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Transformation of aminopyrine during ozonation: Characteristics and pathways

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HIGHLIGHTS

- H_2O_2 addition improved aminopyrine degradation efficiency during ozonation.
- Three degradation pathways were proposed by 21 aminopyrine ozonation by-products.
- Some oxidation by-products could lead to toxicity accumulation during ozonation.
- O_3-BAC showed well removal efficiency for aminopyrine and its oxidation by-products.

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ABSTRACT

Degradation efficiency, mechanism and intermediates' toxicity of aminopyrine (an analgesic and antipyretic drug) upon ozonation were investigated under different oxidation approaches. Results showed that hydroxyl radical pattern (O_3 with H_2O_2 addition) had the highest removal efficiency in aminopyrine, UV_{254} and especially DOC. A total of 21 intermediates from aminopyrine oxidation were assessed by UPLC-Q-TOF-MS, which indicated that aminopyrine was degraded mainly from three pathways. The pyrazole ring break pathway consisted of pyrazole ring opening, demethylation, functional group loss, hydroxylation and substitution, demonstrating the major pathway for aminopyrine oxidation. The demethylation at ^{6}N position pathway was composed of demethylation at the ^{6}N position and further substitution at the ^{4}C position, principally occurred during the aminopyrine ozonation with H_2O_2 addition. The dephenylization pathway was proved by only one intermediate (P21) during the aminopyrine ozonation without addition. Besides, lots of hydroxylated and di-hydroxylated intermediates were detected primarily during the oxidation without addition and with H_2O_2 addition. The toxicity of these intermediates by EPA TEST showed that some of them were intended to be more toxic than aminopyrine. Further test from the toxicity of oxidized mixtures to the bioluminescent marine bacterium *Vibrio fischeri* demonstrated the samples could lead to the accumulation of toxic transformation products, especially for those by the oxidation with HCO_3^- addition. Finally, an O_3-BAC system was applied to treat the raw water spiked with aminopyrine. Although three of the by-products could be detected during aminopyrine ozonation, they were expected to be easily removed by BAC adsorption.

1. Introduction

The occurrence, fate and behavior of pharmaceuticals and personal-care products (PPCPs) in the aquatic environment have been recognized as one of the emerging issues in environmental chemistry as well as the major challenges for the preservation and sustainability of the environment [1]. Although they can fade away by dilution, partial degradation and sorption during migration and transformation process, PPCPs may also occur at low concentrations from the ng L^{-1} to μg L^{-1} range in the aquatic environment [2,3]. Thus, residues of these compounds might get access into drinking water and cause the potential risk in drinking water on human health due to their biologically active nature, accumulation and persistent physico-chemical properties, if drinking water treatment is not able to remove them completely. The presence of small concentration of PPCPs has been associated with chronic toxicity [4,5], endocrine disruption [6] and even the development of pathogen resistance [7].

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Conventional drinking water treatment approaches such as coagulation/flocculation and sand filtration are reported to not effective with regard to the removal of most PPCPs, mainly influenced by the physical–chemical properties of target pollutants [8]. In order to reduce the risk of these contaminants and to meet future challenges, novel methods especially advanced oxidation processes (AOPs) have been introduced to degrade PPCPs [9]. AOPs, characterized by the generation of hydroxyl radicals (OH·) as the primary oxidants, is able to chemically destruct molecular structures of the target pollutants and/or transform them into less toxic pollutants and even non-toxic water and carbon dioxide [10,11]. Among the variety of AOPs such as ozone-based (O_3-based) oxidation, ultrasound-based oxidation and UV-based oxidation processes, ozonation is widely used in water treatment, especially in drinking water disinfection [12,13]. Ozonation is advantageous in drinking water treatment for a number of reasons: (1) it can remove taste and odor compounds, organic micropollutants, and disinfect pathogenic microorganism at lower dosages in shorter contact time compared to other disinfectants; (2) it is able to enhance the efficiency of the coagulation/flocculation process during water treatment; (3) it reduces the formation potential of hazardous chlorination by-products by oxidizing their precursors [14].

