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The mechanism study of efficient degradation of hydrophobic nonylphenol in solution by a chemical-free technology of sonophotolysis

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HIGHLIGHTS

- pH influenced NP sonophotolysis by changing its existing form and light absorption.
- NO_3^- accelerated NP sonophotolysis while HCO_3^- showed insignificant influence.
- Both ortho- and meta-hydroxy-NP species can exist together thermodynamically.
- Only the ortho-4-nonyl-benzoquinone is dominant thermodynamically.
- The mechanism of ortho-hydroxy-NP formation was the addition of $HO^\bullet$ and $H^\bullet$

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ABSTRACT

Nonylphenol is a hydrophobic endocrine disrupting compound, which can inhibit the growth of sewage bacteria in biological processes. This study investigated the degradation of 4-*n*-nonylphenol (NP) in water by a chemical-free technology of sonophotolysis with emphasis on the impacts of several important parameters, including light intensity, solution pH, two commonly seen inorganic ions (i.e. NO_3^- and HCO_3^-), and principally on the examination of degradation mechanisms. It was found that, solution pH could significantly influence both NP degradation efficiency and the synergistic effect of sonophotolytic process, where higher synergistic effect was obtained at more acidic condition. In addition, the presence of NO_3^- accelerated NP degradation by both acting as a photosensitizer and providing $NO_2^\bullet$ radicals, while HCO_3^- had little effect on NP degradation. Identification of intermediates of NP degradation indicated that NP sonophotolysis was mainly initiated by the formation of hydroxy-NP, and a new intermediate di-hydroxy-NP was identified for the first time ever in this study. Through thermodynamic analysis, results indicated that both ortho- and meta-hydroxy-NP species can coexist in the solution but the ortho-4-NBZQ (4-nonyl-benzoquinone) is dominant. In addition, the mechanism of ortho-hydroxy-NP formation was suggested by the addition of $HO^\bullet$ and $H^\bullet$ radicals.

1. Introduction

Nonylphenol (NP) is a xenobiotic compound used in the manufacture of antioxidants, lubricating oil additives and the production of nonylphenol-ethoxylates (NPEOs) surfactants, which accounts for 65% of its major use [1]. The annual production of NP reached 154,200 tons in the USA, 73,500 tons in Europe, and 16,000 tons in China [1]. NPEOs are the most significant alkyl phenol ethoxylates (APEOs), accounting for about 80% of total APEOs used [2]. NPEOs are widely used in industrial, agricultural and household applications, including the production of detergents, emulsifiers, dispersing agents, etc. [1,3]. Due to the extensive use of NPEOs, more than 60% of the total NPEOs produced go into the aquatic environment, where they are incompletely degraded to NP. Therefore, the principal route of exposure to NP for human and wildlife is through water [2]. NP has been found capable of mimicking the effect of hormone estrogen and inducing breast tumor cell proliferation [4,5]. which has caused public concern [2]. The European Union and the United States have gradually phased out nonylphenolic compounds, while many other countries, including China, still produce and use in large quantities.

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The environmental fate of NP is predominantly controlled by its physicochemical properties, which can further influence its degradation in nature. NP is a hydrophobic compound with a LogK_{ow} of 5.71, which favorably enters into the organic matters (e.g. sediment and soil [2]). On the surface of natural waters, NP can be degraded by sunlight photolysis [6], while the half life of NP in sediments was estimated to be more than 60 years [7]. Another important pathway of NP natural degradation is via biodegradation, aerobically or anaerobically, with the half life of several dozen days [8]. Therefore, reducing NP concentration in the effluent of wastewater treatment plants (i.e. the major source of NP) is critical to control NP pollution. The degradation of NP in water by certain advanced oxidation technologies (AOTs) have been reported, including ultraviolet irradiation (UV) [9–11], low-frequency ultrasound [12,13], ozonation [14,15], and photo-catalytic degradation [16–18]. Cravotto et al. have also investigated the sonochemical Fenton process integrated with biosorption for NP removal [19]. In some cases, organic solvents were used (e.g. methanol [11,13]) to increase the solubility of NP so as to facilitate its quantification, which however may influence the investigated processes.

Although the application of ultrasound in industries is not new, its 'green' value has been recognized only recently [20]. Generally, the ultrasonic system requires no chemical additives and generates less or no hazardous byproducts. Due to its 'green' property, ultrasound has been explored with great interest for water/wastewater treatment in an attempt to establish an environmental-friendly treatment technology. Although there is no environmental concern associated with ultrasonic technology, the cost effectiveness issue (i.e. energy input) is still an obstacle for its scale-up. Nevertheless, one effective way to reduce the operational cost and make it economically feasible is to combine ultrasound with other synergistic AOTs. So far, many sono-hybrid processes have been proposed and investigated, such as the sono-persulfate process [21], sono-Fenton process [22–24], sono-electrochemical process [25], sono-photo-ferrioxalate process [26] and sonophotolytic process [27]. Among these hybrid processes, the sonophotolytic process shows more promise for practical application due to its avoidance of chemical addition. A study by Mahamuni and Adewuyi has compared the treatment costs of individual ultrasonic process (US) with some ultrasound-related hybrid processes for 1000 L min^{-1} capacity treatment plant [28], where the cost for trichloroethylene treatment was $91 per 1000 gallons using US, but the cost significantly reduced to $25 for US/UV.

