



Effective degradation of refractory nitrobenzene in water by the natural 4-hydroxycoumarin under solar illumination

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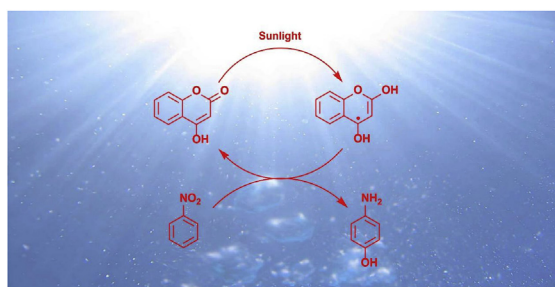
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HIGHLIGHTS

- A new natural organic matter could be activated as reducing agent under illumination.
- 4-hydroxycoumarin as natural compound was found to be an efficient photosensitizer.
- The refractory nitrobenzene was degraded to 4-aminophenol by 4HC as green process.
- 4HC excited state (4H-chromene-2,4-diol radical) as key intermediate was confirmed.
- Reaction pathway between 4HC and NB was completely proposed by product analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, nitrobenzene (NB) as typical refractory organic pollutants was effectively degraded by a new green approach, which was achieved by the chemical effect of natural organic matters (NOMs) under solar illumination as a potential natural degradation process. 4-hydroxycoumarin (4HC), which is natural compound and can be extracted from many plants, was found as an efficient photosensitizer to promote the photoreduction of NB to 4-aminophenol under the solar illumination. The reaction products were definitely identified by LC-MS/MS and ¹H NMR. The response spectrum of 4HC excited state (4H-chromene-2,4-diol radical, S₁) as key intermediate was also obtained by transient absorption spectroscopy (TAS) measurements, which showed that the decay time of S₁ was around 250 ps. Then, the measurements of electron paramagnetic resonance (EPR) confirmed the existence of •OH. As a result, the reaction mechanism between 4HC and NB was proposed. In addition, the influence parameters such as light sources, gas surroundings, solvents, pH values were investigated to further reveal the reaction process.

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1. Introduction

Nitrobenzene (NB) is an important liquid aromatic compound to produce dyes, spices, explosives in organic synthesis industries

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(Andrade and Mascaro, 2018; Zhao et al., 2017a; ElShafei et al., 2015). However, it is highly toxic as potential human carcinogen and readily absorbed through the skin, thus classified as environmental priority pollutant (Gong et al., 2018a; Yang et al., 2018a). About 19 million pounds of NB is released into the environment annually because of its usage, leakage or industrial accidents (Haigler and Spain, 1991). Due to its recalcitrant and hydrophobic nature, NB is dissolved in surface waters with microsolubility or accumulates in the sediment of a water body, posing a concern for ecosystem health. Therefore, it is essential to eliminate NB in contaminated water. In fact, there have been a number of researches on the artificial degradation methods of NB, including physical (Xie et al., 2014; Rajagopal and Kapoor, 2001; Fan et al., 2018), chemical (Vione et al., 2016; Bhatkhande et al., 2003) and biological (Liu et al., 2014) technology; but these technologies entail relatively high cost. However, few researches have investigated the degradation method of aqueous NB under the conditions of natural illumination.

The utilization of natural organic compounds (NOMs) as green and environment-friendly chemicals has become an important field of sustainable chemistry. Among them, coumarin derivatives are useful for assembling enzyme substrates (Lavis and Raines, 2008) and widely used to synthesize laser dyes (Trozzolo et al., 1974) and pharmaceuticals (e.g., analgesia properties, anti-inflammatory and anti-coagulant agents) (Jiang et al., 2017; Wei et al., 2011; Zhao et al., 2018a; Eskandarloo et al., 2018; Palmas et al., 2012), which can be extracted from many plants, notably with high concentration in the tonka bean, *atrichum undulatum*, *polytrichum formosum*, *citrus limonia*, *pelargonium sidoides*, *viola prionantha* (EstevezBraun and Gonzalez, 1997). In addition, coumarin derivatives are also a kind of UV absorbing compounds which can present fast, photoinduced cyclobutane ring formation and cleavage reactions (Jiang et al., 2017). Among them, 4-hydroxycoumarin (4-HC) is an important substance with significant biological activity in nature and in medicine, which also possesses photoactivity (Stanchev et al., 2008). The photochemistry behind these reactions provides the valuable routes for the synthesis of biomedical and photoresponsive reagent in the utilization of coumarins as NOMs (Lavis and Raines, 2008; Jiang et al., 2017; Wei et al., 2011; Zhao et al., 2018a; Eskandarloo et al., 2018; Palmas et al., 2012). However, to our knowledge, coumarin derivatives are not used to explore the photoinduced degradation process of aqueous organic pollutants as new green environment technology.

