Applied Catalysis B: Environmental 150–151 (2014) 380–388

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

# Bismuth oxybromide promoted detoxification of cylindrospermopsin under UV and visible light illumination

Shulian Wang[a,b], Wanhong Ma[a], Yanfen Fang[a], Manke Jia[a], Yingping Huang[a,*]

[a] Engineering Research Center of Eco-environment in Three Gorges Reservoir Region, Ministry of Education, China Three Gorges University, Yichang 443002, China

[b] Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan 430072, China

ARTICLE INFO

*Article history:*
Received 17 September 2013
Received in revised form
23 November 2013
Accepted 8 December 2013
Available online 21 December 2013

*Keywords:*
Cylindrospermopsin
Uracil
BiOBr
Degradation
Mechanism

ABSTRACT

Bismuth oxybromide (BiOBr) was prepared and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and UV–vis diffuse reflectance spectroscopy (DRS). The BiOBr promoted detoxification of cylindrospermopsin (CYN) under UV ($\lambda < 350$ nm) and visible light ($\lambda > 420$ nm) illumination was studied. The results revealed that the toxic uracil unit of CYN was removed, and the carboxylic group of the degraded product was also decomposed, to give the innoxious tricyclic guanidine product under the title conditions. In contrast, the traditional Fenton reagents ($Fe^{2+}$ and $H_2O_2$) limited to remove the uracil moiety of CYN with the carboxylic group intact. Presumably, the decarboxylation ability of BiOBr was induced by Br 4*p* valence band hole ($h_{Br\,4p}^{+}$), and the degradation mechanism was also proposed based on the experimental results and theoretical calculation.



## 1. Introduction

The potential hazard of cyanobacterial toxins is demonstrated by livestock poisoning and human death due to drink the water containing high concentration of cyanobacteria [1]. Cyanobacteria, also known as blue-green algae, are prokaryotic organisms growing in freshwaters and brackish lakes. The toxic cyanotoxins are the secondary metabolites of cyanobacteria [2]. Cylindrospermopsin (CYN) is one of the common members of cyanotoxins which always cause human injury. CYN originates from several cyanobacteria, such as *Cylindrospermopsis raciborskii* [3], *Umezakia natans* [4], *Aphanizomenon ovalisporum* [5], *Anabaena bergii* [6], *Raphidiopsis curvata* [7], *Aphanizomenon flos-aquae* [8], *Anabaena lapponica* [9], *Lyngbya wollei* [10] and *Aphanizomenon gracile* [11]. CYN has neurotoxic effects (inhibition of protein synthesis by binding to liver DNA and forms single DNA adducts which results in liver damage), hepatotoxic effects (inhibition of glutathione synthesis in hepatocytes), and cytotoxic effects (inhibitor of cytochrome P450) [12]. CYN belongs to guanidine alkaloids, and the molecular structure contains tricyclic guanidine moiety and hydroxymethyl uracil (see Fig. 1). CYN acts to inhibit various enzymatic reactions by competing for the binding site of uridine diphosphate (UDP), which serves as a glycosyl group carrier in higher animals. The uracil moiety of CYN structurally resembles the uridine moiety of UDP [13]. The toxicity of CYN comes from the uracil unit, so the decomposition of uracil is regarded as the general method to detoxify it.

As global warming, CYN spreads from the tropics to temperate zone, the peak concentration of CYN can be found in the aqueous media toward the end of a water bloom when the algae are still viable [14]. This phenomena and hazard cause scientific attention on the detoxification of it. The traditional water treatment processes, such as coagulation, flocculation and filtration are ineffective to remove the toxic CYN [15,16]. Some cyanobacterial toxins can be removed by activated carbon via physical adsorption, however, the limited adsorption ability and high cost of activate carbon inhibit its practical application [17]. The effective chemical degradation of CYN by chlorination [18–21] and ozonation [22] has also been realized, but suffering from long degradation time and high cost. Recently, advanced oxidation processes (AOPs) based on high active hydroxyl radical (•OH) have been established as an alternative and superior to conventional chemical oxidation for the degradation of CYN [23]. Among AOPs, photocatalytic degradation with $TiO_2$ under UV irradiation is an attractive alternative for the detoxification of cyanotoxins [24,25]. However, the wide band gap (3.2 eV for anatase) of $TiO_2$ results in the absorption within the UV light region. In addition, only a fraction of pollutants are mineralized to $CO_2$ during the initial phase of $TiO_2$ photocatalysis, and most of them remain with the toxic groups intact.