Since scarce information was available for NP degradation in high-frequency ultrasonic process and sonophotolytic process, especially the potential degradation products, relevant studies are expected to provide some useful information. In this study, the degradation of NP in solution was investigated using a chemical-free technology of sonophotolysis. Several critical influencing factors important for practical application were investigated in detail. The primary degradation intermediates at different conditions were determined based on UPLC/ESI-MS analysis and theoretical calculation.

2. Methodology

2.1. Chemicals

4-*n*-NP (99.9%; Formula: $C_{15}H_{24}O$; Molecular Weight: 220.35; CAS: 25154-52-3) and sodium nitrate (>99%) were purchased from Sigma Aldrich Inc., USA. Sodium bicarbonate ($\geq$99.5%) was purchased from Guangzhou Chemical Reagent Factory. Solvents used for high performance liquid chromatography (HPLC) and liquid chromatography tandem mass spectrometry (LC/MS) were of HPLC grade and LC/MS grade, respectively. Sulfuric acid and sodium hydroxide were used for pH adjustment. Water prepared from a Millipore Waters Milli-Q water purification system with resistivity of 18.3 MΩ cm was used exclusively.

2.2. Apparatus and experimental conditions

A 400 kHz ultrasound was applied in this study, the power density of which was measured to be 0.03 W mL^{-1} by a calorimetric method [29]. The photolytic experiments were conducted using phosphor-coated low pressure mercury lamps emitting 253.7 nm monochromatic UV light. Different light intensities were obtained by varying the number of UV lamps on the ceiling of the photoreactor. The incident light intensity of one UV lamp approximates to be 1.72×10^{-6} einstein L^{-1} s^{-1} as cited by the lamp manufacturer, Southern New England Ultraviolet Co., USA. Details and schematics of the ultrasound and photoreactor have been described elsewhere [30,31]. Sonophotolytic reactions were performed by placing the ultrasonic reactor without lid in the center of the photoreactor. A cooling finger was submerged in the solution to maintain a constant temperature of 29 ± 2 °C during the reaction. NP solutions with the initial concentration of 0.01 mM were prepared and applied for all the tests except for intermediates and total organic carbon (TOC) analysis, in which 0.015 mM NP were used to intensify detection signals. The initial solution volume for the reaction was 250 mL and initial pH was kept at 6.6 ± 0.2 without buffer solutions. All the experiments were duplicated with an observed deviation of less than 5%.

2.3. Analytical method

The NP concentration was determined by HPLC (Waters), consisting of a Waters 515 pump, a Waters 2489 UV detector, a Waters 717 auto sampler, and a Brava C18-BDS column (5 μm, 25 × 0.46 cm). The mobile phase was a mixture of 95% acetonitrile (ACN) and 5% water at a flow rate of 1.0 mL min^{-1}. Dual wavelengths of 224 and 275 nm were selected for NP. Intermediates of NP degradation were identified using a UPLC/ESI-MS system equipped with Bruker amaZon SL ion trap mass analyzer, Dionex UltiMate 3000 ultra performance liquid chromatography (UPLC), and the Thermo Hypersil GOLD column (1.9 μm, 50 × 2.1 mm) for UPLC. Negative ion mode was applied for NP and the intermediates detection. The composition and gradient programme of the mobile phase used for UPLC/ESI-MS at a flow rate of 0.15 mL min^{-1} are shown in Fig. S1 in Supplementary. Intermediates identified by UPLC/ESI-MS were quantified by their relative abundance, which were estimated by comparing their corresponding deprotonated ion intensities to that of the initial NP in solution from the MS analysis. The concentration of hydrogen peroxide was determined by a colorimetric method via reaction with Ti^{4+} [32]. TOC was analyzed by Shimadzu TOC-L analyzer. The UV absorption spectra were obtained by Biochrom Libra S35 UV–vis Spectrophotometer. All the thermodynamic analysis were carried out using Gaussian 09 program package [33]. The structures were optimized at the hybrid density functional B3LYP method with 6-31+G (d, p) basis set in a water solvent, using conductor-like polarizable continuum model (CPCM) combined with a UAKS radii. In addition, the vibrational frequencies were also calculated at the same level to ensure the transition and the local-minima states having only one and no imaginary frequencies, respectively. The zero point energies (ZPEs) of all the optimized structures were included in the calculation of the relative electronic energies (ΔE).