Journal of the Taiwan Institute of Chemical Engineers 60 (2016) 423–429

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Accelerated decomposition of Oxone using graphene-like carbon nitride with visible light irradiation for enhanced decolorization in water

Kun-Yi Andrew Lin*, Yu-Chien Chen

Department of Environmental Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan, ROC

ARTICLE INFO

Article history:
Received 13 May 2015
Revised 27 October 2015
Accepted 29 October 2015
Available online 30 November 2015

Keywords:
Graphene-like carbon nitride
Oxone
Decolorization
Rhodamine B

ABSTRACT

Degradation of organic pollutants using Oxone decomposition has been investigated to address aqueous pollution. Although metallic catalysts can effectively accelerate the Oxone decomposition, using non-metal catalysts to accelerate the Oxone decomposition attract great attention because it minimizes usage of metals and environmental concerns. In this study, graphene-like carbon nitride (GCN) is proposed as a non-metal catalyst to accelerate the Oxone decomposition. Under visible light irradiation (vis), photocatalytic reaction of GCN can initiate the Oxone decomposition to generate sulfate radicals for decolorization in water. A higher GCN loading appeared to enhance the decolorization but over loading could block the light irradiation. The elevated temperature was preferable to this Oxone-GCN/vis process, whereas the alkaline condition was adverse. Despite a high concentration of NaCl in the solution, the decolorization using Oxone-GCN/vis was not noticeably hindered, while ascorbic acid and ethanol could significantly inhibit the Oxone decomposition. Electron paramagnetic resonance spectroscopic results also validated that the combination of GCN/vis successfully accelerated the Oxone decomposition. A multiple-cycle test of using GCN/vis to facilitate the Oxone decomposition was also demonstrated without regeneration treatments on the spent GCN, showing that GCN/vis can be an effective and recyclable catalytic system to decompose Oxone to decolorize dyes in water.

1. Introduction

Advanced oxidation processes (AOPs) are practical and competitive approaches to address aqueous pollution [1–4]. AOPs in general involve usage of oxidants, such as hydrogen peroxide, persulfate and ozone, to generate highly oxidizing radicals including hydroxyl and sulfate radicals to degrade organic contaminants [5,6]. Recently, the powerful oxidizing reagent, Oxone (*i.e.*, monopersulfate), has been intensively used for oxidation reactions, including degradation of organic pollutants [7,8]. Even though Oxone can self-decompose to generate sulfate radicals (*e.g.*, $SO_4^{-\bullet}$) that exhibit the redox potential of +2.5 to +3.1 V [9], the self-decomposition is extremely slow. Therefore, a number of approaches have been employed to accelerate the Oxone decomposition such as heat-activation [10], UV irradiation [11], sonication [12] and addition of catalysts [7,12–16]. Nevertheless, UV irradiation, heat and sonication require intensive energy input and therefore the activation of oxidants using heterogeneous catalysts has attracted more attention. In particular, metallic catalysts are proven to be effective to accelerate the Oxone decomposition [17]. These metallic catalysts include cobalt oxide [12,17], iron oxide [17–19], and manganese oxide [20,21]. Lately, non-metal catalysts for the Oxone decomposition are also proposed to minimize the usage of metals and subsequent environmental concerns. For example, reduced graphene oxide (rGO) was used to accelerate the Oxone decomposition because rGO contains some oxygen groups on the surface which initiates the Oxone decomposition [22]. GO was even doped with nitrogen and sulfur to enhance the Oxone decomposition [23,24]. Granular activated carbon [25] and carbon nanotubes [26] were also proposed to accelerate the Oxone decomposition in order to degrade organic contaminants. These studies reveal that non-metal catalysts are also effective to accelerate the Oxone decomposition. While the Oxone decomposition catalyzed by some non-metal materials had been demonstrated, species of non-metal materials are still very limited.

