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Degradation mechanism of anatoxin-a in UV-C/H_2O_2 reaction

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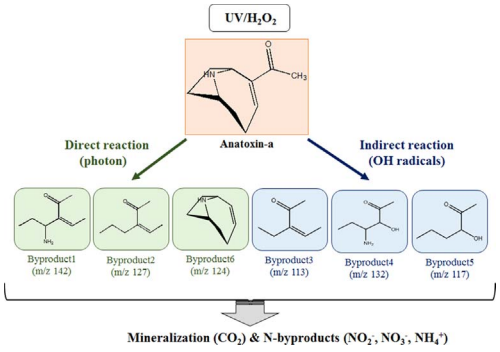
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the kinetics and removal mechanism of anatoxin-a ($C_{10}H_{15}NO$) during a UV-C/H_2O_2 reaction were investigated. The removal of anatoxin-a was more effective during a UV-C/H_2O_2 reaction than with either UV photolysis or H_2O_2 alone, due to the effective production of hydroxyl (OH) radicals. The UV-C/H_2O_2 reaction of anatoxin-a resulted in an approximately 60% decrease in total organic carbon (TOC) within 420 min, while 45% of the carbon in anatoxin-a was converted into acetate, and most of the nitrogen in anatoxin-a was converted into NH_4^+, NO_2^-, and NO_3^- ions. More than 50% of the nitrogen in anatoxin-a was mineralized, mainly into NO_3^- ions, and complete nitrogen recovery was achieved after 120 min of the UV-C/H_2O_2 reaction. Using liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS), we identified six degradation by-products in the UV-C/H_2O_2 reaction ($[M+H]^+$ = 142, 127, 113, 132, 117, and 124, respectively), which were further degraded as the reaction continued. Using these by-products, we proposed a degradation pathway for anatoxin-a during the UV-C/H_2O_2 reaction. Our results indicate that anatoxin-a can be effectively removed by a UV-C/H_2O_2 reaction during water treatment processes.

1. Introduction

Cyanobacteria are prokaryotic photoautotrophs that secrete various secondary metabolites. Certain cyanobacteria produce cyanotoxins including hepatotoxins (microcystins, nodularins, and cylindrospermopsin), neurotoxins (anatoxin-a and saxitoxin), and dermatotoxins [1,2]. There is much concern regarding the secondary metabolites of cyanobacteria, because it has been reported that they are harmful to humans, fish, and animals, despite the low range of concentrations at which they are typically present in the environment [3,4]. Through the ingestion of recreational water, untreated drinking water, and contaminated fish, humans can be exposed to cyanotoxins [5,6].

Anatoxin-a ($C_{10}H_{15}NO$) is a neurotoxin secreted mainly by

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Anabaena flos-aqueae, *Aphanizomenon*, and *Microcystis* [7]. It is an alkaloid neurotoxin, and is not only a tumor promoter but also a tumor initiator. Anatoxin-a can mimic acetylcholine by its amine and carbonyl functionality binding to the acetylcholine receptors [2,8,9]. In the environment, anatoxin-a has been detected at levels of 120 μg/L in lake water in Poland [10], 5.2–35.7 μg/L in fresh water, and 0.71–10.18 μg in plants in the United States [11]. Concentrations of anatoxin-a in water and algae materials in Korea reportedly range from 0.01–0.08 μg/L to 0.61–8.68 μg/g (dry wt), respectively [12].

During drinking water treatment processes, intracellular cyanotoxins such as anatoxin-a can also be released through the degradation of cyanobacteria [13]. Therefore, these residual cyanotoxins in water must be removed during water treatment processes. Cyanobacteria and intracellular cyanotoxins can be removed by conventional water treatment processes such as coagulation, flocculation, sedimentation, and sand filtration. However, extracellular cyanotoxins in the dissolved phase cannot be degraded effectively by such processes [14].

As an alternative, advanced oxidation processes (AOPs) can be applied for the removal of anatoxin-a in water. The degradation of anatoxin-a in water has been studied using ozone (O_3), hydrogen peroxide (H_2O_2), chlorine (Cl), chloroamine (NH_2Cl), and potassium permanganate ($KMnO_4$); while anatoxin-a is not effectively removed by chlorine and chloramine [15], ozone and $KMnO_4$ have proven effective in degrading the anatoxin-a molecule [9,15,16]. Al Momani [17] observed that the combinations of H_2O_2 or Fe(II) with ozone (O_3/H_2O_2 and O_3/Fe(II)) were more efficient than O_3 or H_2O_2 oxidation alone. However, ozonation related process can produce toxic ozonation byproducts.

The UV related AOP processes were effective in degrading anatoxin-a. UV was able to decompose anatoxin-a by direct photolysis or indirect photolysis through an AOP process. UV/H_2O_2 reaction involves the production of hydroxyl (OH) radicals produced by the hemolytic cleavage of H_2O_2, with a wavelength shorter than 280 nm [18–20]. Compared with other AOPs, the UV/H_2O_2 reaction forms two OH radicals due to a single-step dissociation of H_2O_2. Mineralization of organic compounds can be achieved under appropriate conditions without phase transition problems [21].

