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The effect of basic pH and carbonate ion on the mechanism of photocatalytic destruction of cylindrospermopsin

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ABSTRACT

This study investigated the mechanistic effects of basic pH and the presence of high carbonate concentration on the TiO₂ photocatalytic degradation of the cyanobacterial toxin cylindrospermopsin (CYN). High-performance liquid chromatography combined with quadrupole time-of-flight electrospray ionization tandem mass spectrometry (LC/Q-TOF-ESI-MS) was employed for the identification of reaction byproducts. The reaction pathways were proposed based on the identified degradation byproducts and radical chemistry. In high pH system (pH = 10.5) similar reaction byproducts as those in neutral pH system were identified. However, high pH appeared to inhibit sulfate elimination with less sulfate elimination byproducts detected. In the presence of carbonate in the photocatalytic process, hydroxyl radical reaction would be largely inhibited since carbonate ion would react with hydroxyl radical to form carbonate radical. The second order rate constant of carbonate radical with CYN was estimated to be $1.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, which is much smaller than that of hydroxyl radical. However, the more significant abundance of carbonate radical in the reaction solution strongly contributed to the transformation of CYN. Carbonate radical has higher reaction selectivity than hydroxyl radical and hence, played a different role in the photocatalytic reaction. It would promote the formation of byproduct *m/z* 420.12 which has not been identified in the other two studied photocatalytic systems. Besides, the presence of carbonate ion may hinder the removal of toxicity originated from uracil moiety due to the low reaction activity of carbonate radical with uracil moiety in CYN molecule. This work would further support the application of photocatalytic technologies for CYN treatment and provide fundamental information for the complete assessment of CYN removal by using TiO₂ photocatalysis process.

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List of abbreviation

4-CP	4-Cyanophenol
ATZ	Atrazine
AOPs	Advanced oxidation processes
CYN	Cylindrospermopsin
CO ₃ ^{•-}	Carbonate radicals
ESI	Electrospray ionization
HPLC	High performance liquid chromatography
IEP	Isoelectric point
k _{A/B}	Second order rate constant for the reaction of A with •B radical
k _{obs(A)}	Observed degradation rate constant of A
m/z	Mass to charge ratio
MS	Mass spectrometry
•OH	Hydroxyl radical
P25_CO ₃ ²⁻	System with P25 TiO ₂ in the presence of Na ₂ CO ₃ (1.5 mM, pH = 10.5)
P25_HighpH	System with P25 TiO ₂ at high pH (pH = 10.5)
P25_NA	System with P25 TiO ₂ at unadjusted pH (pH = 5.5)
SI	Supporting information
TOF	Time-of-flight

1. Introduction

Cyanotoxins are a group of emerging contaminants that can be produced by certain cyanobacteria as secondary metabolites and released during their cell lysis (Carmichael, 1992; Wiegand and Pflugmacher, 2005). One of the most problematic cyanotoxins, cylindrospermopsin (CYN), has received great public attention due to its high toxicity, prevalent distribution and widespread CYN-producing species (such as strains of *Cylindrospermopsis raciborskii*, *Anabaena bergii*, *Aphanizomenon ovalisporum*, *Rhaphidiopsis curvata* and *Umezakia natans*) in tropical, subtropical and temperate areas (Fergusson and Saint, 2003; Metcalf et al., 2004; Ohtani et al., 1992). The biosynthetic pathways of CYN in *Cylindrospermopsis raciborskii* have been proposed based on the identified gene cluster for the biosynthesis of CYN (Mihali et al., 2008). CYN is a tricyclic guanidine alkaloid containing a hydroxymethyl uracil moiety with high water-solubility. Generally, this toxin is an inhibitor for the synthesis of protein and glutathione (Froschio et al., 2003; Lopez-Alonso et al., 2013; Young et al., 2008). It has a negative effect on many organs and has been reported as a potent hepatotoxin, cytotoxin and genotoxin (Bazin et al., 2010; Mazmouz et al., 2010; Ohtani et al., 1992). Moreover, CYN has been proven to have carcinogenic potential at a concentration as low as 1×10^{-7} µg/L (Maire et al., 2010). The cattle deaths and human poisonings in Palm Island of Australia in 1979 have been attributed to the CYN contamination in drinking water (Griffiths and Saker, 2003; Wiegand and Pflugmacher, 2005). Besides, the natural photodegradation of CYN is very limited and highly dependent on UV-A radiation (Wormer et al., 2010). Therefore, the effective treatment for this toxin is of extreme significance for public health and environmental safety.

