



Supercritical water oxidation of 2-, 3- and 4-nitroaniline: A study on nitrogen transformation mechanism



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HIGHLIGHTS

- SCWO was an effective method for removing 2-, 3- and 4-nitroaniline (NA), in an order of 2-NA > 3-NA > 4-NA.
- The amino and nitro preferred to interact within the molecule rather than between the molecules.
- The NH₄⁺ and NO₃⁻ did convert into N₂ during SCWO, but the conversion was little without auxiliary fuel.
- The result of Fukui indices verified that amino was more easily to be attacked than nitro.
- The conceivable reaction pathways of 2-, 3- and 4-NA were proposed.

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ABSTRACT

Supercritical water oxidation (SCWO) of 2-, 3- and 4-nitroaniline (NA) was investigated under residence time of 1–6 min, pressure of 18–26 MPa, temperature of 350–500 °C, with initial concentration of 1 mM and 300% excess oxygen. Among these operating conditions, temperature and residence time played a more significant role in decomposing TOC and TN than pressure. Moreover, the products of N-containing species were mainly N₂, ammonia and nitrate. When temperature, pressure and retention time enhanced, the yields of NO₃⁻ and org-N were reduced, the amount of N₂ was increasing, the proportion of NH₄⁺, however, presented a general trend from rise to decline in general. The experiment of aniline/nitrobenzene indicated that TN removal behavior between amino and nitro groups would prefer to happen in the molecule rather than between the molecules, therefore, the smaller interval between the amino and nitro group was the more easily to interreact. This might explain the reason why TN removal efficiency was in an order that 2-NA > 3-NA > 4-NA. The NH₄⁺/NO₃⁻ experiment result demonstrated that ammonia and nitrate did convert into N₂ during SCWO, however, the formation of N₂ was little without auxiliary fuel. Density functional theory (DFT) method was used to calculate the molecular structures of 2-, 3- and 4-NA to further explore reaction mechanism, which verified that amino group was more easily to be attacked than nitro group. Based on these results, the conceivable reaction pathways of 2-, 3- and 4-NA were proposed, which contained three parts, namely denitrification, ring-open and mineralization.

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1. Introduction

2-, 3- and 4-nitroaniline (2-, 3- and 4-NA), as the isomeric compounds of nitroaniline, are important intermediates or precursor in the synthesis of azo dyes, antioxidants, fuel additives, pharmaceuticals, pesticides etc. Nowadays, 4-nitroaniline (4NA)

has been listed as a priority pollutant by the Environmental Protection Agency (EPA) of the United States, due to its high toxicity, potential carcinogenic and mutagenic effects (Cheng et al., 1998; Ye et al., 2004). Moreover, traditional purification of wastewater polluted with 2-, 3- and 4-NA is a very hard task because the presence of a nitro group in the aromatic ring enhances the stability to chemical and biodegradation, while the anaerobic degradation would generate nitroso- and hydroxyamino-group compounds which are known as carcinogenic substances.

In recent years, advanced oxidation processes (AOPs) have

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shown great advantages over treating nitroanilines. Gautam et al. studied the photocatalytic degradation of 4-nitroaniline (4-NA) in a batch reactor with TiO₂ suspensions and found that 4-NA was best degraded under basic pH after 4 h (Gautam et al., 2005). Subbulekshmi and Subramanian used nano CuO immobilized fly ash zeolite to examine catalytic wet peroxide oxidative degradation of 4-NA, the results indicated that the best degradation rate of 84% occurred at 20 mg L⁻¹ 4-NA, catalyst dose 500 mg L⁻¹, pH = 6.5 and 2 mL H₂O₂ after 180 min (Subbulekshmi and Subramanian, 2017). Sun et al. investigated the decomposition of 4-NA by Fenton oxidation in various pH values, H₂O₂ concentrations and Fe²⁺ levels, and found that the degradation of 4-NA proceeded rapidly at pH value of 3 with the activation energy of 53.96 kJ mol⁻¹ (Sun et al., 2007). Moreover, Sun et al. also examined the decomposition of 4-NA by solar photo-Fenton and obtained the degradation rates of 4-NA more than 98% under pH value of 3, 0.05 mM Fe²⁺, 10 mM H₂O₂ and 20 °C (Sun et al., 2008). Although the above mentioned AOPs have an effective removal over 4-NA, there are still shortcomings. The addition of Fe²⁺, CuO and other transition metals would not only activate reactions, but cause potential secondary pollution as well. Moreover, the highly toxic intermediate products, such as 4-nitrophenol and hydroquinone, might produce and accumulate as a result of weak mineralization of 4-NA (Subbulekshmi and Subramanian, 2017).

Supercritical water oxidation (SCWO), therefore, were took into our consideration, for the refractory hazardous compounds can be available and successfully oxidized into CO₂, H₂O, N₂ as well as inorganic salt during SCWO process (Liu et al., 2009). Previous studies have proved SCWO as an innovative technology could successfully mineralize 2-chlorophenol (Lee et al., 2002), indole (Guo et al., 2014), quinoline (Pinto et al., 2006b), pyridine (Aki and Abraham, 1999), and 4-nitrophenol (Dong et al., 2015). Unfortunately, although these N-containing compounds could completely mineralized and mainly generate N₂ after SCWO process, there were still inorganic salt, such as ammonia, nitrate and nitrite, which would contribute to TN and potentially resulted in exacerbating the occurrence of eutrophication in receiving water. Based on our previous study (Yang et al., 2017), the amino- and nitro-group compounds could generate ammonia and nitrate, respectively, after SCWO process. Interestingly, 2-nitroaniline, containing the both amino and nitro groups, would directly produce nitrogen gas. As a result, it is significant to further explore TN removal, N-containing products and reaction pathways of 2-, 3- and 4-nitroaniline during SCWO.