Recent studies have examined the removal of anatoxin-a using vacuum-UV photolysis and UV/H_2O_2 [22], and UV-C LED and UV-C LED/H_2O_2 reactions [23]. Afzal et al. [22] reported that low pressure UV lamp was not effective in degrading anatoxin-a through direct photolysis; however medium pressure UV lamp was able to degrade 88% of anatoxin-a. Use of H_2O_2 along with low pressure UV lamp resulted in above 70% degradation of anatoxin-a. Verma and Sillanpää [23] observed that 96% removal of anatoxin-a was achieved by photolysis using UV-C LED, and 79% removal was achieved with UV-C/H_2O_2 process in raw water sample. Verma et al. [24] also found that UV-C/peroxylmonosulfate (PMS) were efficient in the degradation of anatoxin-a, even in a lake water. However, these UV related AOP processes and the UV/H_2O_2 reaction only observed degradation kinetics of anatoxin-a. Although anatoxin-a can be removed from water, the major concern is the formation of unknown by-products that can lead to the secondary contamination of drinking water. Until now, no studies have examined anatoxin-a degradation by-products or pathways during the UV/H_2O_2 reaction or any AOP process.

In this study, we investigated the kinetics and removal mechanism of anatoxin-a during a UV-C/H_2O_2 reaction, and compared it with UV photolysis and a H_2O_2 only reaction. To investigate the degradation mechanism of anatoxin-a during the UV-C/H_2O_2 reaction, we examined the mineralization of anatoxin-a by measuring various parameters such as total organic carbon (TOC), acetate, NH_4^+, NO_2^-, and NO_3^- ions, and identified the organic by-products formed during the UV-C/H_2O_2 reaction using liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS) and ACD/MS Fragmenter software. Finally, using the by-products identified, we proposed a possible degradation pathway of anatoxin-a during the UV-C/H_2O_2 reaction.

2. Materials and methods

2.1. Chemicals

Anatoxin-a ($C_{10}H_{15}NO$) was purchased from Enzo Life Sciences (Farmingdale, NY, USA). Table S1 shows the physicochemical properties of anatoxin-a. A stock solution of anatoxin-a was prepared by dissolving 1 mg anatoxin-a in 1 mL Milli-Q water deionized water (Millipore, Billerica, MA, USA). A 10 mg/L stock solution was prepared by diluting with deionized water. The stock solution was kept in darkness at −20 °C to inhibit degradation.

Hydrogen peroxide (30%, v/v), formic acid (FA: 88%, v/v), and catalase (10,000–40,000 units/mg protein) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile and distilled water (J.T. Baker, Waltham, MA, USA) were used as mobile phase eluents for LC-ESI-MS/MS.

2.2. Experimental procedures

To investigate the rate of anatoxin-a removal, UV photolysis and UV-C/H_2O_2 reactions were performed using a UV photoreactor. A schematic diagram of the photolysis reactor system is shown in Fig. 1(a). The reactor consisted of a 2-L glass bottle, a stirrer, and a UV-C lamp (6 W, 254 nm, Sankyo Electronics Co., Ltd., Inazawa, Japan). UV intensity was measured with a radiometer (VLX-3W Radiometer 9811–50, Cole-Parmer, Vernon Hills, IL, USA). The single UV lamp had

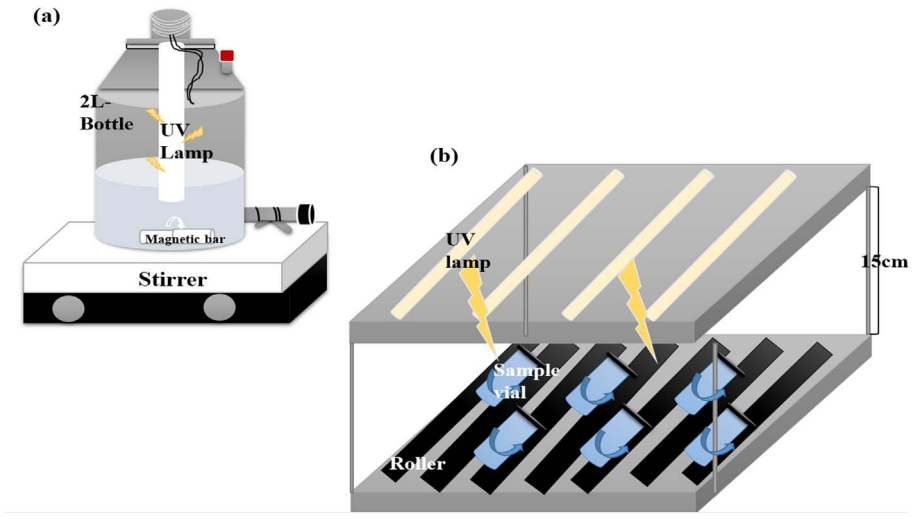

Fig. 1. Schematic diagram of the photolytic reactors.