In fact, the study on photochemistry processes of coumarins in various environments is insufficient, which generally focused on their spectral properties and photoexcitation mechanism (EstevezBraun and Gonzalez, 1997). In organic solvent systems, the photoexcitation pathway of some coumarin derivatives under illumination is deduced mainly with transient characterization techniques and theoretical calculations (D'Auria and Racioppi, 2004; da Silva et al., 2017; de Melo and Fernandes, 2001). For example, under light illumination, coumarins would firstly turn into their excited states, which can be traced by the measurement of transient absorption spectroscopy (TAS) (Murdock et al., 2016). A study on excited state of hydroxycoumarin indicated that the likely protonation site of 4-hydroxycoumarin (4HC) in its excited states is the carbonyl oxygen (de Melo and Fernandes, 2001). In addition, combining quantum chemical calculations, some studies on photochemistry mechanism show that excited coumarin molecules decay in two pathways: 1) a ring-opening approach initiated by excited state; 2) transition into dark state along the carbonyl stretching mode (Murdock et al., 2016; Krauter et al., 2013). However, as for the aqueous system, there is not a report to exhaustively reveal the reaction process of coumarins under solar illumination, especially for these reactions between coumarins and other

compounds.

In this work, a new sustainable method under natural illumination is presented to degrade the refractory NB into 4-aminophenol, which is easily biodegradable (O'Connor and Young, 1996). 4HC as the readily available NOM was selected as photosensitizer to conduct NB degradation. Additionally, it was elucidated for the degradation pathway of NB to 4-aminophenol by the analysis of HPLC, LC-MS/MS, and ^1H NMR. The TAS measurements were conducted to justify the formation of the organic free radicals (4H-chromene-2,4-diol radical, S_1) as the key intermediate of 4HC photolysis. And electron paramagnetic resonance (EPR) confirmed the existence of $\cdot\text{OH}$. Subsequently, comparative experiments under various gas surroundings, solvent systems, and different pH values were investigated to explore the effects of different parameters on NB degradation efficiency.

2. Experimental methods

2.1. Materials and reagents

4-hydroxycoumarin (4HC) (98%), isopropanol (99.5%), ethyl acetate (99.5%), 4-aminophenol (99%) and salicylic acid (99%) were provided by J&K Scientific. Nitrobenzene (NB) (99%), petroleum ether (AR, boiling range 30–60 °C), p-nitrophenol (98%), and sodium sulfate anhydrous (99%) were purchased from Aladdin. NaOH (98.0%) and HCl (36–38%) were obtained from Tianjin Guangfu Technology Development Co., Ltd. and Dongguan Dongjiang Chemical Reagent Co., Ltd., respectively. Sigma-Aldrich provided 5,5-dimethyl-1-pyrroline N-oxide (DMPO) for ESR-spectroscopy, dimethyl sulfoxide- d_6 (DMSO, 99.9 atom % D, containing 0.03% (v/v) TMS), ethyl alcohol (HPLC grade) and methanol (HPLC grade). Argon gas (Ar) of high purity ($\geq 99.99\%$) was utilized. Hydrogen gas (H_2) used in experiments was mixture gas (95% Ar+5% H_2). All gases used in the experiment were provided by Shenzhen Huatepeng Special Gas Co., Ltd. All solutions were prepared with ultrapure water.

2.2. Experimental procedure

2.2.1. Photodegradation of NB

An aqueous solution (30 mL) containing 4HC (160 μM , unless otherwise mention) and NB (80 μM) was added into quartz reaction tube (Diameter 22 mm \times Length 180 mm). All solution used in the experiments were sealed after deoxygenation with argon unless otherwise specified. The photoreduction experiments were conducted in CEL-LAB500 photocatalytic reaction system (Beijing China Education Au-light Co., Ltd). 500 W mercury lamp and 500 W xenon lamp (Beijing China Education Au-light Co., Ltd) were used to provide UV and simulate solar irradiation, respectively. The lamp was positioned at cylindrical quartz cold trap. The distance between the quartz reaction tube and the light source was 130 mm. A magnetic stir bar was placed in each tube to provide constant stirring. The temperature of the reaction maintained at 25 °C in water bath. Samples were taken at the interval of 0.5 h (within 1 h) and 1 h (after 1 h) to analyze the degradation efficiency of NB. Dark control experiments were carried out by wrapping the tubes with aluminum foil. Each experiment was repeated at least three times.

Similar experiments were conducted directly in the daylight solar irradiation. Samples were exposed to the sunlight from 10 a.m. to 4 p.m., May 11, 2018 to May 12, 2018, at the roof of the Chemistry and Environmental Engineering building of Shenzhen University (Shenzhen, Guangdong province, 113°56'E, 22°32' N, altitude: 15 m). Samples were kept in the dark prior exposed to the sunlight. The information of the photon intensity, humidity, and temperature at the experimental site were recorded with a CEL-

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