



Photoreactivity of hydroxylated multi-walled carbon nanotubes and its effects on the photodegradation of atenolol in water



Ya Zhang^a, Lei Zhou^a, Chao Zeng^a, Qi Wang^a, Zunyao Wang^a, Shixiang Gao^a, Yuefei Ji^{a,b}, Xi Yang^{a,*}

^a State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, PR China

^b Université Lyon 1, UMR CNRS 5256, Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), 2 Avenue Albert Einstein, F-69626 Villeurbanne, France

HIGHLIGHTS

- MWNT-OH produced ¹O₂ and ·OH upon simulated solar irradiation.
- MWNT-OH promoted photodegradation of atenolol.
- MWNT-OH-induced degradation of atenolol was influenced by natural water components.
- Degradation pathways of atenolol were hydroxylation and chain cleavage oxidation.

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ABSTRACT

In spite of the increasing concerns about the fate of pharmaceuticals and personal care products (PPCPs) and the nanomaterial pollution in aquatic ecosystem, the effects of carbon nanotubes on the photochemical transformation of PPCPs are less considered. In this study, the photochemical production of reactive oxygen species (ROS) were examined in colloidal dispersions of hydroxylated multi-walled carbon nanotubes (MWNT-OH) under simulated solar irradiation using a Xenon lamp. Two kinds of ROS, ¹O₂ and ·OH, were confirmed by their molecular probes, furfuryl alcohol (FFA) and *p*-chlorobenzoic acid (PCBA). The steady-state concentrations of ¹O₂ and ·OH were calculated as 1.30×10^{-14} M and 5.02×10^{-16} M, respectively. The effects of MWNT-OH on photodegradation of atenolol (ATL) were investigated in the presence of natural water components, i.e., dissolved organic matters (DOMs), nitrate (NO₃⁻) and ferric ions (Fe³⁺). Photoproducts of atenolol were identified by solid phase extraction-liquid chromatography-mass spectrometry (SPE-LC-MS) analysis techniques. Three potential photochemical pathways of atenolol, including the hydroxylation on aromatic ring, the loss of amide group and the cleavage of ether oxygen bond as well as di-polymerization of reaction intermediates were tentatively proposed. Using the radical quenching method, reaction with ·OH was determined as the major photolysis pathway of atenolol in irradiated MWNT-OH suspensions. These findings of the production of ROS and their effects on the photodegradation of organic contaminants provided useful information for assessing environmental risk of MWNT-OH.

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1. Introduction

Due to their unique electronic, thermal, optical and mechanical properties, carbon nanotubes (CNTs) have been used in a wide range of applications in the past 20 years (Köhler et al., 2008). While CNTs can aggregate and hardly disperse equably in water due to their extremely hydrophobic nature (Dujardin et al., 1998), it has been functionalized with different moieties to obtain a high solubility and to avoid aggregation in water in the past decade. Hydroxylated multi-walled carbon nanotubes (MWNT-OH) is one kind of functionalized CNTs. Because the functionalization

processes of MWNT-OH result in sp³ hybridization of C–C bonds, “structural defects” occur on the grapheme surface with altered electronic properties (Zhao et al., 2004; Curran et al., 2005; Bradley et al., 2012). Such structural defects enhance the reactivity of MWNT-OH during the natural environmental processes.

The impacts of CNTs become a major issue of environmental concern recently due to their extensive application and huge production (Lam et al., 2006; Helland et al., 2007; Nowack and Bucheli, 2007). For example, an increasing number of studies have reported the cytotoxicity and acute toxicity of CNTs (Jia et al., 2005; Pulskamp et al., 2007; Hussain et al., 2009). Although the adsorption of organic chemicals by CNTs in waters have been frequently studied (Yang et al., 2006, 2008; Chen et al., 2007, 2008a,b), the environmental impacts of water-dispersible CNTs are still largely

* Corresponding author. Tel./fax: +86 (0)2589680357.

E-mail address: yangxi@nju.edu.cn (X. Yang).

unknown. The production of reactive oxygen species (ROS) of aqueous C₆₀ nanoparticles in sunlight (Hou and Jafvert, 2009a,b) has been observed for some CNTs. Carboxylated single-walled carbon nanotubes (SWNT-COOH) under sunlight has been known to produce ROS in water (Chen and Jafvert, 2010). Previous studies have revealed that C₆₀ and CNTs could destruct 2-chlorophenol under ultraviolet irradiation (Chae et al., 2012). Based on these observations, clarifying the photochemical behaviors of MWNT-OH in water is of great importance for understanding its environmental impacts and ecology risk assessment.

In order to test the possible effects of MWNT-OH on the transformation of organic pollutants upon irradiation, atenolol (ATL), an emerging environmental pollutant, was chosen as a model compound in the current investigation because of its wide occurrence, relative recalcitrant and resistant to direct photolysis (Routledge and Sumpter, 1996; Anette et al., 2010; Chen et al., 2012). Previous reports have demonstrated that atenolol is resistant to direct photolysis, but it can be eliminated through aquatic photodegradation by dissolved organic matters (DOMs) and nitrate (Ji et al., 2012; Zeng et al., 2012). Natural aqueous compositions, e.g., DOMs, NO₃⁻ and Fe³⁺, can influence the photochemical fate of organic pollutants in water significantly through energy transfer, charge transfer or oxidation with photo-generated ROS (Zepp et al., 1987; Zuo and Jones, 1997; Halle and Richard, 2006; Zuo et al., 2006; Jacobs et al., 2011; Xu et al., 2011). Therefore, the study on photodegradation of atenolol in MWNT-OH solutions in the presence of natural aqueous compositions is of great interest.