Aminopyrine as an over-the-counter drug, has been extensively used for decades since 1990s with its analgesic, antipyretic and anti-inflammatory properties [15]. Although it is no longer licensed for use in most countries because of the risk of agranulocytosis, it is still used in "herbal" medication on treating febrile patients in many countries, especially in China [16]. Furthermore, due to its biochemical-persistence, removal efficiency for aminopyrine in wastewater treatment plant was only ~38%, which mean sizable part of aminopyrine would be discharged into natural waters and subsequently threaten human health [17]. Given low removal efficiencies of aminopyrine by conventional wastewater and drinking water treatment, aminopyrine is supposed to widely exist throughout the environment and the elimination of aminopyrine in the water treatment plant (WTP) may be largely attributed to the disinfection process [18,19]. A survey about the occurrence and distribution of aminopyrine in WTPs in Beijing revealed that aminopyrine widely existed in the raw water at the concentration ranged from 0.17 to 0.64 ng L^{-1}, and ozonation showed high removal efficiency of it [20]. However, even though ozonation can remove the target drugs quickly and effectively, oxidation process could not mineralize the organics completely and in some cases, highly toxic by-products might be produced inevitably [21]. These intermediates often differ in their toxicity and potential for accumulation compared to the parent compounds. Moreover, these undesired degradation by-products may be more difficult to be removed than the original compound and become new chemical entities within the environment or in the drinking water [22]. Therefore, evaluation, determination and removal of these by-products as well as aminopyrine after ozonation is also important considerations for drinking water safety purpose. Unfortunately, most of the previous studies regarding aminopyrine removal in drinking water treatment were mainly focused on the degradation efficiency of oxidation [18,23], and few publications reported degradation intermediates and mechanism of aminopyrine by chlorination [24]. To the best of our knowledge, there has not been any investigation on degradation mechanism and intermediates' toxicity of aminopyrine by ozonation.

In the light of these concerns, the objective of this work was to technically evaluate the degradation efficiency, mechanism and intermediates' toxicity of aminopyrine during the different O_3-based oxidation processes such as single ozonation, ozonation with OH· promoter addition and ozonation with OH· scavenger addition. The elaboration of degradation mechanism and the characteristics of intermediates by the different oxidation approaches are the main subject of this paper. Firstly, aminopyrine degradation efficiency and the transformation products' characteristics during the different oxidation approaches were investigated. Secondly, the tentative degradation pathway for aminopyrine ozonation was proposed for the first time. Thirdly, toxicity of the intermediate products obtained by ozonation is estimated using US Environmental Protection Agency Toxicity Estimation Software Tool (US-EPA TEST) and further affirmed by the bioluminescence inhibition test. Finally, removal efficiencies of aminopyrine and its ozonation by-products were evaluated in an ozonation coupled with biological activated carbon adsorption (O_3-BAC) system during the raw water treatment.

2. Materials and methods

2.1. Chemicals and reagents

Aminopyrine with physico-chemical characteristics of formula $C_{13}H_{17}N_3O$, molecular weight 231.15 and density 1.17 g cm^{-3} was purchased from Sigma–Aldrich (USA), and used without further purification. Aminopyrine stock solution of 8.65 mM was prepared in ultrapure deionized water, stored in the amber glass bottle at 4 °C, and diluted as necessary. HPLC-grade methanol (MeOH) and acetonitrile (ACN) were supplied from Merck (Darmstadt, Germany). Formic acid (0.1%) for HPLC–MS was bought from Sigma–Aldrich (USA). Other reagents used in this study were obtained from Sinopharm (Shanghai, China). Ultrapure deionized water (18 MΩ cm) was prepared in the lab using a Milli-Q water system (Millipore, USA).

The raw water was collected from an intake in the Meiliang Bay of Taihu Lake, where is one of the main potable water sources of Wuxi City. The quality of the raw water is shown in Supplementary material Table S1.

2.2. Bench-scale ozonation experiments

For aminopyrine degradation efficiency and mechanism investigation, ozonation experiments were performed in a 100 mL cylindrical jacketed borosilicate glass reactor, in batch mode [25]. Firstly, the O_3 stock solution was freshly obtained by bubbling O_3 gas through the phosphate buffer solution (5 mM with pH 7.0) maintained at 25 ± 1 °C to maximize O_3 dissolution. O_3 was produced from purified oxygen gas (99.8%) by a COM-AD-01 O_3 generator (Anseros, Germany). Aqueous concentration of O_3 in the stock solution was tested right before the ozonation experiments. Secondly, the ozonation was started by injecting aminopyrine solution into the O_3 stock solution by using a gas-tight syringe, and shaking the reaction vessel vigorously for 10 s. Temperature of the reaction was kept at 25 ± 1 °C. If needed, radical promoter (H_2O_2) or radical scavenger (HCO_3^-) was added into the O_3 stock solution right before the aminopyrine solution injection. Finally, samples for analysis were obtained at defined time intervals and quenched by aeration with nitrogen gas to remove the residual O_3.

Bench-scale experiments for aminopyrine ozonation efficiency were mainly carried out under conditions of the aminopyrine initial concentration 0.173 mM, pH 7.0 and the O_3 dosage of 5:1 (O_3:aminopyrine). Different oxidation approaches such as molecular O_3 pathway, OH· pathway and ozonation were examined by the addition of OH· scavenger bicarbonate (HCO_3^-) at the dosage of 5:1 (HCO_3^-:O_3), addition of OH· promoter hydrogen peroxide (H_2O_2) at the dosage of 1:2 (H_2O_2:O_3) and no addition, respectively. All the experiments were repeated at least 3 times. For aminopyrine ozonation mechanism investigation, experiments were also performed with the aminopyrine initial concentration 0.173 mM and