



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Enhanced photocatalytic degradation of atenolol using graphene TiO₂ composite

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ARTICLE INFO

Article history:

Received 23 December 2015

Received in revised form 13 July 2016

Accepted 28 August 2016

Available online 29 August 2016

Keywords:

Photocatalysis

Graphene

Hydrothermal method

Atenolol

Pharmaceuticals

ABSTRACT

Graphene oxide-TiO₂ (TiO₂-G) composite synthesized by a facile route is able to exhibit significantly higher photocatalytic activity under visible light irradiation. The prepared composite was characterized by means of powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS), UV–vis diffuse reflectance spectroscopy (DRS), and Brunauer Emmett Teller (BET). The photocatalytic activity was evaluated by photo-degradation of the Atenolol (ATL) as model pharmaceutical pollutant under UV–vis light and “simulated Sun” irradiation conditions. The results showed that TiO₂-G exhibited much higher photocatalytic performance than that of bare TiO₂. The enhanced activity can be ascribed to the incorporation of graphene. The effect of various factors such as variation of pH, catalyst concentration, initial substrate concentration, light intensity, and source of light as well as reaction kinetics were investigated. The results showed that 72% degradation of ATL (25 ppm) can be achieved with 1.5 g/L TiO₂-G in 1 h under solar irradiation. Complete TOC removal for atenolol degradation was obtained in 7 h. The work is expected to shed new light on the development of graphene composite nanostructures for gathering visible light energy and on the improvement of new photocatalytic materials for the exclusion of environmental pollutants.

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1. Introduction

In the early 1980s the active pharmaceutical ingredients (APIs) are identified in the water stream [1]. An emerging environmental issue includes the presence of pharmaceutical compounds in surface water and offers a challenge to water treatment systems [2]. Pharmaceuticals are basically designed so that they can physiologically effect humans and animals even at low concentrations. These compounds remain in the environment for a long time and are not degraded biologically or by natural reduction [3]. The APIs consumed by the patients are excreted either as metabolites or as the unchanged main compounds. Beta blockers are involved in treatment of various of cardiovascular diseases such as hypertension, artery disease etc., by blocking the action of hormones such as epinephrine and norepinephrine in the body [4]. Due to its limited human metabolism and extensive usage, ATL was widely detected in sewage effluents and surface water, usually with a concentration ranging from ng/L to μm/L

[5,6]. The studies also concluded that 2.2–50.8 g/d is the daily output loads of the ATL compound in the treated wastewater.

For the treatment of these pharmaceutical compounds, Conventional wastewater treatment methods such as use of activated sludge [7] is not effective. Furthermore, many studies have reported that the growth of human embryonic cells could be inhibited by ATL and was also found to be ecotoxic to freshwater species [8]. It has also been found that ATL possesses phytotoxic activity during its chlorination after the process of wastewater disinfection [9]. Therefore, it is need of an hour to develop the advanced treatment technologies for ensuring complete removal of ATL from wastewater before release into water stream. Recently, it has been reported in several studies that advanced oxidation processes (AOPs) are used for the degradation of beta-blockers [10–14]. Oxidation of organic and inorganic species can achieved by heterogeneous photocatalysis [15,16].

Composites consisting of carbonaceous materials have been studied, in order to further improve the photocatalytic efficiency. In particular, to take advantage of graphene's superior properties, many efforts have been devoted through coupling it with semiconductors. Graphene has a two-dimensional sp² hybridized carbon network [17,18]. Its unique properties include large specific surface area (2600 m²/g), high thermal conductivity (3000 W/m/K), and high

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intrinsic electron mobility ($15,000 \text{ m}^2/\text{V/s}$) [20]. Therefore, to form a hybrid structure with different nanomaterials for photocatalytic applications it is highly advantageous and desirable to explore its potential. Several graphene-semiconductor composites have been reported in literature using either growing on surfactants or by physical mixing of pre-synthesized nanoparticles and graphene [19–22]. Recently, it has been studied that methylene blue in an aqueous solution has been degraded by photocatalysis using TiO_2 -graphene based photocatalyst [19].

As a novel material, many extraordinary properties has been observed for graphene, such as it is chemically stable, having high specific surface area ($\sim 2600 \text{ m}^2/\text{g}$), tremendous motion of charge carriers ($20,000 \text{ cm}^2/\text{V/s}$) and worthy optical transparency [23–25]. On the basis of above described properties, the graphene can leads to charge separation and function when used as an electron carrier in composite materials, thus composites of graphene and TiO_2 have shown enhancement of photocatalytic activity in different studies [26–28].

Several reports are published for the photocatalytic degradation of organic molecules by enhancements in photocatalytic activity of TiO_2 nanoparticle-reduced graphene composites. Zhang et al. and co-workers [29–31] have reported increased photocatalytic degradation of methylene blue by preparing a Graphene- TiO_2 nanoparticle composite. Xiaoyan et al. [32] studied the production of H_2 by splitting of water using TiO_2 nanoparticles on graphene and observed enhanced photocatalytic activity than that of only TiO_2 .

