Photodegradation of nonylphenol by simulated sunlight

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ABSTRACT

The photodegradation of nonylphenol (NP) was studied to simulate its photolysis process in natural seawater. The effects of the initial NP concentration, the light intensity, the temperature, the initial pH, the dissolved oxygen content and the presence of common water constituents (i.e., Fe(III), NO_3^- and HCO_3^-) on the photodegradation of NP in pure water have been assessed. The degradation rate increased in the presence of Fe(III), NO_3^- or HCO_3^-, and the photolysis rate of 4-NP was more rapid in alkaline solution than in an acidic medium. The DO content is a key factor in the photodegradation, and the rate of the photoreaction depended on the O_2 concentration. The degradation rate was slower in natural seawater than in pure water. 4-Nonylcatechol was identified as the intermediate of photodegradation of nonylphenol in natural seawater. The proposed pathway involved a reaction between irradiated NP and the reactive oxygen species that existed in the seawater.

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1. Introduction

The most common aquatic pollutant, nonylphenol (NP), has been used as an intermediate material to synthesize a nonionic surfactant (nonylphenol ethoxylates, NPEOs) that can be widely used in household products and in agricultural and industrial applications (Nice et al., 2000). More than 60% of the total NPEOs produced in the world go into the aquatic environment, and NPEOs in the environment generate NP, which has greater toxicity, greater stability and a stronger biologically cumulative effect than the parent compound (Ying et al., 2002). The estrogenic character of NP in organisms has caused public concern. The primary route of exposure to NP for human and wildlife is through water (Ying et al., 2002). Research on the degradation of NP, which strongly influences the behavior and fate of NP in aquatic environment, is necessary.

Photodegradation is an important abiotic process for the elimination of NP in water. Recent studies have focused on the degradation of NP with photocatalysts such as TiO_2 (Tanizak et al., 2002) and $BiVO_4$ (Kohtani et al., 2003). Related research on the environmental transformations of NP is sparse. Ahel et al. (1994) studied the photodegradation of NP in filtered lake water by sunlight; however, they did not systematically study the influence of different environmental factors on the NP photolysis. Neamtu and Frimmel (2006) investigated the photolysis of NP using a solar simulator in aqueous solution and determined the intermediates using HPLC; however, the existence of methanol, which was used to dissolve NP, may influence the photodegradation process. Consequently, these studies were limited in their ability to help us understand the environmental fate of NP, and no mechanism study has been reported.

In this study, we are particularly interested in simulating the NP photolysis process in natural seawater (NSW) by sunlight. To elucidate the respective role of these environmental factors, the effects of the photodegradation conditions (i.e., the initial NP concentration, the light intensity, the temperature, the dissolved oxygen concentration and the pH) and those of common water constituents (i.e., nitrate, bicarbonate and iron) on the photodegradation of NP were assessed in pure water (PW). The intermediate product was identified using GC–MS, and a degradation mechanism is proposed. The experimental range of the factors was selected based on their occurrence in the aquatic environment, and 4-*n*-NP was chosen as the target compound.

2. Methods

A detailed description of the photodegradation processes has been reported elsewhere (Li et al., 2012), although the authors provided only a simple description of the experimental process.

2.1. Photolysis experiments

Each NP sample solution was placed in a quartz tube, and all of the tubes were then fixed in the groove of the photolysis device (Suntest-CPS+, Atlas, Germany). The groove was filled with water, and the water temperature was controlled by a circulator bath.

A schematic of the photolysis device is provided in Fig. 1.

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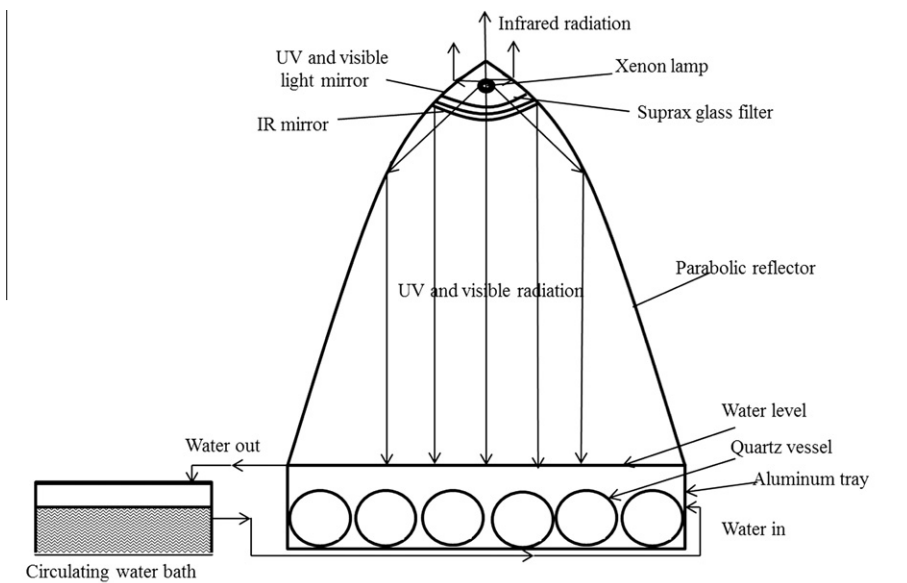
E-mail address: lixg@ouc.edu.cn (X. Li).