TiO₂ photocatalysis has been applied in many areas including water treatment for emerging contaminants (Antoniou et al., 2009b; Miranda-Garcia et al., 2011; Pelaez et al., 2009). It has been proven to be an effective and efficient approach for CYN removal (Senogles et al., 2001; Zhang et al., 2014). Hydroxyl radical (•OH) is considered to be the main reactive agent in the TiO₂ photocatalysis process (Antoniou et al., 2009a; Kim and Choi, 2002; Tachikawa et al., 2007). Our previous work has shown that hydroxylation and ring opening on the hydroxymethyl uracil moiety and tricyclic guanidine moiety, along with sulfate elimination, are the main reaction pathways for the TiO₂ photocatalytic degradation of CYN in water (Zhang et al., 2015). Since the hydroxymethyl uracil moiety is believed to be responsible for the toxicity of CYN (Banker et al., 2001; Norris et al., 1999), the toxicity of water sample after TiO₂ photocatalytic treatment can be reduced (Zhang et al., 2015).

In the molecule of CYN, there is a negatively charged sulfate group and a positively charged guanidine group. The pK_a of CYN was estimated to be around 8.8 (Onstad et al., 2007). Therefore, the CYN molecule has both negatively and positively charged groups at pH < 8.8, while the CYN molecule is negatively charged at high pH condition (e.g., pH = 10.5). The isoelectric point (IEP) of TiO₂ catalysts is around 7 (Gumy et al., 2006; Zhang et al., 2014), which means TiO₂ would be positively charged at acidic pH and negatively charged at basic pH. In our previous study (Zhang et al., 2015), we have identified the reaction byproducts and pathways of photocatalytic degradation of CYN at pH around 5.5 (without pH adjustment). Hence, it would be very scientifically meaningful to explore the differences in the mechanism at a high pH. Besides, carbonates are widely present in various waters, and would therefore significantly affect the chemistry of the photocatalytic process (Dimitrijevic et al., 2011). When carbonate ions are in the system, they would result in not only higher pH but also other possible effects. Many studies have shown that •OH radical generated by photocatalytic activity can react with carbonate and bicarbonate ions to form carbonate radicals (CO₃^{•-}) with second-order reaction rate constants of 3.9×10^8 and 8.5×10^6 M⁻¹s⁻¹, respectively (He et al., 2012; Pelaez et al., 2011). Moreover, the concentration of CO₃^{•-} in surface water under solar light has been estimated to be two orders of magnitude higher than that of •OH radical (Sulzberger et al., 1997). Thus, it is interesting to examine the effect of carbonate (or the generated carbonate radicals) on the photocatalytic degradation byproducts and pathways of CYN.

In this study, we report for the first time the effects of initial high pH (pH = 10.5) and the presence of carbonate ion on the TiO₂ photocatalytic degradation of CYN from the mechanism aspects, including the reaction byproducts and pathways. The reaction byproducts were detected and identified by using a high-performance liquid chromatography combined with quadrupole time-of-flight electrospray ionization tandem mass spectrometry (LC/Q-TOF-ESI-MS). The degradation pathways were proposed based on the identified byproducts and radical chemistry. This work can provide not only better understanding about the mechanism of CYN photocatalytic destruction but also further insights on the assessment of this technology for the treatment of CYN contaminated water.

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