Chemosphere 148 (2016) 34–40

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Improvement of phenol photodegradation efficiency by a combined g-C_3N_4/Fe(III)/persulfate system

Jian-Yang Hu, Ke Tian, Hong Jiang*

CAS Key Laboratory of Urban Pollutant Conversion, Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

HIGHLIGHTS

- Unmodified g-C_3N_4 was employed to degrade refractory pollutant for the first time.
- The synergistic interaction of g-C_3N_4/Fe(III)/persulfate can improve the reactivity.
- An integrated radical and light Fenton mechanism was experimentally verified.

ARTICLE INFO

Article history:
Received 11 August 2015
Received in revised form
8 December 2015
Accepted 4 January 2016
Available online 21 January 2016

Handling Editor: Jun Huang

Keywords:
g-C_3N_4
Photocatalyst
Persulfate
Fenton
Phenol degradation

ABSTRACT

Graphite-like C_3N_4 (g-C_3N_4) is an efficient visible-light-driven photocatalyst commonly used in dye decolorization with very poor photocatalytic efficiency for degrading recalcitrant organic pollutants, such as phenol. In this study, we designed a g-C_3N_4/Fe(III)/persulfate system to significantly improve the phenol photodegradation efficacy by combining photocatalysis and light Fenton interaction. The phenol removal ratio and degradation rate of the g-C_3N_4/Fe(III)/persulfate system are 16.5- and 240-fold higher than those of individual g-C_3N_4 system. Sulfate radicals ($SO_4^{\bullet -}$) and H_2O_2 are detected in the g-C_3N_4/Fe(III)/persulfate system, suggesting that both radical decomposition and light Fenton interaction play important roles in phenol degradation. The efficient coupled photocatalytic system of g-C_3N_4 combined with Fe(III) and persulfate shows significant potential for application in large-scale degradation of environmental pollutants.

1. Introduction

Organic pollutants are widely existed in natural environment because of the development of industries. Phenol, a typical toxic organic pollutant, was produced from chemical, resin, pharmacy, and electronic industries (Jiang et al., 2003; Yang et al., 2006; Yotova et al., 2009; Liu et al., 2012), and inevitably released to environment. These phenolic compounds pose great risk to various creatures and human beings. Currently, the main methods to remove phenol from wastewater include biological oxidation (Ortega Méndez et al., 2015), adsorption onto the surface of porous materials (Yousef et al., 2011), and advanced oxidation processes (AOPs) using strong oxidizing agents such as hydrogen peroxide (Cartaxo et al., 2012).

Photocatalytic technology using metal oxide semiconductors has recently attracted much attention as one of the energy-efficient techniques in wastewater treatment and surface water remediation (Hoffmann et al., 1995; Gnayem and Sasson, 2013). However, most metal oxide photocatalysts release toxic metal ions and can only utilize UV light to generate conduction band electrons (e^-) and valence band holes (h^+) for contaminant decomposition (Li et al., 2011; Ma-Hock et al., 2012). Graphitic carbon nitride (g-C_3N_4), which consists only of carbon and nitrogen, has been applied to different photocatalytic fields (Maeda, 2009; Dong and Zhang, 2012; Zhang et al., 2015a,b) under visible light to minimize environmental risk and increase the efficiency of solar utilization. This polymeric semiconductor is environment friendly, highly stable, inexpensive, and presents intrinsic visible light response (Wang et al., 2012).

Despite its advantages, g-C_3N_4 exhibits low photoreactive efficiency because of the high recombination rate of its photogenerated charges (Zhang et al., 2010), and thus limit its practical

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* Corresponding author.
E-mail address: jhong@ustc.edu.cn (H. Jiang).

http://dx.doi.org/10.1016/j.chemosphere.2016.01.002
0045-6535/

application. Most previous studies just focused on the use of pure $g\text{-}C_3N_4$ for decolorizing organic dyes (Dong et al., 2011; Xin and Meng, 2013). Several methods, such as fabrication of a porous structure (Wang et al., 2009), doping with metal or nonmetal elements (Liu et al., 2010), coupling with grapheme (Xiang et al., 2011), and combining with other semiconductors (Xu et al., 2011), have been developed to enhance the photocatalytic capability of $g\text{-}C_3N_4$. Zhang et al. reported that the introduction of different species of Ag or Fe, like Ag@AgCl, 1D $Ag@AgVO_3$ nanowires, C + Fe, or $ZnFe_2O_4$ nanoparticles, to the $g\text{-}C_3N_4$ by kinds of synthesis routes, all of them have a huge enhancement in photocatalysis activity (Zhang et al., 2013a, 2013b, 2015a, 2015b). Although these methods obviously improve $g\text{-}C_3N_4$ photocatalytic activity, the complex preparation process, high cost, and biological toxicity of the resultant photocatalysts reveal the need for further studies.

A simple method combining photocatalysis and radicals, such as addition of H_2O_2 to a photocatalytic system to generate more hydroxyl radicals (HO•), can significantly improve the efficiency of pollutant degradation in water (Xu, 2001). Liu et al. (2014) recently found that adding persulfate to a photodegradation system dramatically increases the degradation performance of this system, during which the sulfate radical ($SO_4^{\bullet-}$) is produced by thermolytic cleavage of the peroxide bond. Persulfate can be oxidized and reduced, similar to the mechanism of H_2O_2 activity in a light Fenton system (Avetta et al., 2015). The presence of Fe(III) contributes to electron trapping at the semiconductor surface, facilitates efficient separation and utilization of the electron–hole pairs, and finally promotes pollutant degradation. Thus, we assume that if persulfate and ferric ions are added to the $g\text{-}C_3N_4$ photodegradation system, an enhanced light Fenton system may be built to improve organic pollutant decomposition.

