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# Photodegradation of nonylphenol in aqueous solution by simulated solar UV-irradiation: The comprehensive effect of nitrate, ferric ion and bicarbonate



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### Jialin Peng, Guoguang Wang, Dahai Zhang, Dongmei Zhang, Xianguo Li\*

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China

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#### ABSTRACT

A Suntest-CPS+ sunlight simulator was used to investigate the direct and indirect photolysis of nonylphenol (NP) exposing to simulated sunlight in aqueous solution. The degradation reaction of NP obeyed a pseudo-first-order kinetics. Based on the pseudo-first-order rate constant (k) obtained from experimental data, the half-life of NP was calculated under different conditions, which ranged from 0.41 to 2.39 h. The affecting factors (NO<sub>3</sub><sup>-</sup>, Fe<sup>3+</sup> and HCO<sub>3</sub><sup>-</sup>), especially their interactions on NP photodegradation, were systematically studied for the first time in the present study. The results showed that NO<sub>3</sub><sup>-</sup> significantly influenced the photodegradation of NP and had a degradation ceiling. NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup> exhibited a synergistic effect on the photodegradation of NP and this interaction was very strong, which showed an abnormal phenomenon in dynamics, whereas the influence of  $Fe^{3+}/HCO_3^{-}$  was slight on the photodegradation of NP. In addition, Fe<sup>3+</sup> contributed little to the interaction in combining with other ions ( $NO_3^-$  and  $HCO_3^-$ ). The light-absorbing ions ( $NO_3^-$  and  $Fe^{3+}$ ) with low concentration could inhibit the photolysis of NP only at the beginning of degradation process, indicating that the competition for energy and photons between NP molecule and light-absorbing ions is stronger than the photosensitizing effect at the initial stage. But this effect diminished with prolonged irradiation. Additionally, it was proved that the formation of free radicals during the photodegradation reaction was not the rate-determining step in NP indirect photodegradation. Meanwhile, compared with HO•, CO3had a higher oxidation rate on NP degradation, attributed to the generation of the more stable transition state between NP and CO<sub>3</sub><sup>-•</sup> during the degradation process.

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#### 1. Introduction

Emerging organic contaminants in rivers, lakes and reservoirs are becoming a worldwide concern due to their adverse effects on the environment [24,33,41]. An example is nonylphenol (NP), which is widely used in the production of nonylphenol ethoxylates surfactants, lubricating oil additives and the manufacture of antioxidants [39]. NP is known to accumulate in the aquatic environment [5], which causes extremely damages to a variety of aquatic organisms [36] via acting as an estrogen mimic by competing for the binding site of the receptor for the natural estrogen [25,42]. Based on the previous reports, the production and usage of NP had been increasing exponentially, since it was first synthesized in 1940 [28,36]. The annual output of NP reached

http://dx.doi.org/10.1016/j.jphotochem.2016.04.015 1010-6030/© 2016 Elsevier B.V. All rights reserved. to 16,000 tons in China [3], 16,500 tons in Japan [22], 73,500 tons in Europe [20] and 154,200 tons in the USA [36]. Due to the bioaccumulation and toxicity of NP, its manufacture and application have been restricted in the European Union since 2003 and the concentration of NP in water bodies is limited to  $2 \mu g/L$  [8]. The major sources of NP in the environmental matrixes are closely connected with the discharge of industrial and domestic wastewater as well as the surface runoff [1,15,19]. Moreover, for human and wildlife, one of the primary pathways of exposure to NP is via water consumption [46]. Accordingly, the degradation of NP, which strongly affects the behavior and fate of NP in aquatic environment, is of significant interest.

Photolysis is one of the main degradation pathways in surface waters for many organic contaminants [37]. This process can simultaneously impact the environmental fate of these pollutants and the ecological risk that they represent [11,43,44]. Photo-transformation of pollutants mainly proceed via two pathways, where the direct way refers to photodecomposition of the



<sup>\*</sup> Corresponding author. E-mail addresses: 1540124605@qq.com (J. Peng), lixg@ouc.edu.cn (X. Li).

pollutant itself after the absorption of photons from irradiation, and the indirect way refers to its transformation induced by reactions with excited states from other components or oxide radicals such as hydroxyl radicals (HO<sup>•</sup>) and carbonate radicals ( $CO_3^{-\bullet}$ ). The degradation of hazardous organic pollutants in natural waters occurs with these radicals, which initiate rapid reactions with organic compounds. Then the resulting organic radicals react with oxygen to originate a series of degradation oxidation reactions which ultimately lead to complete mineralization to  $CO_2$  and  $H_2O$  [26].

It was reported that the HO<sup>•</sup> radical can be formed from nitrate [10], nitrite [32], ferric ion [9] as well as other species and quenched by carbonate, bicarbonate and other solutes [10,32,40] in sunlit surface water. Meanwhile, the  $CO_3^{-\bullet}$  radical can be generated through the interactions between bicarbonate and other radicals, such as HO<sup>•</sup> and  $SO_4^{-\bullet}$  [12]. Due to the widespread distributions of the photoreactive constituents in aquatic systems, these factors deserve extensive attention on the photodegradation of organic contaminations. Several studies have proved that the concentration of NP can be reduced via photolysis induced by sunlight in the surface waters [2], and the degradation time of NP varies depending on various environment parameters [27,34].

