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Kinetics and mechanisms of cylindrospermopsin destruction by sulfate radical-based advanced oxidation processes

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ABSTRACT

Cylindrospermopsin (CYN) is a potent cyanobacterial toxin frequently found in water bodies worldwide raising concerns over the safety of drinking and recreational waters. A number of technologies have been investigated to remove and/or degrade cyanotoxins with advanced oxidation processes (AOPs) being among the most promising and effective for water detoxification. In this study, the degradation of CYN by sulfate radical-based UV-254 nm-AOPs was evaluated. The UV/$S_2O_8^{2-}$ (UV/peroxydisulfate) was more efficient than UV/HSO_5^- (UV/peroxysulfate) and UV/H_2O_2 (UV/hydrogen peroxide) processes when natural water samples were used as reaction matrices. The observed UV fluence based *pseudo-first-order* rate constants followed the expected order of radical quantum yields. The presence of 200 μM natural organic matter (NOM) as carbon slightly inhibited the destruction of CYN; 1.24 mg L^{-1} NO_3^- (nitrate) had no significant influence on the removal efficiency and 50 μg L^{-1} Fe^{2+} [iron (2+)] or Cu^{2+} [copper (2+)] improved the performance of UV/$S_2O_8^{2-}$. The addition of tert-butyl alcohol (t-BuOH; hydroxyl radical scavenger) in the reaction yielded byproducts that indicated specific sites in CYN preferentially attacked by sulfate radicals (SRs). The predominant CYN degradation byproduct was P_{448} consistent with fragmentation of the C5=C6 bond of the uracil ring. The subsequent formation of P_{420} and P_{392} through a stepwise loss of carbonyl group(s) further supported the fragmentation pathway at C5=C6. The byproduct P_{432} was identified exclusively as mono-hydroxylation of CYN at tricyclic guanidine ring, whereas P_{414} was detected as dehydrogenation at the tricyclic ring. The elimination of sulfate group and the opening of tricyclic ring were also observed. The possible degradation pathways of CYN by SR-AOP were presented.

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1. Introduction

Cyanobacterial harmful algal blooms in aquatic environments are a common and worldwide problem causing a significant adverse impact on public health and ecosystems (Smith, 2003; Paerl et al., 2011). Cyanobacteria produce a wide variety of secondary metabolites, and most importantly, potent toxins frequently called cyanobacterial toxins or cyanotoxins known to affect a wide range of living organisms including humans (Codd et al., 2005; Ibelings and Chorus, 2007; Merel et al., 2013; Pearson et al., 2010). Cylindrospermopsin (CYN, Fig. 1) is one of the most widely distributed cyanotoxins in water bodies (de la Cruz et al., 2013; Merel et al., 2013). CYN can be produced by a large group of cyanobacteria that are highly adaptive and invasive and have been detected in tropical, subtropical and even in temperate areas (de la Cruz et al., 2013; Kinnear, 2010). Compared with microcystins, CYN can be actively released into the environment leading to higher extracellular toxin concentrations than the intracellular levels (de la Cruz et al., 2013; Schembri et al., 2001). No regulation on this cyanotoxin is currently available, although a guideline safety value of 1 μg L^{-1} was proposed (Humpage and Falconer, 2003). It has also been included in the US EPA Contaminant Candidate List 3 that is being evaluated within the regulatory framework (US EPA, 2009).

CYN is highly water soluble and stable in a wide range of light (including UV light), heat, and pH conditions and may thus be resistant to some standard water treatment processes (de la Cruz et al., 2013; Kinnear, 2010; Merel et al., 2013). Conventional water treatment technologies have been evaluated for the removal/degradation of CYN and have shown to be unreliable especially when the concentration of natural organic matter (NOM) is high (de la Cruz et al., 2013; Dixon et al., 2011; Ho et al., 2011; Onstad et al., 2007). Therefore, it is desirable to develop an efficient treatment technology for the detoxification of water contaminated with such micropollutants. Advanced oxidation processes (AOPs) have received considerable attention as an alternative for the destruction of recalcitrant organic contaminants and biological toxins. Most of the AOPs evaluated for the degradation of cyanotoxins involve the generation of hydroxyl radical ($^{\bullet}$OH; HR-AOP) as the main oxidizing species (He et al., 2012; Onstad et al., 2007; Sharma et al., 2012). Previous studies on the heterogeneous photocatalytic degradation of CYN via hydroxyl radical reaction revealed insignificant adsorption of CYN onto the catalyst materials with an effective elimination of CYN by UV activated Evonik P25 TiO_2 or UV-100 TiO_2 (Senogles et al., 2001), as well as UV–vis activated anatase–brookite–rutile polymorphic TiO_2 materials (Zhang et al., 2014). With the second order reaction rate constant of CYN with hydroxyl radical reported to be 5.5, 5.08 and 5.1×10^9 M^{-1} s^{-1} by either pulse radiolysis (Song et al., 2012) or by competition studies (He et al., 2013; Onstad et al., 2007), HR-AOPs are most likely effective in degrading CYN. Alternatively, sulfate radical ($SO_4^{\bullet -}$; SR-AOP), with an oxidizing ability comparable to $^{\bullet}$OH, has been previously reported (Antoniou et al., 2010; He et al., 2013). In some cases, SR-AOPs may be more advantageous than HR-AOPs, due to the slower reaction of NOM with SRs (Gara et al., 2009).

