeOOH) solution catalyst was prepared according to the method used by Lin (Lin et al., 2012). The α-FeOOH/ACF was prepared according to the method used by Kaneko (1986).

2.2. Photo-Fenton degradation experiment

First, 0.05 g of catalyst was added to 100 mL of a phenol solution with an initial concentration of 100 mg/L and stirred by a magnetic stirrer. Different initial pH values (from 4.5 to 9.5) were obtained using 3 mol/L H_2SO_4 or 1 mol/L NaOH, as measured by a PB-10 (Sartorius) pH meter. After stabilizing the pH, 1 mmol of H_2O_2 was added to the phenol solution to begin the reaction. Simultaneously, a 500 W long arc xenon lamp was turned on, and the timer was started. Samples were collected at different times and then filtered by a 0.45 μm membrane for analysis. Finally, 30 μL of NaOH (8 mol/L) was dripped into the samples to terminate the reaction. The experimental procedure for quinoline degradation was the same as that used for phenol degradation. The catalyst was recycled 4 times to evaluate its stability.

2.3. Characterization of the catalysts

The structure and morphology characteristics of materials were observed by scanning electron microscopy (SEM, HITACHI, ×650, Japan). The structural features were tested by polycrystalline X-ray diffraction (X′ Pert PRO MPD, PANalytical, the Netherlands). The chemical valence state and morphological characteristics were determined by X-ray photoelectron spectroscopy (XPS) analysis. Raman spectra were recorded on a laser confocal micro-Raman scattering spectrometer (LabRAM Aramis, HJY Company). The specific surface area and pore size distribution were determined by a high-speed automated surface-area and pore-size analyzer (Quantachrome, Autosorb-iQ3, USA).

2.4. Chemical analytical methods

The phenol concentration was determined using high-performance liquid chromatography (HPLC). The flow phase for analysis was methanol/ultrapure water (0.1% phosphoric acid) = 50/50 (v/v); the column temperature was maintained at 30 ± 1 °C; the flow rate was 1 mL/min; and the detection wavelength was 270 nm. The concentration of quinolone was determined in the same way. Chemical oxygen demand (COD) was determined spectrophotometrically (UV-2500, Shimadzu) using the $K_2Cr_2O_7$-oxidation method, in which an optimal combination of Na_2CO_3 and heating time (90 °C for 90 min) were used to eliminate the influence of residual H_2O_2 on COD determination (Wu and