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Effects of pH and H_2O_2 on ammonia, nitrite, and nitrate transformations during UV_{254nm} irradiation: Implications to nitrogen removal and analysis

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HIGHLIGHTS

- Conversions among DINs were studied by UV_{254nm} photolysis with and without H_2O_2.
- Complete oxidation of NH_3 was obtained within 1 h with proper pH & H_2O_2 controls.
- Nitrite photo-oxidation depended strongly on H_2O_2 dose but less so on pH.
- Nitrate photo-reduction generally increased with increasing pH.
- Nitrogen balance was achieved in all irradiation experiments.

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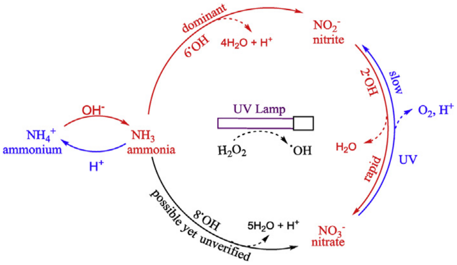
GRAPHICAL ABSTRACT



ABSTRACT

In order to achieve better removal and analyses of three dissolved inorganic nitrogen (DIN) species via ultraviolet-activated hydrogen peroxide (UV/H_2O_2) process, this study systematically investigated the rates of photo-oxidations of ammonia/ammonium (NH_3/NH_4^+) and nitrite (NO_2^-) as well as the photo-reduction of nitrate (NO_3^-) at varying pH and H_2O_2 conditions. The results showed that the mass balances of nitrogen were maintained along irradiation despite of interconversions of DIN species, suggesting that no nitrogen gas (N_2) or other nitrogen-containing compound was formed. NH_3 was more reactive than NH_4^+ with hydroxyl radical (•OH), and by a stepwise H_2O_2 addition method NH_3/NH_4^+ can be completely converted to NO_x^-; NO_2^- underwent rapid oxidation to form NO_3^- when H_2O_2 was present, suggesting that it is an intermediate compound linking NH_3/NH_4^+ and NO_3^-; but once H_2O_2 was depleted, NO_3^- can be gradually photo-reduced back to NO_2^- at high pH conditions. Other than H_2O_2, the transformation kinetics of DINs were all dependent on pH, but to varying aspects and extents: the NH_3 photo-oxidation favored a pH of 10.3, which fell within the pK_a values of NH_4^+ (9.24) and H_2O_2 (11.6); the NO_3^- photo-reduction increased with increasing pH provided that it exceeds the pK_a of peroxynitrous acid (6.8); while the NO_2^- photo-oxidation remained stable unless the pH neared the pK_a of H_2O_2 (11.6). The study thereby demonstrates a picture of the evolutions of DIN species together during UV/H_2O_2 irradiation process, and for the first time presents a method to achieve complete conversion of NH_4^+ to NO_3^- with UV/H_2O_2 process.

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1. Introduction

Ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-) are the three most common dissolved inorganic nitrogen (DIN) compounds in water, and their widespread existences may pose many negative impacts, such as eutrophication and acidification (Camargo and Alonso, 2006), on aquatic systems, and cause certain toxicological effects, like methemoglobinemia, to humans (Manassaram et al., 2005; Camargo and Alonso, 2006). Consequently, they have been regulated by many water and wastewater authorities around the world typically including USA, China, and Germany. To mitigate their risks, researchers have taken the initiative in applying measures to transform or remove them from water, including biological nitrification and denitrification (Rittmann and McCarty, 2001), air stripping (Liao et al., 1995), ion exchange (Jorgensen and Weatherley, 2003), and chemical precipitation (Li et al., 1999).

Recently, the uses of ultraviolet (UV)-based methods for DINs removal have received significant attention (Pollema et al., 1992; Mack and Bolton, 1999; Lee et al., 2002; Zhang et al., 2005; Zhu et al., 2005; Doudrick et al., 2013; Krasae and Wantala, 2016). In general, these photochemical processes might undergo two reaction routes. One route involves the photo-oxidation of ammonia/ammonium (NH_3/NH_4^+) to yield NO_2^-, NO_3^-, and nitrogen gas (N_2) (Wang et al., 1994; Zhu et al., 2005), and the other route involves photo-reduction of NO_3^- to form NO_2^- or N_2 (Mack and Bolton, 1999; Zhang et al., 2005; Doudrick et al., 2013; Krasae and Wantala, 2016). However, earlier studies usually examine ammonia oxidation, nitrite oxidation, and nitrate reduction separately, but seldom look into the concurring evolutions of all three DIN species together in a UV process. In addition, although many mechanistic and radicals formation insights have been provided on NH_3/NH_4^+ oxidation by UV and hydrogen peroxide (H_2O_2) (Huang et al., 2008), the reported treatment efficiency appeared not satisfying considering its large consumption of H_2O_2. Meanwhile, since NO_2^- formation has been documented in both NH_3/NH_4^+ photo-oxidation and NO_3^- photo-reduction processes (Motomizu and Sanada, 1995; Mack and Bolton, 1999; Sharpless and Linden, 2001; Keen et al., 2012), it is also important to know which one is quicker and what conditions are favorable.

