Chemosphere xxx (2015) 1–9

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Oxidative degradation of N-Nitrosopyrrolidine by the ozone/UV process: Kinetics and pathways

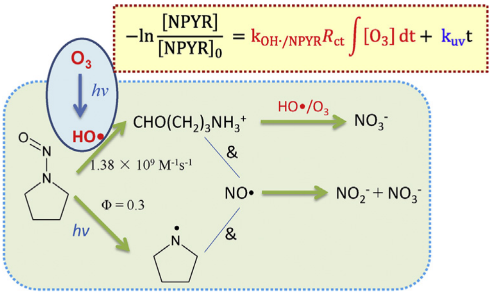
Zhi Chen [a, 1], Jingyun Fang [b, *], Chihhao Fan [c, **], Chii Shang [a, d]

[a] Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
[b] Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, China
[c] Department of Bioenvironmental Systems Engineering, National Taiwan University, Taipei 10617, Taiwan
[d] Hong Kong Branch of Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Hong Kong

HIGHLIGHTS

- Degradation of N-Nitrosopyrrolidine by the O_3/UV process was investigated.
- The degradation was attributable to both UV photolysis and OH• oxidation.
- Synergistic effects of O_3 and UV were observed and more pronounced at higher O_3 dosages.
- An empirical kinetics model was established for NPYR degradation.
- Nitrate is the major inorganic product after the O_3/UV and ozonation treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 October 2015
Received in revised form
13 December 2015
Accepted 14 December 2015
Available online xxx

Handling Editor. J. de Boer.

Keywords:
Nitrosamines
Ozone
Ultraviolet
Advanced oxidation process (AOP)
Hydroxyl radicals
Water treatment

ABSTRACT

N-Nitrosopyrrolidine (NPYR) is an emerging contaminant in drinking water and wastewater. The degradation kinetics and mechanisms of NPYR degradation by the O_3/UV process were investigated and compared with those of UV direct photolysis and ozonation. A synergistic effect of ozone and UV was observed in the degradation of NPYR due to the accelerated production of OH• by ozone photolysis. This effect was more pronounced at higher ozone dosages. The second-order rate constants of NPYR reacting with OH• and ozone was determined to be $1.38\ (\pm\ 0.05) \times 10^9\ M^{-1}\ s^{-1}$ and $0.31\ (\pm\ 0.02)\ M^{-1}\ s^{-1}$, respectively. The quantum yield by direct UV photolysis was 0.3 (± 0.01). An empirical model using Rct (the ratio of the exposure of OH• to that of ozone) was established for NPYR degradation in treated drinking water and showed that the contributions of direct UV photolysis and OH• oxidation on NPYR degradation were both significant. As the reaction proceeded, the contribution by OH• became less important due to the exhausting of ozone. Nitrate was the major product in the O_3/UV process by two possible pathways. One is through the cleavage of nitroso group to form NO• followed by hydrolysis, and the other is the oxidation of the intermediates of amines by ozonation.

---

* Corresponding author.
** Corresponding author.
E-mail addresses: fangjy3@mail.sysu.edu.cn (J. Fang), chfan@ntu.edu.tw (C. Fan).
[1] Present address: Oil & Gas Engineering Company, China Huanqiu Contracting & Engineering Corp. (HQC), Beijing, China.

http://dx.doi.org/10.1016/j.chemosphere.2015.12.046
0045-6535/© 2015 Elsevier Ltd. All rights reserved.

Please cite this article in press as: Chen, Z., et al., Oxidative degradation of N-Nitrosopyrrolidine by the ozone/UV process: Kinetics and pathways, Chemosphere (2015), http://dx.doi.org/10.1016/j.chemosphere.2015.12.046

1. Introduction

Nitrosamines are a group of emerging nitrogen-containing micropollutants classified as probable human carcinogens by U.S. EPA. They have attracted considerable attentions (Mitch et al., 2003; Charrois et al., 2004; Zhao et al., 2006; Krasner et al., 2013) because of their presence in the U.S and Canada drinking water distribution systems at the concentrations up to several hundred ng L^{-1} (Zhao et al., 2006; Krasner et al., 2013; California Department of Public Health (2015)). N-Nitrosodimethylamie (NDMA), a frequently-detected nitrosamine in the aquatic environment, was reported at concentration levels up to 180 ng L^{-1} and several thousand ng L^{-1} in drinking water and wastewater, respectively (Krasner et al., 2009).

Another often-detected nitrosamine is N-Nitrosopyrrolidine (NPYR) which has been also found in drinking water distribution systems at the concentration up to 70.5 ng L^{-1} (Charrois et al., 2004; Zhao et al., 2006, 2008; Krasner et al., 2013). Additionally, the detection of NPYR has been reported at the concentration up to several hundred ng L^{-1} in wastewater and the municipal sludge (Krasner et al., 2009; Padhye et al., 2009). NPYR with concentrations from 53 ng L^{-1} to 127 ng L^{-1} in pool samples has been reported and its existence might pose potential threats to human health due to dermal absorption or inhalation during swimming activities (Pozzi et al., 2011). Given its repetitive occurrence in the aquatic environment and possible 10^{-6} cancer risk at 20 ng L^{-1} concentration level, NPYR is listed in the Unregulated Contaminant Monitoring Regulation (UCMR 2) and the Contaminant Candidate List 3 (CCL 3) by the U.S. EPA (USEPA, 2009, 2012). Despite its potential threats to the public health, the formation of NPYR, possible associations with the nitrogen-containing organic precursor of pyrrolidine which is an important ingredient for pharmaceutical drugs or pesticides, is unclear (Huxel et al., 1974; Pozzi et al., 2011). The existence of other NPYR precursors and their removal by the conventional water and wastewater processes remained to be investigated.