Recently, graphene-like carbon nitride (GCN) has been developed and extensively used as a non-metal photocatalyst to degrade organic pollutants [27–29]. Although GCN alone is ineffective to accelerate the Oxone decomposition [24], GCN can be employed as a photo-Fenton-like catalyst to accelerate decomposition of oxidants under light irradiation [30]. GCN with visible light irradiation (GCN/vis) is also expected to be a metal-free technique to accelerate the Oxone decomposition [28,31]. Therefore, in the present study we aim to investigate the capability of GCN/vis to accelerate the Oxone decomposition and underlying mechanism. To evaluate this Oxone-GCN/vis

---

* Corresponding author. Tel.: +886 4 22854709.
E-mail address: linky@nchu.edu.tw (K.-Y.A. Lin).

http://dx.doi.org/10.1016/j.jtice.2015.10.046

process, decolorization of Rhodamine B (RB) dye in water was selected as a model reaction.

GCN was prepared by a heat treatment of melamine and characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometer (XRD), Fourier-Transfer Infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and diffusion reflectance spectroscopy (DRS). Factors affecting this Oxone-GCN/vis process to decolorize RB were examined. Electron paramagnetic resonance (EPR) spectroscopy was employed to provide insight into the mechanism of Oxone-GCN/vis process. Recyclability of GCN for accelerating Oxone decomposition was also evaluated.

2. Experimental

2.1. Synthesis and characterization of graphene-like carbon nitride (GCN)

GCN was prepared according to the reported protocol [32] as follows: 5 g of melamine powder (Sigma-Aldrich, USA) was placed into a ceramic crucible and heated to 550 °C for 4 h with a heating rate of 2 °C min^{-1}. After the heat treatment, white melamine powder was converted to yellow GCN powder.

The as-synthesized GCN was first characterized using a Field Emission SEM (JEOL JSM-6700, Japan) and transmission electronic microscopy (TEM) (JEOL JEM-2010, Japan) to observe its morphology. The crystalline structure of GCN was measured by an X-ray diffractometer (PANalytical, the Netherlands) with copper as an anode material (40 mA, 45 kV). Absorption infrared (IR) spectrum of GCN was determined by a Fourier-Transform Infrared spectrometer (4100, Jasco, Japan) with KBr pellets as sample holders. The chemical composition of GCN was analyzed using a X-ray Photoelectron Spectroscopy (XPS) (PHI 5000 Versa Probe/Scanning ESCA Microprobe, ULVAC-PHI, Inc., Japan) with a monochromatized Mg Kα (1253.6 eV) X-ray source. The optical property of GCN was determined using a UV–vis spectrophotometer equipped with integrating spheres (V650 Jasco, Japan) to collect diffuse reflectance spectrum.

2.2. Decolorization using Oxone-GCN/vis process

The RB decolorization using Oxone-GCN/vis process was conducted by batch-type experiments. First, a certain amount of Oxone powder (*e.g.*, 60 mg) (Sigma-Aldrich, USA) was added a batch reactor containing 200 ml of RB solution with an initial concentration (C_0) of 10 mg L^{-1}. The batch reactor was irradiated by visible light lamp (150 W Philips, Netherland) and equipped with a water-circulation system to maintain temperature of reaction solutions. Upon the dissolution of Oxone, a given amount of GCN (*e.g.*, 100 mg L^{-1}) was immediately added to the RB solution. Sample aliquots were withdrawn from the batch reactor at pre-set times, and the remaining RB concentration was determined using a UV–vis spectrophotometer (e-ChomTech CT-2000, Taiwan). The detailed procedures for investigating other effects and subsequent analyses can be found in the supporting information (Text S1).

