

The Study of Photolysis of Single Nonylphenol Isomer

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Abstract: To better understand the photolysis behavior of technical nonylphenol (tNP) under low-pressure mercury lamp (20 W) with light source ($\lambda=253.7$ nm), the study of the photolysis of single nonylphenol isomer (NP₃₈) and tNP were carried out. The result showed that NP₃₈ and tNP were removed quickly, the photolysis rate of tNP was higher than that of NP₃₈. H₂O₂ accelerated remarkably the degradation of NP₃₈. Identified products of photolysis of NP₃₈ were probably 4 (2,6-dimethyl-2-heptyl)-1,2-benzenediol or 2 (2,6-dimethyl-2-heptyl)-1,5-benzenediol. The photolysis of NP₃₈ seemed to proceed through two pathway: 4 (2,6-dimethyl-2-heptyl)-1,2-benzenediol was generated by the reaction of NP₃₈ and O₂[·] radicals, the reaction of NP₃₈ and [·]OH radicals that produced by the photolysis of H₂O maybe the precursor of 2 (2,6-dimethyl-2-heptyl)-1, 5-benzenediol, but the H₂O₂ oxidised the intermediate products could not be detected by GC-MS.

1 INTRODUCTION

Nonylphenol (tNP) was one of endocrine disruptors (EDCs) due to its estrogenic effect, which was produced by the degradation of the nonionic surfactant (NPEO). tNP was more stable, toxic and accumulate than the NPEO, which was stable in water (Kannan et al., 2003; Xia et al., 2013) and had a significant toxicity effect on zebrafish embryos at 2 $\mu\text{g}\cdot\text{L}^{-1}$ (Zhang et al., 2017). tNP was found in sewage sludge during the 80s (Giger et al., 1984), and a large amount of tNP were detected on surface water, groundwater, soil, sediment, air and so on (Guenther et al., 2002; Liu et al., 2013; Careghini et al., 2015; Chen et al., 2013; Peng et al., 2016). tNP was included in the European Union water framework directive as a new hazardous substance. The tNP levels was limited at 6.6 $\mu\text{g}\cdot\text{L}^{-1}$ in fresh water and 1.7 $\mu\text{g}\cdot\text{L}^{-1}$ in the seawater (Brooke and Thursby, 2005).

The degradation rate of tNP under the UV was about 1.3 times higher than that of natural light source (Neamtu and Frimmel, 2006). The straight

chain of NP (4-n-NP) degradation rate reached 90%, after 4 h under certain conditions (Martinez et al., 2013; Li et al., 2012). The study of degradation of tNP showed that hydroxyl free ([·]OH) could promoted the degradation of tNP under the 266 nm laser flash photolysis and 254 nm photolysis (Zhang et al., 2012). The above researchers mainly studied the photolysis of nonylphenol with tNP or 4-n-NP as the research object, but tNP was composed of a variety of nonylphenol monomers, and the para nonylphenol (4-NPs) was mainly composed of alkyl side chains, which accounted for 86~94% (Eganhouse et al., 2009). Some study showed that the photolysis products of the tNP was 4-nonyl-catechol (Li et al., 2012), but others showed that the photolysis products of the tNP might be phenols, aldehydes and carboxylic acids. Therefore, further research was needed for the photolysis mechanism of nonylphenol. NP₃₈ monomer was one of 4-NPs, which was common in the tNP (Eganhouse et al., 2009; Shan et al., 2011). In this study, NP₃₈ was chosen as the research object, and its photolysis

pathway was discussed, which provided a theoretical basis for the final fate of tNP in water environment.

2 MATERIALS AND METHODS

2.1 Materials

tNP was bought from Fluka with 99.9% (Germany), NP₃₈ (purity, >99%) was synthesized by Friedel-Crafts alkylation with 2, 6-dimethyl-2-heptyl and phenol in laboratory (Vinken et al., 2002), Methanol, n-hexane and Dichloromethane were chromatographic grade (CNW, Germany). Ultrapure water (18.2 MΩ·cm) produced by a Milli-Q system, 200 mg·L⁻¹ stock solutions of NP₃₈ was prepared with methanol, the solutions were prepared by adding an appropriate amount of stock solution in methanol with ultrapure water to obtain final concentration 5 mg·L⁻¹ of NP₃₈.

2.2 Experiment Design

Photolysis batch experiments in water: each photolysis experiment had two replicates. The irradiation device with quartz test tubes (volume: 35 cm³, average optical path length: 6 cm) in this study referred to our previous work (Jia et al., 2009). In brief, the experiment was carried out by using low-pressure mercury lamp (20 W) as light source (λ=253.7 nm). Those samples that were wrapped by the aluminum foil and kept in the dark set as control group. All samples were taken at certain time intervals during the irradiation.