In the real practice of water treatment, the installation of an advance treatment unit has been regarded as an efficient way to control nitrosamines in water. For example, photodecomposition, advanced oxidation (e.g. O_3/H_2O_2, UV/H_2O_2, UV/TiO_2), reverse osmosis and chemical reduction processes have been considered and verified being capable of removing nitrosamines from water efficiently (Gui et al., 2000; Stefan and Bolton, 2002; Sharpless and Linden, 2003; Mezyk et al., 2004; Lee et al., 2005a, 2005b; Davie et al., 2006; Landsman et al., 2007; Lee et al., 2007; Plumlee and Reinhard, 2007; Frierdich et al., 2008; Zhou et al., 2012; Mestankova et al., 2014). In addition to its wide application as a mean for disinfection, UV irradiation is an effective process to decompose nitrosamines including NDMA and NPYR (Stefan and Bolton, 2002; Lee et al., 2005a; Xu et al., 2009). Similar to the photodecomposition of NDMA, UV photolysis initiates the degradation process by breaking the N–N bond of NPYR (Lee et al., 2005a). Pyrrolidine and some low-molecular weight aliphatic amines were identified as the degradation products (Xu et al., 2009). Ozonation is another widely-used water treatment process for oxidation and disinfection (von Gunten, 2003). However, ozonation is less effective in NDMA decomposition at neutral pH (Lee et al., 2007; Mestankova et al., 2014), while increasing solution pH or adding H_2O_2 during ozonation could enhance the removal efficiency of NDMA due to the rapid production of hydroxyl radicals (OH•), a non-selective strong oxidant (Sharpless and Linden, 2003; Zhou et al., 2012). Hydrogen abstraction was found as the first step of NDMA oxidation by OH•, followed by the release of the NO group and the formation of methylamine (MA), nitrite (NO_2^-) and nitrate (NO_3^-) (Lee et al., 2007). The rate constant of NPYR reacting with OH• produced from linear accelerator electron-pulse radiolysis has been reported 2-time higher than that of NDMA with OH• (Landsman et al., 2007). We therefore hypothesized that the simultaneous exposure to UV and ozone (hereafter referred to as the O_3/UV process) might be more effective than to UV irradiation only in degrading NPYR, in which process NPYR can be degraded by both UV and OH•.

In this study, the degradation of NPYR by the O_3/UV process was investigated. The kinetics of NPYR degradation by the O_3/UV process at low ozone dosages (up to 1 mg/L) were studied and compared with those by UV irradiation and ozonation at pH 7 in deionized and treated drinking water. The low ozone dosages were selected to reflect the ozone concentrations in post-treatment of drinking water by end-user water purification devices where NPYR concentrations are expected to be the highest. A kinetic model that considered the degradation by UV photolysis and the oxidation by ozone and OH• was established to delineate the contributions by UV, OH• and ozone on NPYR degradation. Moreover, since there are two nitrogen atoms in NPYR (one in the NO group and the other in the pyrrolidine group) and the NO group is expected to be transformed into NO_2^- and NO_3^- while the pyrrolidine group does not, the mechanisms of NPYR degradation by the O_3/UV process were explored by studying the formation of inorganic products of NO_2^- and NO_3^-.

2. Materials and methods

2.1. Chemicals

N-Nitrosopyrrolidine (NPYR), nitrobenzene (NB), para-chloribenzoic acid (*p*CBA) and tert-butyl alcohol (TBA) of reagent grade were purchased from Sigma–Aldrich. The chemicals of $NaNO_2$, $NaNO_3$, Na_2SO_3, H_2SO_4 and NaOH of reagent grade were purchased from Sigma–Aldrich, and used without further purification. Stock solutions were prepared with deionized water (18.2 MΩ-cm) purified by a NANOpure system (Barnstead). An ozone stock solution was prepared by bubbling ozone/oxygen gas mixture from an ozone generator (Guolin, China) into the deionized water conditioned with ice.

The treated drinking water sample without final disinfection was collected from the Shatin Water Treatment Works in Hong Kong, where the source water from a river is treated through coagulation, sedimentation and filtration processes. The water sample was further filtered through a 0.45-μm membrane before degradation experiments. The basic characteristics of the water sample were measured as following: pH 7.0, DOC 0.6 mg L^{-1}, and alkalinity 25 mg L^{-1} as $CaCO_3$.

2.2. Experimental procedures

UV irradiation was carried out using a bench-scale UV irradiator, consisting of four LP Hg UV lamps (254 nm, G15T8, 10 W, Sankyo Denki) housed in a shuttered box, with a vertical tube extending from the bottom (Fang et al., 2014). A 250 mL sample with a water depth of 5 cm was placed in a glass reactor with an inner diameter of 8 cm, which was directly beneath the collimated tube for UV treatment. A quartz cap was used to reduce the volatilization of ozone and the sample was stirred rapidly at ambient temperature 22 (± 2) °C. The distance between the solution and the lamps was about 30 cm. The photon flux (I_0) entering the solution was determined to be 0.062 (± 0.003) μE s^{-1} in a separate experiment using iodide/iodate chemical actinometry (Bolton et al., 2011). Since the UV light in the reactor was not a standard collimated beam (Fang et al., 2014), the effective path length (L) was used to characterize the photoreactor and measured to be 4.9 ± 0.1 cm from

Please cite this article in press as: Chen, Z., et al., Oxidative degradation of N-Nitrosopyrrolidine by the ozone/UV process: Kinetics and pathways, Chemosphere (2015), http://dx.doi.org/10.1016/j.chemosphere.2015.12.046