In this study, we measured the production of singlet oxygen (¹O₂) and hydroxyl radicals (·OH) in the MWNT-OH solutions and investigated the effects of MWNT-OH on atenolol photolysis in the presence of DOMs, NO₃⁻ and Fe³⁺ under the irradiation of a xenon lamp as a simulated sunlight source. The photolysis kinetics, photoproducts, and possible photodegradation pathways of atenolol in MWNT-OH solutions with DOMs, NO₃⁻ and Fe³⁺ were reported.

2. Materials and methods

2.1. Chemicals and reagents

Hydroxylated multi-walled carbon nanotubes were purchased from Nanotech Port Co. (Shenzhen, Guangdong Province, China). The parameters of MWNT-OH are 20–40 nm in diameter, <5 μm in length, <3% in ash, 97% in purity and 30–50 m² g⁻¹ in special surface area. Atenolol (+98%) and *p*-chlorobenzoic acid (PCBA, 99%) were purchased from Tokyo Chemical Industry. Furfuryl alcohol (FFA, 99%) was purchased from Sigma–Aldrich (St. Louis, Missouri). Suwannee River Fulvic Acid (SRFA), Suwannee River Humic Acid (SRHA), Nordic Lake Fulvic Acid (NOFA) and Nordic Lake Humic Acid (NOHA) were obtained from International Humic Substance Society (IHSS). HPLC grade methanol, acetic acid and isopropanol were supplied from Tedia Company (Fairfield, USA). Deionized (DI) water was prepared by a Millipore Milli-Q System. Except for MWNT-OH, all the reagents were dissolved directly in DI water without further purification. Stock solutions were stored in a refrigerator under 4 °C and used within one month.

2.2. Preparation and characterization of MWNT-OH samples

Aqueous suspensions of the MWNT-OH were prepared in DI water via intermittent and ice-bath sonication (60–80 W, 5 s on and 3 s off, JY88-II Ultrasonic cell disruptor, Nanjing Emmanuel Instrument Equipment Co., China) until the absorbance at 400 nm reached 1.9. The suspensions were stable with no phase separation for 100 days, and their absorbance remained no change

within two weeks. The MWNT-OH samples were diluted with DI water directly.

2.3. Irradiation experiments

Steady irradiation experiments were performed by a XPA-II photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China) equipped with a 1000 W xenon arc lamp (Beijing Electric Light Source Institute, China) placed in a quartz cooling well as the simulated solar irradiation source. Irradiance at the surface of cuvettes was monitored by an UV radiometer (Beijing Normal University Photoelectrical Company, China). Pyrex colorimetric tubes ($\lambda < 290$ nm radiopacity) containing 50 mL reaction solutions were placed in a merry-go-round unit at a fixed distance around the lamp. Aliquots (1 mL) were sampled at selected time intervals. Each photolysis experiment was carried out in triplicate.

2.4. Analytical methods

The concentrations of ATL, FFA and PCBA were determined by high performance liquid chromatography (HPLC, Agilent 1100, USA). The HPLC analytical methods of the three compounds are listed in Table S1 (Supplementary material). The concentrations of MWNT-OH and DOMs were measured by a TOC 5000A analyzer (Shimadzu, Japan) in terms of total organic carbon (TOC, mgC L⁻¹). The absorption spectrums of ATL, PCBA, FFA, DOMs and NO₃⁻ solutions were scanned by a UV–vis spectrometer (UV2450, Shimadzu, Japan).

The photoproducts of atenolol were concentrated by solid phase extraction (SPE) method equipped with Oasis HLB prepackaged cartridges (200 mg/6 mL, Waters). The HLB cartridges were activated by 6 mL methanol and 6 mL DI water in sequence. Irradiated solutions (100 mL) were percolated through the HLB cartridges at 0.5 mL min⁻¹. After washed with 4 mL DI water, the photoproducts in the cartridges were eluted with 2 × 1 mL methanol.

Photoproducts of atenolol were identified by the Thermo Finnigan Surveyor Modular HPLC system with a Finnigan LCQ Advantage MAX ion trap mass spectrometer (LC–MS). In this system, LC separation was achieved by employing an Agilent SB-C18 column (5 μm, 150 mm × 4.6 mm). The mobile phase was consisted of 10 mM ammonium acetate solution (A) and methanol (B). At a flow rate of 0.2 mL min⁻¹, the ratio of mobile phase was changing with linear gradient from 5% B to 95% B in 25 min. An electrospray interface (ESI) was used for the MS and MS² measurement in positive ionization mode and full scan acquisition between *m/z* 100–600. The injection volume, spray voltage and ion-transfer capillary temperature were 10 μL, 4.5 kV and 200 °C, respectively. Nitrogen was used as nebulizer and sheath gas at a flow rate of 35 arbitrary unit and argon was used as a collision gas at 0.25 MPa.

3. Results and discussion

3.1. ROS production of MWNT-OH under irradiation

In the present study, molecular probes were used to identify the production of different ROS species and measure their steady-state concentrations, which have been proved to be reliable and useful in environmental photochemistry studies (Haag et al., 1984; Haag and Hoigne, 1986). To monitor ¹O₂, furfuryl alcohol (FFA) was added into the reaction solution. The production and steady-state concentration of ¹O₂ were determined by the loss of FFA, that reacts with ¹O₂ at a second order reaction rate constant of $k_{1O_2, FFA} = 1.20 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, using the following equations (Haag et al., 1984; Haag and Hoigne, 1986).



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