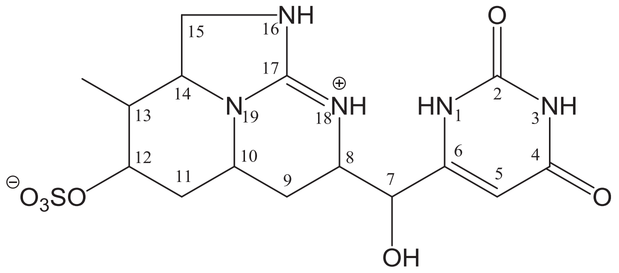

Fig. 1 – Structure of cylindrospermopsin (CYN), *m/z* 416, $C_{15}H_{21}N_5O_7S$.

Peroxydisulfate ($S_2O_8^{2-}$, commonly known as persulfate) is the most commonly used chemical for the generation of SRs (Tsitonaki et al., 2010). The radical quantum yields of persulfate by UV-254 nm in de-oxygenated (1.4) and oxygen saturated (1.8) water are much higher than those of peroxysulfate (HSO_5^-, commonly known as peroxymonosulfate) and hydrogen peroxide (H_2O_2), 1.04 and 1.0, respectively, as shown in Eqs (1)–(3) (Baxendale and Wilson, 1957; Guan et al., 2011; Mark et al., 1990). Previous studies using these three UV-254 nm-based AOPs on the removal of CYN in Milli-Q water revealed that UV/$S_2O_8^{2-}$ was the most efficient followed by UV/HSO_5^- and UV/H_2O_2 at an initial concentration of 1 μM CYN, 1 mM individual peroxide and 5 mM phosphate buffer (pH 7.4, He et al., 2013). Hence, UV/$S_2O_8^{2-}$ is highly effective in the destruction of organic pollutants in water.

$$S_2O_8^{2-} \rightarrow h\nu \rightarrow 2SO_4^{\bullet -} \quad \Phi = 1.4(\text{de}-\text{oxygenated}), \; 1.8(\text{oxygen saturated}) \tag{1}$$

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \quad \Phi = 1.0 \tag{2}$$

$$HSO_5^- + h\nu \rightarrow SO_4^{\bullet -} + {}^{\bullet}OH \quad \Phi = 1.04 \tag{3}$$

The reaction mechanism of HR with CYN has been reported in detail previously (He et al., 2014), but only limited information is available on the kinetic and mechanistic reaction of SR with CYN. SR is strongly electrophilic and can function as a one electron transfer oxidant (Davies et al., 1985), with three possible routes of reaction: (1) formation of sulfate adduct at the unsaturated double bond, with a subsequent formation of active carbocation for further reaction; (2) electron abstraction at the carboxylate anion, with the loss of CO_2, and (3) relatively weak hydrogen abstraction (H-abstraction), so that the corresponding organic radical can go through similar reaction pathways as those in HR reaction (as shown in Figs. S1–S3, Davies et al., 1985; Norman et al., 1970).

In this study, the degradation of CYN by UV 254 nm-AOPs (i.e., UV/$S_2O_8^{2-}$, UV/HSO_5^-, and UV/H_2O_2), with a specific focus on SR-AOPs, was evaluated. The influence of natural radical scavengers in various natural water samples was determined. The simultaneous activation of persulfate by UV and transition metals, i.e., Fe^{2+} [iron (2+)] or Cu^{2+} [copper (2+)], were also investigated on both the destruction of CYN and the formation/degradation of the byproducts that were detected by mass spectrometry. A common HR scavenger, tert-butyl alcohol (t-BuOH), was used to examine the type of oxidizing radical species responsible for the reaction. Finally, the