3. Results and discussion

3.1. Characterization of GCN

Morphology of the as-prepared GCN can be seen in Fig. 1(a) and (b). In the SEM image (Fig. 1(a)), the sheet-like morphology can be still clearly identified. Some of GCN sheets even curled to exhibit a roll-like shape. Single-sheet morphology of GCN can be better revealed in the TEM image (Fig. 1(b)), confirming graphene-like morphology. Fig. 1(c) shows an XRD pattern of GCN, in which two significant peaks are observed. The peaks at 13.1° and 27.4° can be indexed to the (100) and (200) planes of hexagonal GCN, respectively (JCPDS card #87-1526). The FT-IR spectrum of GCN is revealed in Fig. 1(d), in which several peaks occur in 800–1700 cm^{-1}, derived from the chemical bonding between carbon and nitrogen. The peak at 808 cm^{-1} can be assigned to the characteristic breathing mode of the triazine units [33]. The peaks at 1238, 1412 and 1563 cm^{-1} can be attributed to the stretching modes of C–N heterocyclics [34]. The peak at 1336 cm^{-1} corresponds to the C-N bonding, while the peak at 1634 cm^{-1} results from the C = N stretching mode [29]. The chemical composition and valence states of various species of GCN can be further determined using XPS as shown in Fig. 2. The full scan spectrum (Fig. 2(a)) indicates that GCN consists of carbon, nitrogen and oxygen as three noticeable peaks are observed at 288 eV (C 1s), 399 eV (N 1s), and 531 eV (O 1s), respectively [35]. In the C 1s core level spectrum (Fig. 2(b)), two distinct peaks are also detected at 284.6 and 288.0 eV, corresponding to the C–C bond and the sp^2-bonded carbon in N–C=N, respectively. On the other hand, the peak located at around 399 eV can be deconvoluted into three peaks at 398.3, 399.1 and 400.3 eV (Fig. 2(c)). The peak at 398.3 eV is attributed to the sp^2-hybridized aromatic N bonded to carbon (*i.e.*, C=N−C), whereas the peak at 399.1 eV is derived from the tertiary N bonded to carbon (*i.e.*, $\text{N}-(\text{C})_3$ or $\text{H}-\text{N}-(\text{C})_2$). The shorter peak at 400.3 eV corresponds to N−H side groups [35]. The optical property of the as-synthesized GCN was determined by diffusion reflectance spectroscopic (DRS) analysis. As shown in Fig. 3, GCN exhibits an onset of adsorption at 460 nm as reported in other literatures [36].

3.2. Decolorization using the Oxone-GCN/vis process

Prior to investigating the RB dcolorization using Oxone-GCN/vis process, RB adsorption to GCN was evaluated and shown in Fig. 4(a). Nevertheless, the adsorption of RB to GCN was negligible, indicating that GCN did not possess strong affinity towards RB. We also examined the RB decolorization by Oxone alone to be a reference considering that Oxone can self-decompose. The decolorization by Oxone alone reached $C_t / C_0 = 0.25$, revealing that the self-decomposition of Oxone, even though capable, was extremely slow. When 500 mg L^{-1} of GCN was added to the RB solution with Oxone, the decolorization kinetics rapidly increased as seen in Fig. 4(a), indicating that the combination of Oxone, GCN and visible light can effectively decolorize. An analysis of total organic carbon (TOC) of the RB decolorization (Fig. S1, see ESI†) also validates that RB was gradually degraded and mineralized by Oxone-GCN/vis process.

To quantitatively evaluate the effectiveness of GCN, the decolorization kinetics was analyzed using the pseudo first order equation as follows (Eq. (1)):

$$C_t = C_0 \exp(-k_1 t) \tag{1}$$

where k_1 represents the first order rate constant of RB decolorization. The rate constants of Oxone alone and Oxone-GCN/vis processes are listed in Table 1. With GCN, the k_1 can increase from 0.0088 (*i.e.*, Oxone alone) to 0.0440 min^{-1}, a 5-fold increase, validating that the Oxone decomposition was significantly accelerated by GCN in the presence of visible light irradiation. When GCN was irradiated by visible light, several active species may occur such as photo-generated electrons (e^-) and photo-generated holes (h^+) as follows [28] (Eq. (2)):

$$\text{GCN} + h\nu \rightarrow e^- + h^+ \tag{2}$$

The photo-generated electron (e^-) and hole (h^+) can also react with Oxone to generate sulfate radicals as follows (Eqs. (3)–(5)) [37]:

$$\text{HSO}_5^- + e^- \rightarrow \text{SO}_4^{-\bullet} + \text{HO}^- \tag{3}$$

$$\text{HSO}_5^- + h^+ \rightarrow \text{SO}_5^{-\bullet} + \text{H}^+ \tag{4}$$