2.3 Extraction and Analysis

tNP and NP₃₈ determination in water: the water samples were extracted by liquid-liquid extraction method. 10 ml of sample was transferred to separating funnel and extracted three times with 10 ml of DCM, the collected samples were enriched to about 0.5 ml by a rotary evaporator (Buchi, Switzerland) and transferred into 2 ml of blown bottle. They were dried under a gentle nitrogen stream and redissolved in 0.4 ml of methanol to be detected by High Performance Liquid Chromatography (HPLC, 1100-UVD, Agilent Technologies, USA) (Jia et al., 2009), the crude products of NP₃₈ were identified by Gas Chromatograph-Mass Spectrometer (GC-MS, 6890-

5975N, Agilent Technologies, USA) (Shan et al., 2011).

3 THE RESULTS AND DISCUSSION

3.1 The Photolysis of tNP and NP₃₈

In the text, Figure 1 shows that tNP and NP₃₈ can be efficiently degraded by 78.36% and 69.61% respectively in an hour through UV photolysis, it was similar to the degradation of octylphenol (4-OP) under low pressure mercury lamp (Liao et al., 2009). The photolysis rate of tNP was faster than NP₃₈, due to the presence of more isomers in tNP that was easy to degradation than NP₃₈. The decay of the tNP in our study was prominently faster than reported under the simulate sunlight (Li et al., 2012), which proved UV light could efficiently decompose tNP.

3.2 The Effect of H₂O₂ to the Photolysis of NP₃₈

Figure 2 shows that only 6.4% and 4.3% of NP₃₈ existed in the experimental group containing 20 mmol·L⁻¹ and 50 mmol·L⁻¹ H₂O₂ solution, but the NP₃₈ monomer still had 58.2%, after 60 min, in the solution without H₂O₂. This indicates that H₂O₂ greatly promoted the photolysis process of NP₃₈, and the higher concentration of H₂O₂ was more beneficial to the photolysis of NP₃₈ monomers.

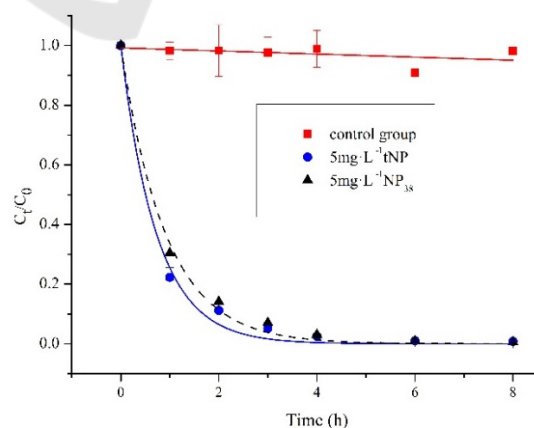


Figure 1: Photolysis of NP₃₈ and tNP in ultrapure water, Control group (tNP, 5 mg·L⁻¹). Initial condition: pH=6.59, T=25 °C, t=8 hours.

Figure 3 shows that the degradation products of NP₃₈ in H₂O₂ solution were different from those of NP₃₈ in ultrapure water system, the total ion chromatogram (TIC) was shown. A was NP₃₈ (the peak time is 12.26 min). B was intermediate photolysis product (the peak time is 19.72 min), but it wasn't detected in the TIC diagram of H₂O₂ solution, because its intermediate product was further oxidized to be other substances had different photolysis pathways.

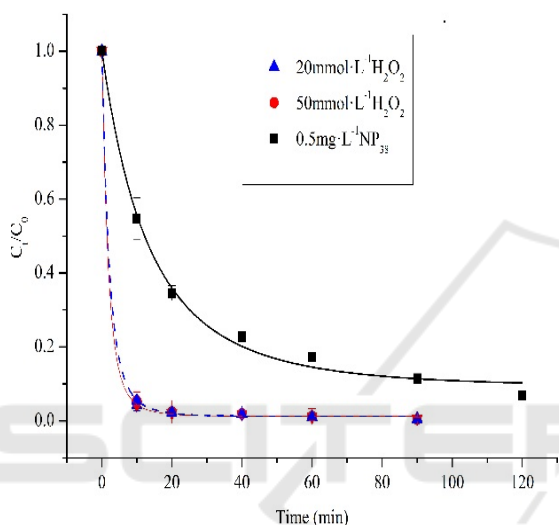


Figure 2: The effect of H₂O₂ upon the photolysis of NP₃₈. Initial conditions: C₀= 0.5 mg·L⁻¹, pH= 6.59, T = 25 °C, t=120 min.

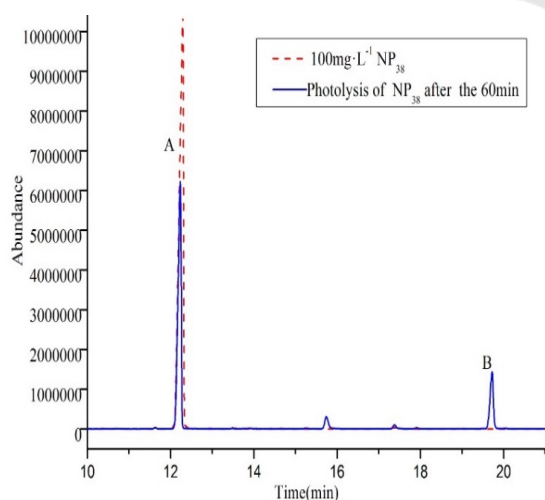


Figure 3: TIC analysis of NP₃₈ in ultrapure water after UV illumination for 60 min.

