Chemosphere 153 (2016) 531–540

Contents lists available at ScienceDirect

Chemosphere

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

An efficient and environment-friendly method of removing graphene oxide in wastewater and its degradation mechanisms

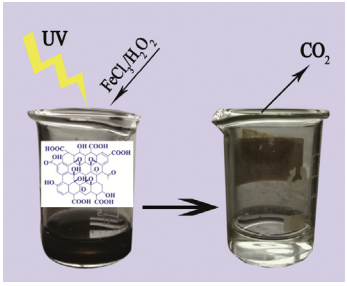
Chao-Zhi Zhang [a, *], Ting Li [a], Yang Yuan [b], Jianqiang Xu [b]

[a] School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, PR China
[b] Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Nanjing University of Information Science and Technology, Nanjing 210044, PR China

HIGHLIGHTS

- An efficient and environment-friendly method of degrading GO in wastewater.
- Graphene oxide being completely degraded by Photo-Fenton to give CO_2.
- The degradation mechanisms of graphene oxide.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 September 2015
Received in revised form
17 March 2016
Accepted 20 March 2016
Available online 1 April 2016

Handling Editor: Jörg E. Drewes

Keywords:
Graphene oxide
Photo-Fenton
Degradation
Mechanism

ABSTRACT

Graphene and graphene oxide (GO) have already existed in air, water and soil due to their popular application in functional materials. However, degradation of graphene and GO in wastewater has not been reported. Degradation of GO plays a key role in the elimination of graphene and GO in wastewater due to graphene being easily oxidized to GO. In this paper, GO was completely degraded to give CO_2 by Photo-Fenton. The degradation intermediates were determined by UV–vis absorption spectra, elemental analysis (EA), fourier transform infrared (FT-IR) and liquid chromatography-mass spectrometry (LC-MS). Experimental results showed that graphene oxide was completely degraded to give CO_2 after 28 days. Based on UV, FT-IR, LC-MS spectra and EA data of these degradation intermediates, the degradation mechanisms of GO were supposed. This paper suggests an efficient and environment-friendly method to degrade GO and graphene.

1. Introduction

Graphene and graphene oxide (GO) have widely been applied in optoelectronic materials (Tang et al., 2010), biomedicine (Kuila et al., 2011), adsorbent (Zhao et al., 2011; Upadhyay et al., 2014; Gao et al., 2011) and photocatalyst (Sun et al., 2012) since graphene was discovered in 2004 (Novoselov et al., 2004). In 2014, requirement of graphene was up to 10,000 tons in the world. GO was also popularly applied in functional materials, such as bacteriostatic and anti-viral (Akhavan and Ghaderi, 2010, 2012; Hu et al., 2010; Akhavan et al., 2012; Liu et al., 2011; Kostarelos and Kostya, 2014; Wu et al., 2014), optoelectronic (Loh et al., 2010; Zhang et al., 2012) and environmental (Zhang et al., 2011; Mi and Hu, 2013; Khan et al., 2012; Pham et al., 2011) materials. Graphene

* Corresponding author.
E-mail address: zhangchaozhi@nuist.edu.cn (C.-Z. Zhang).

http://dx.doi.org/10.1016/j.chemosphere.2016.03.094
0045-6535/

and GO are released into the water (Zhao et al., 2014) in the process of their production and application (Marcano et al., 2010; Choi et al., 2010). Graphene and GO in water can easily enter organisms (Sanchez et al., 2012) to interact with tissues (Hu and Zhou, 2013), cells (Luan et al., 2015), organelles and other biological macromolecules (Hu and Zhou, 2013). It would further result in abnormal function of organisms.

Graphene is easily oxidized to GO by H_2O_2 (Marcano et al., 2010). Therefore, graphene in wastewater would be removed by a method of degradation of GO. It is significant that an efficient and environment-friendly method would be developed to remove graphene oxide from wastewater. However, degradation method of graphene and GO in wastewater has not been reported. Allen et al. (2008, 2009) employed biological and enzymatic method to degrade single-walled carbon nanotubes. Russier et al. (2011) reported degradation of single- and multi-walled carbon nanotubes with horseradish peroxidase. However, the enzyme is too expensive to apply in degradation of graphene and GO in wastewater. Feng et al. degraded ^{14}C-labeled few layer graphene with Fenton. The hazardous products containing conjugated double bonds were given. The products had dramatically ecological effects (Feng et al., 2015).