In recent years, BiOBr has received remarkable interest in the potential photocatalysis to remove contaminants from aqueous

* Corresponding author. Tel.: +86 717 6397488; fax: +86 717 6395966.
*E-mail addresses:* huangyp@ctgu.edu.cn, yingpinghuang@126.com (Y. Huang).

0926-3373/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.12.016

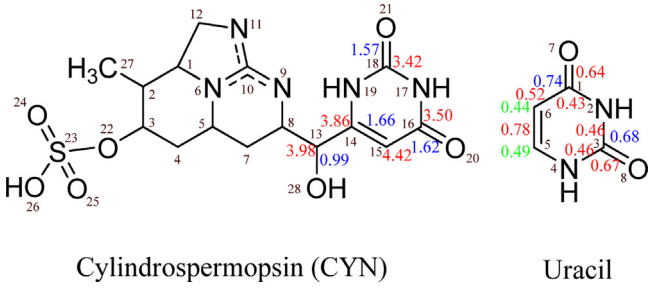


**Fig. 1.** The structures of CYN and uracil. The red, blue and green numbers represent electron population, bond order and free valence, respectively.

solution, owing to its stability, suitable band gap and relatively superior photocatalytic abilities [26–28]. Both O 2*p* and Br 4*p* states of BiOBr dominate the valence band, whereas Bi 6*p* state contributes the most to the conduction band [29]. Very recently, our group discovered that BiOBr photocatalyst had ability to selectively remove the free carboxylic groups from D-Glu and D-MeAsp of microsystin-LR (MC-LR). In contrast, the $TiO_2$ photocatalyst cannot do so [30]. BiOBr crystallizes in the tetragonal matlockite structure and has layered structure characterized by $[Bi_2O_2]$ slabs interleaved by double slabs of bromine atoms [31]. Our previous research indicated that BiOBr had two separate valence bands, instead of hybridized valence band, which had different oxidation abilities and responded to UV and visible light, respectively [32]. Furthermore, the valence hole energy of BiOBr (~2.25 V) is not high enough to oxidize $H_2O$ ($E^0_{\bullet OH/H_2O} = +2.7$ V, NHE) [29]. Thus, separate valence bands and lower redox potential could lead to different degradation pathways compared with other AOP systems. Song et al. originally reported the detailed mechanism of degradation and transformation of CYN by •OH generated from γ radiolysis [33]. They found that CYN was detoxified through removal of the uracil moiety. In this paper, we reported BiOBr promoted photocatalytic detoxification of CYN respectively under UV and visible light illumination through decomposition of the uracil unit and decarboxylation from CYN to eliminate its toxicity. As a compare, traditional Fenton system was employed to degrade CYN. The degradation of uracil was also studied as a control experiment to further verify the detoxification mechanism.

## 2. Materials and methods

### 2.1. Reagents

CYN and uracil (Fig. 1) were purchased from Express Technology Co. and Aladdin Industrial Inc., respectively. CPB (hexadecylpyridinium bromide) was purchased from Aladdin Industrial Inc. DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) was obtained from Sigma–Aldrich Co. $TiO_2$ (Degussa P25), containing 80% anatase and 20% rutile, was used. Chromatographically pure methanol was received from J.T. Baker Co. All reagents were used without further purification. Deionized and redistilled water was used.