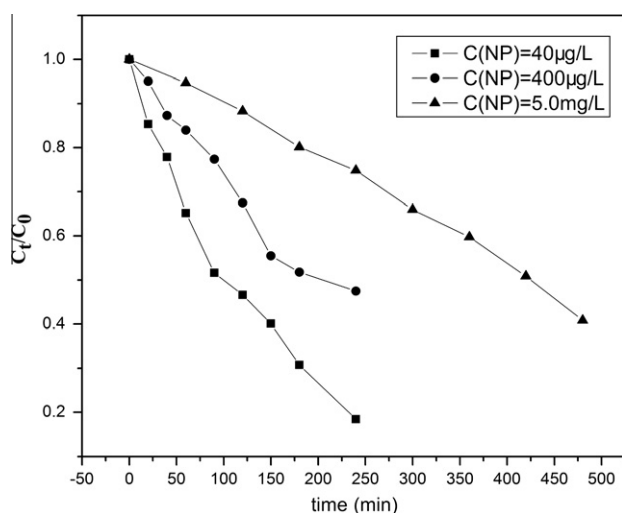Fig. 1. Schematic diagram of the irradiation equipment.

Fig. 2. The influence of the initial NP concentration on the photodegradation (40 µg/L NP and 400 µg/L NP under conditions of 500 W/m^2 and 20 °C; 5.0 mg/L NP under conditions of 750 W/m^2 and 30 °C).

2.2. Sample analyses

The pH and the dissolved oxygen (DO) content of the NP solutions were determined using an HQ40d portable meter (Hach, USA).

The concentrations of NP were determined using a GC–FID (6890, Agilent, USA) after extraction. The GC was equipped with a capillary column (DB-5MS(UI), 30 m × 0.25 mm i.d., film thickness 0.25 µm). High-purity nitrogen carrier gas was used with a constant pressure of 93.8 kPa. The sample injection volume was 2 µL (splitless mode).

The temperatures of the injector and detector were 280 °C and 300 °C, respectively. The column oven temperature was programmed as follows: 100 °C for 2 min, 100–180 °C at 10 °C/min, 180–230 °C at 5 °C/min, 230–290 °C at 10 °C/min, and a 290 °C hold for 7 min.

The degradation products were identified using a GC–MS (6890/5973, Agilent, USA) equipped with a capillary column (HP-35MS, 30 m × 0.25 mm i.d., film thickness 0.25 µm). High-purity helium carrier gas was used with a flow rate of 1.0 mL/min. The mass spectrometer was set to scan mass units of 29–550 for electron-impact ionization with a source temperature of 280 °C.

3. Results and discussion

3.1. Influences of photodegradation conditions

3.1.1. Initial NP concentration

The influence of the initial NP concentration on the photodegradation was investigated. A greater degradation efficiency was obtained under conditions where the initial NP concentration was lower (Fig. 2). The pseudo-first order rate constants for NP concentrations of 5.0 mg/L, 400 µg/L and 40 µg/L were 1.57×10^{-3} min^{-1}, 3.36×10^{-3} min^{-1} and 6.73×10^{-3} min^{-1}, respectively (Table 1). The pseudo-first order rate constant decreased as the initial NP concentration was increased. The higher concentration of NP acts as an inner filter that makes the solution less permeable to light irradiation under the same light intensity. Additionally, the additional intermediates produced at higher concentrations can compete with NP molecules and decrease the degradation efficiency (Daneshvar et al., 2007).

However, the reaction rate was higher when the initial concentration in the photolysis process was greater, which can be explained by the increased light absorption and by the greater reactant concentration (Błędzka et al., 2009).

The photodegradation rate was obviously influenced by the initial concentration, and we therefore chose a single concentration to study in follow-up experiments. To simulate natural water conditions, a concentration of 40 µg/L was selected.

3.1.2. Temperature

The degradation rates at 20 °C and 30 °C were faster than that at 10 °C; however, the difference in degradation rates between 20 °C and 30 °C was not obvious (Fig. 3). Therefore, the influence of temperature was not significant.

In general, an increase in temperature accelerates the movement rate of NP molecules, and the change in interatomic interactions weakens the chemical bonds. Therefore, the reaction rate increased at higher temperatures. However, the activation energy