The present study was performed to broaden the application of C_3N_4 in the degradation of recalcitrant organic pollutants and enhance the understanding of photochemical systems combined with $SO_4^{\bullet-}$ and Fenton reagents. To this end, (1) photochemical degradation of phenol was investigated by adding persulfate and ferric ions to a visible-light-$g\text{-}C_3N_4$ system, and (2) an integrated light Fenton and radical photocatalytic system was verified through a series of photodegradation experiments and characterizations. This work proposed a new $g\text{-}C_3N_4$/Fe(III)/persulfate system which can significantly improve the phenol photodegradation efficacy, while deepened the understanding on the degradation mechanism of organic compounds in light Fenton and radical photocatalytic system.

2. Materials and methods

2.1. Preparation

The $g\text{-}C_3N_4$ photocatalyst was prepared by directly heating melamine in a semiclosed system to prevent melamine sublimation. Then, 10 g of melamine powder was placed in an alumina crucible with a cover and then heated to 600 °C in a muffle furnace for 8 h at a heating rate of 4.17 °C/min. The resultant yellow powder was collected and used without further treatment.

2.2. Characterization

Fourier Transform infrared (FTIR) spectra in the range of 4000–400 cm^{-1} were collected on a VERTEX 70 FT-IR spectrometer (Bruker Inc., Germany) by the KBr pellet method. Each spectrum represents the average of 64 scans at a spectral resolution of 4 cm^{-1}. The morphologies of $g\text{-}C_3N_4$ were observed on a SIRION-200 scanning electron microscope (SEM) that was operated at a 30-kV accelerating voltage and a JEOL-2100F transmission electron microscope (TEM) that was operated at a 200-kV accelerating voltage.

2.3. Photodegradation experiment

Photocatalytic degradation of phenol was performed in a 125 mL magnetically stirred cylindrical reactor top-irradiated by a 350 W Xenon lamp (XD-300, Nanjing Yanan Special Lighting Co., Ltd.) at room temperature (26 °C). In a typical run, 80 mL of 10 mg L^{-1} phenol aqueous solution was added to the reactor. The pH of the phenol solution was kept at the initial state. A 150 mg portion of the photocatalyst was added to the reactor, and the system was stirred in the dark for 30 min to achieve adsorption equilibrium. This degradation process is similar to that described in our previous work (Zhang et al., 2014). The samples were centrifuged to sediment the photocatalyst, and the phenol concentration in the supernatants was monitored by measuring solution absorbance using a UV-2450 spectrophotometer (Shimadzu Inc., Japan) at 510 nm wavelength. Aromatic intermediates were identified by LC-100 high-performance liquid chromatograph (HPLC; Wufeng Inc., China) using 1.2 mL min^{-1} of acetonitrile (25 vol.%) and water (75 vol.%) as the mobile phase at 280 nm. The reactor was left open to air over the entire process to ensure aerobic conditions.

Based on the initial experimental conditions above, $Fe(NO_3)_3$ (350 mg L^{-1}) and $K_2S_2O_8$ (300 mg L^{-1}) were added to the reaction system to investigate the effects of Fe(III) and sulfate on phenol degradation. Several comparative experiments were performed by changing the dosages of reagents. Most conditions were tested at least in triplicate. In a ultrasound treatment experiment, we put the system in ultrasound for 15 min before the dark absorption and light irradiation, other conditions are the same as other experiments.

The photocatalytic degradation process accords with the pseudo first-order kinetics (Eq. (1)) by data fitting, thus the apparent kinetic constant (k_{app}) can be used to compare the photocatalytic activity of each photocatalytic system quantitatively (Yan et al., 2010; Dong et al., 2012):

$$\ln(C/C_0) = -k_{app}\, t \tag{1}$$

3. Results and discussion

3.1. Characterization

The FTIR spectra (Fig. 1a) show little difference between the $g\text{-}C_3N_4$ samples before and after light irradiation. Both molecules possess characteristic functional groups on the carbon nitride polymer. The broad peak around 3174 cm^{-1} is attributed to primary and secondary amino groups, and the presence of the peaks indicates that thermo-condensation during the synthesis of $g\text{-}C_3N_4$ is incomplete (Thomas et al., 2008). For example, some $-NH_2$ or $-NH$ groups existed in the side of the layer after the thermal treatment (Zhang et al., 2014). Strong absorption bands ranging from 1200 to 1600 cm^{-1} correspond to the skeletal stretching of the tri-s-triazine heterocycle motif, and the peak at 801 cm^{-1} shows the typical ring-breathing vibration of the tri-s-triazine heterocycle, which indicates that degradation experiment does not destroy the in-plane tri-s-triazine structural motif of $g\text{-}C_3N_4$. Moreover, there was no obvious characteristic peak of phenol in the curve, suggesting the negligible adsorption of phenol on $g\text{-}C_3N_4$ in the dark.

Fig. 1b shows the SEM image of $g\text{-}C_3N_4$ samples. The morphology of sample is highly ordered and dominantly comprises aggregated layers with a size of several micrometers.