### 2.2. Theoretical calculation of substrate molecules

Semi-empirical method is used to calculate molecular parameters and helpful to seek rules of structure and property. Semi-empirical self-consistent-field molecular orbital method (AM1) and Huckel molecular orbital method (HMO) are widely applied among them [34–36]. Electron population, bond order and free valence are frequently used parameters to evaluate π charge density in organic conjugated systems. Generally, atoms with the highest electron population are the sites easily attacked by electrophilic groups; atoms with the lowest electron population are the sites easily attacked by nucleophilic groups; reactions involved free radicals easily occur at atoms with the highest free valence; nucleophilic, electrophilic and free radical reactions are inclined to occur at atoms with the highest free valence when electron populations are equal. Bond order represents the intensity of bond energy. The higher the bond energy, the more stable the molecules.

AM1 was employed to optimize the geometric configuration and calculate electron population and bond order of CYN. Uracil has planar configuration, so the π electronic structure of it was processed according to HMO. The electron population, bond order and free valence of different atoms were calculated using self-compiled computer program. The numbers of atoms in CYN and uracil were shown in Fig. 1.

### 2.3. Synthesis and characterization of BiOBr

BiOBr was prepared according to Ref. [30]. In a typical operation, $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 1.2 mol/L $HNO_3$ solution, and 0.05 mol/L CPB aqueous solution was kept in 40 °C temperature bath all the time. The molar ratio of CPB/$Bi(NO_3)_3{\cdot}5H_2O$ was set as 3:2. Yellow precipitates produced when acidic solution of $Bi(NO_3)_3{\cdot}5H_2O$ was added dropwise into the CPB solution. The pH of the mixture was then adjusted to 7 with NaOH (0.5 mol/L) and the solution was vigorously stirred for 1 h at room temperature. Finally, the above solution was heated at 170 °C for 17 h. The resulting precipitates were washed with plenty of water and dried at 50 °C in air.

The crystalline phases of the samples were characterized by Ultima IV XRD (Rigaku, Japan) with Cu $K_\alpha$ radiation ($\lambda$ = 1.54178 Å). The surface morphology of BiOBr was observed by JSM-7500F field SEM (JEOL, Japan). Surface element compositions were analyzed by an Axis-Ultra DLD multi-technique XPS (Kratos, Britain) employing a monochromated $K_\alpha$ X-ray source ($h\nu$ = 1486.6 eV). The specific surface area was determined by an ASAP 2020 model BET surface area and pore size analyzer (Micrometritics, USA). The DRS of BiOBr was recorded on a U-3010 UV-Vis spectrophotometer (Hitachi, Japan) using spectral grade $BaSO_4$ as the reference material.

### 2.4. Degradation of CYN and uracil

A 100 W mercury lamp (2.8 mW/m$^2$) and 500 W halogen lamp (22.9 mW/m$^2$), purchased from Nanjing Xujiang Electromechanical Plant, were used as the UV light and visible light source, respectively. They were positioned inside the XPA photochemical reaction instrument (Xujiang Electromechanical Plant, China). To ensure that the system was irradiated only by UV light with wavelength below 350 nm, 6 pieces of cutoff filter (17.5 cm × 4.5 cm × 0.2 cm) were placed outside the Pyrex jacket to eliminate any radiation with wavelength above 350 nm. The wavelength of visible light source is above 420 nm.

All the CYN and uracil photocatalytic degradation experiments were carried out in a Pyrex vessel (10 mL) with 5 mL 2 mg/L CYN (uracil) and certain amount of BiOBr. Prior to the irradiation, the suspensions were magnetically stirred in dark for approximately 1 h to ensure that CYN (uracil) reached an adsorption–desorption equilibrium on the surface of BiOBr. At specific time intervals, aliquots (300 μL) were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.22 μm) to remove the solid catalyst particles prior to high performance liquid chromatography (HPLC) analysis.

### 2.5. Analysis methods

HPLC analysis was performed with a Waters 2998 photodiode array (PDA) detector and a $C_{18}$ reverse-phase column (5 μm; 4.6 mm i.d. × 250 mm, kromasil). Gradient elution for the