The present work includes the degradation of atenolol via synthesized Graphene Oxide- TiO_2 (GO-TiO_2) and Degussa TiO_2 photocatalyst and different parameters has been studied, including catalyst loading, initial substrate concentration, variation of light intensity, pH of the solution, and introduction of UV filter in solar simulator on the atenolol degradation. The new features of this study include the interpretation of the kinetics of the atenolol removal with GO-TiO_2 and Degussa TiO_2 during photocatalysis. Adding to this, to the authors' knowledge, this is the first study that comprises a well-organized exploration of the various parameters that can affect the oxidation process of the model compound including the catalyst concentration, initial substrate concentration, variation of light intensity and pH using GO-TiO_2 and its comparison with commercial available Degussa TiO_2 .

2. Experimental section

2.1. Materials

Atenolol (its chemical structure is shown in Fig. 1) was procured from Sigma-Aldrich and was used as such without further purification. Solutions of the ATL was prepared in deionized water at concentrations up to 25 mg/L and stirred for one 1 h to ensure complete mixing. Such concentrations, more than those usually found in water, were taken so as to (a) assess the efficiency of process within a measurable time period, and (b) accurately determining the remaining concentration of ATL with the analytical techniques employed in this work. Commercially available TiO_2 was employed by Aeroxide P25.

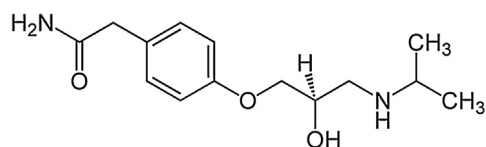


Fig. 1. Structure of Atenolol.

2.2. Synthesis of graphene – TiO_2 composite

To obtain graphite oxide (GO) from graphite powder, modified Hummers method was applied as described previously [33]. To obtain graphene- TiO_2 composite, 2 mg of GO was poured to a solution of water and ethanol (2:1) followed by ultrasonic treatment of 1 h. Then weighed amount of TiO_2 (200 mg) was added and further stirring was done for 2 h. The mixture was then transferred to a Teflon-lined autoclave, for the hydrothermal treatment process for 3 h at 120°C . During this process, GO could be reduced to graphene and simultaneously the deposition of TiO_2 achieved. The obtained composites were centrifuged, rinsed with deionized water, and vacuum-dried at 60°C . The prepared samples are denoted as GO-TiO_2 .

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku-Ultima IV Advance X-ray diffraction meter using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15 \text{ \AA}$). The microstructures of the samples were analyzed by a Hitachi S-4500 scanning electron microscope (SEM) and transmission electron microscopy (TEM; JEOL 2010F). UV-vis diffuse reflectance spectra (DRS) were measured using a UV-vis spectrophotometer (UV-3600, Shimadzu). Raman spectroscopy was performed on a Renishaw Raman spectrometer Model 2000 using a 632.8 nm laser at 100% power. The X-ray photoelectron spectroscopic (XPS) analyses was done with a Kratos Axis Ultra spectrometer with a monochromatic $\text{Al K}\alpha$ source (15 mA , 14 kV).

2.4. Photocatalytic measurement

Experiments of Photocatalysis were carried out as follows: Appropriate amount of photocatalyst in the range $0.5\text{--}2.0 \text{ g/L}$ was added to 150 mL of an aqueous solution and was allowed to mix and poured into the reactor. Further, continuous mixing was done with magnetic stirrer at 800 rpm for 45 min in the dark to ensure complete adsorption of the ATL molecule on the surface of catalyst. Simulated Air Mass (AM) 1.5 solar light was produced by means of a solar simulator (model SS1KW, Sciencetech, Ontario, Canada, with a 1000 W Xe arc lamp and an AM 1.5G filter). During the photocatalytic experiments, the reaction mixture was continuously aerated. Samples were withdrawn after fixed interval of time and filtered through a $0.45 \text{ }\mu\text{m}$ filter to separate catalyst particles. pH of the ATL solution were varied from 4, 6, 8 and 9.

2.5. Analytical technique

The absorbance of the sample was measured with a UV-vis spectrophotometer. Absorbance was measured at 224 nm for photocatalytic experiments, as this wavelength agrees to the characteristic peak of the ATL in the UV spectrum. The straight line curve has been obtained between absorbance and concentration with ATL concentration ranging from 5 to 25 mg/L .

3. Results and discussion

3.1. Characterization of graphene oxide – TiO_2 composite

The characterization of synthesized catalyst includes XRD, SEM, TEM, XPS and UV-DRS, which has been described and explained in details elsewhere [33]. The BET specific surface area ($54\text{--}70 \text{ m}^2/\text{g}$) and pore volume ($0.25\text{--}0.38 \text{ mL/g}$) of the Graphene- TiO_2 composite were controlled by graphene compared with those of TiO_2 . The pore diameter ($\sim 3 \text{ nm}$) was quite uniform. The BET surface area of the Graphene- TiO_2 composite increased from 54 to $73 \text{ m}^2/\text{g}$ with increasing graphene content. This result can be ascribed to the

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