To our best knowledge, however, data is still sparse on the treatment of 2-, 3- and 4-nitroaniline through SCWO. This study, therefore, aims to explore the potential of nitroanilines degradation during SCWO. Bench scale experiments were conducted to examine the effects of temperature, pressure and reaction time on TOC/TN degradation and N-containing products' distribution of 2-, 3- and 4-NA during SCWO. Furthermore, density functional theory (DFT) method was used to optimize and calculate the structures of 2-, 3- and 4-NA for further exploring the reaction mechanism of these target compounds in SCWO.

2. Experimental

2.1. Apparatus and experimental procedures

The SCWO schematic diagram was shown in Fig. 1. It was similar to the reactors reported elsewhere (Tan et al., 2014; Yang et al., 2017). The continuous tubular reactor is made of Hastelloy alloy whose designed maximum operating pressure and temperature were 40 MPa and 600 °C, respectively, with 2.5 mm ID and 2 m long, resulted in an approximately effective volume of 10 mL.

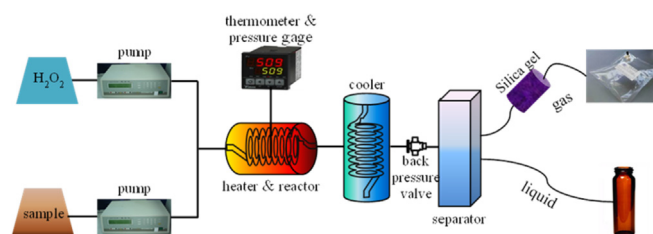


Fig. 1. Scheme of SCWO equipment.

Firstly, the sample and oxidant (H₂O₂) were pumped through two separate pumps at a desired flow rate, before mixing at the reactor entrance. Then, the reactor was heated within an electric temperature furnace, and could reach the desired temperature in few minutes (e.g., 1.5 min at 350 °C). Temperatures were measured at the reactor inlet and outlet points, to make sure that the temperature along the reactor remained constant. The cooling system consisted of a tank with circulating water at room temperature. Finally, a separator was applied to separate gas and liquid effluent, after a back-pressure regulator. Gas sample would undergo allochromic silica gel for dewatering before collection by gas collecting bag. Prior to the experiment, the equipment underwent 30 min to keep the balance of temperature and pressure. H₂O₂ (30 wt%) was used in SCWO experiments as the oxidant and all reagents were analytic grade. Considering the initial concentration was 1 mM, 300% excess oxygen was used into this study to keep sufficient oxidation. Sampling temperature was designed as 350, 400, 450, 500 and 550 °C, pressure was 18, 20, 22, 24 and 26 MPa, and reaction time was 1, 1.5, 3, 4.5 and 6 min. It is generally believed that SCWO reactions are feasible under the above conditions (Cocero and Martinez, 2004; Bermejo et al., 2006).

2.2. Materials and analytical methods

Molecular descriptors of 2-, 3- and 4-NA were calculated using the Density Functional Theory (DFT) method using Material Studio 6.1 (Dmol3/GGA-BLYP/DNP(3.5) basis). Fukui indices based on ·OH radical attack (*F*(0)) are important for analysis of site reactive selectivity among the reaction pathways, because hydrogen substitution by radicals, like ·OH, is the most events during SCWO. Therefore the calculations of *F*(0) and the basis set with Double Numerical plus Polarization (DNP) were adopted, as carried out in Dmol3 code in Material Studio 6.1. Meanwhile, the self-consistent field procedure was implemented with a convergence criterion of 10⁻⁶ a. u. on energy and electron density. Density mixing and the smearing of electronic occupations were set as 0.2 charge and 0.5 spin, as well as 0.005 Ha, respectively. These parameters were successfully conducted into our previous researches (Ogunsola and Berkowitz, 1995; Jia et al., 2015; Zhu et al., 2015; Su et al., 2016).

Measurement of total nitrogen (TN), NH₄⁺, NO₂⁻ and NO₃⁻ concentration was using a photometer (Model Spectroquant® NOVA 60, Merck Limited). Gas samples, such as N₂ and N_xO, were analyzed by GC-TCD (Agilent Technologies 6890 N) with Alltech CTR 1 column. Total organic carbon (TOC) was measured by the TOC Analyzer multi N/C 3000 (ChD) with detection limit of 0.01 mg L⁻¹. In brief, the spectrometry tended to a constant temperature after 30 min of warm-up. Ammonium and nitrite were analyzed under the wavelength of 420 and 540 nm, respectively, and nitrate was analyzed under 220 and 275 nm wavelength. The detection limits of NH₄⁺, NO₂⁻ and NO₃⁻ were 0.025, 0.003 and 0.08 mg L⁻¹, respectively. All experiments were repeated three times, and only the mean values were shown.

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