Photo-Fenton is a very efficient method for degradation of pollutants in wastewater (Pérez-Estrada et al., 2005; Sirtori et al., 2009; Sabaikai et al., 2014; Zhang et al., 2013; Elmorsi et al., 2010). UV irradiation can improve the rate of degradation via Fenton process (Sun and Pignatello, 1993). Therefore, Photo-Fenton method has widely been applied in degradation of organic pollutants (Pérez-Estrada et al., 2005; Sirtori et al., 2009; Sabaikai et al., 2014; Zhang et al., 2013; Elmorsi et al., 2010).

In this paper, the Photo-Fenton method was used to degrade GO in wastewater. $FeCl_3$ and H_2O_2 were added into a suspension containing GO. The suspension was irradiated under UV lights at 185 nm wavelength. The degradation intermediates were characterized by EA, FT-IR, LC-MS and UV–vis absorption spectra. Experimental results showed that the Photo-Fenton method would be used to degrade completely graphene oxide to CO_2. Based on elemental analyses and MS data of degradation intermediates, degradation mechanism of GO was suggested.

2. Materials and methods

2.1. Materials

All chemicals except GO were purchased from Sigma-Aldrich. GO was synthesized in our laboratory. Digital light incubator was customized from Jintan Kejie Equipment Company.

2.2. Synthesis of GO

A modified Hummers' method (Hummers and Offeman, 1958) was used to synthesize graphene oxide. Graphite (1 g) was added into a solution of HNO_3 (68 wt%, 30 mL, 0.45 mol) and H_2SO_4 (98 wt %, 60 mL, 1.10 mol) at 0–5 °C. The reactive mixture was stirred for 10 min. Then, $KMnO_4$ (6 g, 38 mmol) was slowly added into the mixture within 2 h at 0–10 °C. The reaction mixture was heated to 50 °C, stirred continuously for 15 h. Distilled water (100 mL) and H_2O_2 (30 wt%, 5 mL, 44 mmol) were added into above reactive mixture. The reactive mixture was filtered to give crude product. The crude product was washed with 5% HCl aqueous solution (5 mL × 3) and distilled water (5 mL × 3) until pH = 7. The product was dried at 60 °C for 2 days, to give GO, a brown solid (1.39 g).

2.3. Degradation of GO by Photo-Fenton

Graphene oxide (0.2 g) in distilled water (200 mL) was ultrasonicated with power 100 W for 1 h to give a suspension. The pH value of suspension was adjusted to pH = 2 by 5% HCl aqueous solution. A solution of $FeCl_3$ (2 mg) in water (2 mL) was added into the suspension containing GO, after 4 mL H_2O_2 was added. At last, the sample was irradiated (λ = 185 nm) with ultraviolet light for 1, 2, 4, 8, 12, 24, 72, 264, 336, 384, 480 and 672 h at 20 °C.

2.4. Elemental analysis

Water was removed from the suspension (10 mL) containing degraded GO to give a solid. The solid was dried at 80 °C and characterized using elemental analysis (Vario EL-III) with CNH mode.

2.5. UV–vis absorption spectrum

The suspension (1 mL) of GO or degradation samples were added into distilled water (100 mL). UV–vis absorption spectra of the GO and the degradation samples were determined using a lambda 25 Perkin-Elmer spectrophotometer. The spectrophotometer worked at a wavelength range from 200 nm to 800 nm.

2.6. FT-IR spectrum

Water was removed from the suspension (10 mL) containing degraded GO to give a solid. The degradation samples were dried at 80 °C. The FT-IR spectra of GO and degradation samples in KBr pellets were recorded using a Bruker Vector 22 Fourier transform infrared spectrometer.

2.7. Liquid chromatography-mass spectrometry

The final degradation products were analyzed by LC-MS (Finnigan LCQ Advantage MAX). A 10 μL solution was injected to a column. Mobile phase was a solution of methanol in water with a flow rate of 0.2 mL/min. Ratio of methanol volume and water volume was 3 versus 7. Samples were analyzed in a $^{+}$PESI-MS mode.

3. Results and discussion

3.1. Degradation process of GO

Similar to literature (Feng et al., 2015), GO was degraded by Fenton without a light to give hazardous products containing

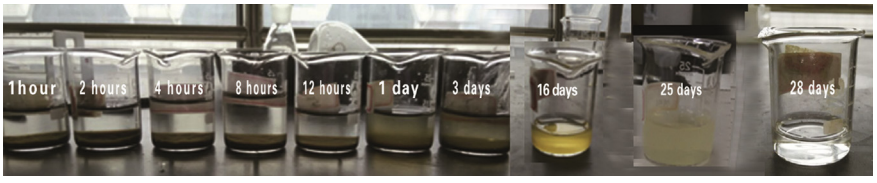


Fig. 1. Degradation process of GO samples.