3.3 The Photolysis Pathways of NP₃₈

Figure 4 and Figure 5 shows that the MS spectrum of the NP₃₈ was mainly included 135 (100), 136 (10), 121 (5), 119 (2), 107 (15) and the MS spectrum of the B was mainly included 151 (100), 152 (10), 137 (5), 123 (11), 135 (2), because Hydrogen atom on the benzene ring of the NP₃₈ was substituted by hydroxyl group produced B, 135→151, 107→123, 136→152, 121→137, 119→135. 4 (2, 6-dimethyl-2-heptyl)-1, 2-benzenedio and 2 (2, 6-dimethyl-2-heptyl)-1, 5-benzenediol was produced by photolysis of NP₃₈ (Corvini et al., 2005).



Figure 4: A bar graph of NP₃₈.

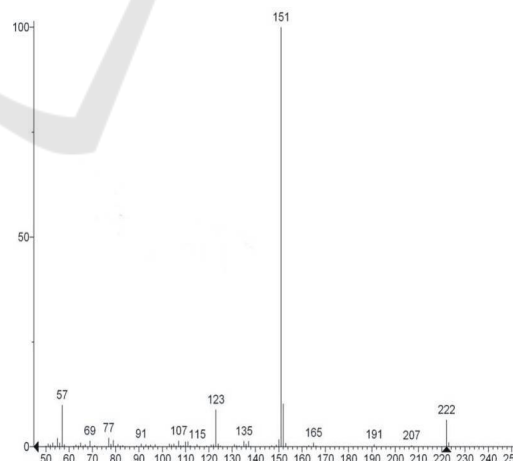


Figure 5: A bar graph of B.

Figure 6 showed two photolysis pathways of NP₃₈. On the one hand, NP₃₈ was in the excited state and transferred into the 4-nonyl benzoxy radical with active ortho hydroxyl group at low-pressure mercury lamp (20 W), O₂^{·-} was formed after the O₂

captured electron. The 4 (2, 6-dimethyl-2-heptyl)-1, 2-benzenedio (Figure 6-A) was produced when the 4- nonyl benzoxy radical was attacked by the $O_2^{\cdot-}$. On the other hand, hydrogen atoms on adjacent carbon atoms of NP_{38} were more susceptible to be replaced by the hydroxyl and was converted to 2 (2, 6-dimethyl-2-heptyl)-1, 5-benzenedio (Figure 6-B), due to the alkyl side chain of NP_{38} had the electron cloud density on the opposite substituent of the benzene ring (Vinken et al., 2002). There were different products from 4-n-NP after photolysis (Li et al., 2012), because of more complex structure of the alkyl side chain on NP_{38} than that of 4-n-NP. This study indicated that the structure of tNP had a certain effect on its photolysis behavior.

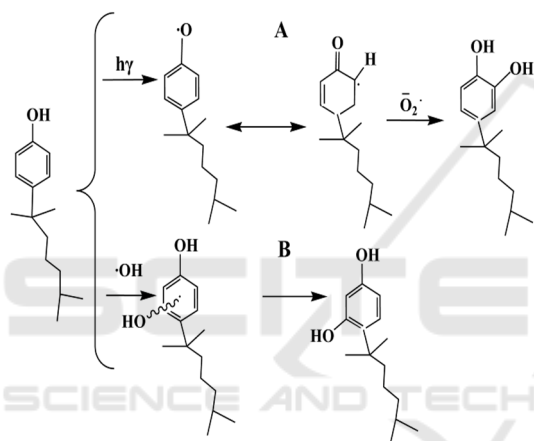


Figure 6: The possible photolysis pathways of NP_{38} .

4 CONCLUSIONS

The photolysis behavior of NP_{38} was studied under the conditions of different initial concentration and different concentration of H_2O_2 with low pressure mercury lamp as the light source. the degradation products of NP_{38} were identified by GC-MS, and the possible degradation pathways of NP_{38} were analyzed. NP_{38} and tNP were removed quickly under the UV radiation. The photolysis rate of tNP was higher than that of NP_{38} . Photolysis would not stop until all of them disappeared from solution. H_2O_2 accelerated remarkably the degradation of NP_{38} , NP_{38} was degraded about 93.6% and 95.4% in H_2O_2 20 $mmol \cdot L^{-1}$ and 50 $mmol \cdot L^{-1}$. Identified resulting products were probably 4 (2, 6-dimethyl-2-heptyl) -1, 2-benzenedio or 2 (2, 6-dimethyl-2-heptyl)-1, 5-benzenedio. The photolysis of NP_{38} seemed to

proceed through two pathway mechanisms: 4 (2, 6-dimethyl-2-heptyl)-1, 2-benzenedio was generated by the reaction of NP_{38} and $O_2^{\cdot-}$ radicals; The reaction of NP_{38} and $\cdot OH$ that produced by the photolysis of H_2O maybe the precursor of 2 (2, 6-dimethyl-2-heptyl) -1, 5-benzenedio, but the H_2O_2 oxidized the intermediate products so that it could not be detected by GC-MS.

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