Other than water and wastewater treatment, the use of UV methods for analyses of nitrogen-containing compounds is another arena of interest for a long time. To the best of our knowledge, some studies have applied UV (Baxley et al., 2004), UV-activated hydrogen peroxide (UV/H_2O_2) (Scheuer et al., 1995), UV/TiO_2 (Takeda and Fujiwara, 1996), and vacuum UV (Gonzalez and Braun, 1995) to convert dissolved organic nitrogen (DON) into DINs to enable determination of total nitrogen (TN) in water by colorimeter or ion chromatographer (IC) (Westerhoff and Mash, 2002; Ma et al., 2014). Although the oxidation efficiency is not as high as other methods for resistant compounds and nitrogen-enriched samples (Bronk et al., 2000), these UV-based TN analytical methods are superior to high temperature combustion (HTC) and high temperature catalytic oxidation (HTCO) methods in not requiring expensive instruments (e.g., combustor), and are also more advantageous than UV persulfate oxidation (UPO) method because they do not introduce external ions into samples so that it is possible to analyze μg/L (i.e., ppb) level of nitrogen in irradiated water by IC, thus making them appealing to measure traces of nitrogen. However, based upon earlier study, the conversion of NH_4^+ into NO_x^- remained challenging for UV/H_2O_2 process, with the maximum efficiency being only 26.4% even at favorable experimental conditions (Huang et al., 2008). So, it is necessary to optimize the process. In addition, because NO_2^- features the lowest detection limit of all DIN species by spectrophotometric methods (Westerhoff and Mash, 2002; Huang et al., 2008), there were once also desires to convert NO_3^- into NO_2^- to allow handy detection of traces of NO_x^- for water and wastewater operators (Zhang and Wu, 1986; Takeda and Fujiwara, 1993; Motomizu and Sanada, 1995). However, up to date, few applications have been reported out of laboratory for real waters using this approach, suggesting that there are probably some unresolved problems that require clarification and further understandings.

In order to achieve better transformation efficiency, an in-depth understanding of the kinetics and influencing factors is needed. Based on existing information, •OH was believed to be responsible for the NH_3/NH_4^+ photo-oxidation in TiO_2 or H_2O_2-based methods (Lee et al., 2002; Huang et al., 2008). Hence, the additions of H_2O_2 are expected to promote transformation of NH_3/NH_4^+. However, contrary to expectations, lower-than-expected removals of NH_3/NH_4^+ via UV/H_2O_2 was observed even with sufficient dosages H_2O_2 (Huang et al., 2008), suggesting that scavenging effect of •OH was probably present and therefore a higher NH_3/NH_4^+ oxidation may require consideration of other important factors and/or other approaches (Zhu et al., 2005). Hence, the influences of pH, H_2O_2, H_2O_2 dosing method, and feeding NH_3/NH_4^+ concentration on NH_3/NH_4^+ removal deserve to be further explored.

Herein, we systematically examined three photolysis processes step-by-step, including: 1) photo-oxidation of NH_3/NH_4^+ to yield NO_2^- and NO_3^- in the presence of H_2O_2; 2) photo-oxidation of NO_2^- to produce NO_3^- with H_2O_2; and 3) photo-reduction of NO_3^- to form NO_2^- without H_2O_2. Low pressure UV lamps emitting 254 nm wavelength (UV_{254nm}) were employed as the energy source, and H_2O_2 was used as the only oxidant to yield •OH. In addition, although emphasis were put on the influences of pH and H_2O_2, the effects of H_2O_2 dosing mode and feeding DIN concentration was also evaluated. Noteworthy is that since earlier studies have already provided the details of DIN transformation mechanisms and radical formation pathways (Mack and Bolton, 1999; Huang et al., 2008), this study mainly intended to enhance the DIN transformation efficiency and kinetics, instead of repeating the efforts on mechanistic explorations, despite that the results of this study may also help enhance current understanding of these processes.

2. Materials and methods

2.1. Chemicals

The three dissolved inorganic nitrogen (DIN) compounds used in this study were ammonium chloride, sodium nitrite, and sodium nitrate, all in analytical grades. A stock solution of H_2O_2 (20 g/L) was made by using a 30% reagent grade solution. Sodium hydroxide (NaOH, 1 or 0.1 M) and sulfuric acid (H_2SO_4, 0.1 M) were used to adjust water pH in case of need. All solutions were prepared by ultrapure water with electric resistance of 18.2 MΩ cm and ≤10 μg/L organic carbon.

2.2. Analytical methods

NH_3/NH_4^+ was detected by a spectrophotometer (DR 3900, Hach Co., Ltd.) using the EPA method 350.2, with a method detection limit (MDL) of 0.02 mg-N/L. NO_3^- and NO_2^- were measured by an ion chromatograph (IC2010, Tosoh Inc., Japan) equipped with a SuperIC-AZ column (Tosoh Inc.) and a 100 μL injection loop