In the photochemical degradation of NP in aquatic systems, previous studies have identified nitrate, ferric ion and bicarbonate as significant participants [27,34]. However, no studies investigated the interaction of these three factors on the photodegradation of NP. Therefore, the aim of the present study was to simulate natural aquatic environment to investigate the direct and indirect photolysis of nonylphenol (NP) exposing to solar irradiation, with particular emphasis on the possible interactive impact of these three ions (NO<sub>3</sub><sup>-</sup>, Fe<sup>3+</sup> and HCO<sub>3</sub><sup>-</sup>). The selection of their concentration ranges was based on the real level typically observed in natural aquatic environment [29,48]. To our knowledge, this is the first attempt to systematically investigate the removal of NP by incorporation of all these three water constituents under the irradiation.

#### 2. Materials and methods

#### 2.1. Reagents

NP was purchased from Dr. Ehrenstorfer-Gmbh (Germany, CAS: 104-40-5). Hexamethylbenzene, purchased from Aldrich Chemical (USA, CAS: 87-85-4), was added as the internal standard for quantification of targeted NP. Solvents including *n*-hexane and dichloromethane were of HPLC grade from Burdick & Jackson. Salts, such as sodium nitrate (NaNO<sub>3</sub>), ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O) and sodium bicarbonate (NaHCO<sub>3</sub>), were guaranteed reagents. Anhydrous sodium sulfate was baked at 450 °C for 4 h and stored in sealed container after cooling. Ultrapure water was produced using Gradient A10 Millie-Q system from Millipore (USA). Fuming hydrochloric acid (HCl, 37%) was used to obtain a final acid solution in 3 mol/L.

#### 2.2. Sample preparation

Individual stock solution of NP was prepared by dissolving 2.8 mg of the solute in 10 mL *n*-hexane to achieve a final concentration of 280 mg/L; this solution was stored at 4 °C and was protected from light. NP solution for irradiation experiments was prepared by adding an appropriate volume of stock solution in *n*-hexane (280 mg/L) to ultrapure water to obtain an initial concentration of 0.056 mg/L, and stirred for several hours in the dark to ensure sufficient dissolution. Shortly before the irradiation,

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The concentration of  $NO_3^-$ ,  $Fe^{3+}$  and  $HCO_3^-$  in the experiment.

Treatment	NO <sub>3</sub> <sup>-</sup> mg/L	Fe <sup>3+</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L
1	0.88	0	0
2	26.40	0	0
3	52.80	0	0
4	0	0.15	0
5	0	0.45	0
6	0	0.75	0
7	0	0	120
8	0	0	600
9	0	0	960
10	26.40	0.75	0
11	26.40	0	120
12	0	0.75	120
13	26.40	0.75	120

the solution was spiked with nitrate, ferric ion and bicarbonate, the concentrations of which were shown in Table 1.

#### 2.3. Irradiation experiments

The photolysis experiments were operated using a Suntest-CPS + sunlight simulator from Atlas (Germany) equipped with a xenon lamp filtered by a UV filter that delivered a light emission spectrum similar to that of sunlight  $(500 \text{ W/m}^2)$ . The volume of each NP sample solution was 100 mL and placed in a quartz tube for irradiation. All quartz tubes soaked in the water bath were ensconced in the groove of sunlight simulator under the same conditions, and the water temperature was controlled by a circulator cooling bath. The initial concentration of NP was constant (0.056 mg/L) for each batch of samples. No extra oxygen was supplied in the system, but there existed dissolved oxygen (DO), which was normally saturated and kept the same with an initial concentration of DO = 7.91 mg/L in any case. Assays were performed for 4.5 h, with samples collected at 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.5 and 4.5 h for a total of 8 samples as well as an extra dark control. Quartz tubes were removed at selected time intervals in turn, acidified to pH 2 and then extracted with 30 mL of dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). Finally, all the extracts were dewatered by a column packed with anhydrous sodium sulfate (5g). Each experiment was performed in duplicate.

#### 2.4. GC analyses

The degradation efficiency of target compound was examined by measuring the residual concentration. NP was analyzed by a Shimadzu 2010plus gas chromatograph coupled with flame ionization detector (GC-FID) and a DB-5MS ( $30 \text{ m} \times 0.25 \text{ mm}$  i. d.  $\times 0.25 \mu \text{m}$  film thickness) capillary column was used for the identification. The oven temperature was initiated at 100 °C for 2 min, ramped at 10 °C/min to 180 °C, 5 °C/min to 230 °C for 1 min, then up to 290 °C at 10 °C/min and held for 7 min. Automatic injection of 1  $\mu$ L sample was conducted in the splitless mode. Helium was used as the carrier gas at a flow rate of 3 mL/min. Injector and detector temperatures were fixed at 290 °C and 300 °C, respectively.

Limit of detection (LOD) of NP, calculated as signal-to noise ratio of 3, was 0.006 ng/mL. The recoveries of NP without irradiation ranged from 84.6% to 96.3% (n = 6, in the concentration range of 0.01 mg/L-0.1 mg/L).

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