Chemosphere 165 (2016) 381–387

Contents lists available at ScienceDirect

Chemosphere

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

A comparative study of microcystin-LR degradation by electrogenerated oxidants at BDD and MMO anodes

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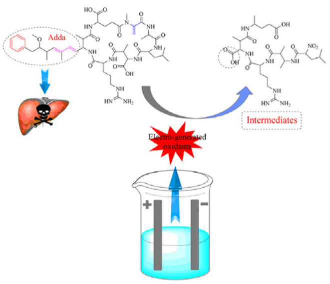
HIGHLIGHTS

- Electrogenerated oxidants were responsible for MC-LR degradation.
- BDD anode showed better performance in all medium in this study.
- Possible pathways of MC-LR degradation were proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 August 2016
Received in revised form
13 September 2016
Accepted 14 September 2016
Available online 30 September 2016

Handling Editor: E. Brillas

Keywords:
Electrochemical oxidation
In-situ generated oxidants
Microcystin-LR
Intermediates

ABSTRACT

This study investigated the electrochemical degradation of microcystin-LR (MC-LR) using boron-doped diamond (BDD) anode and mixed metal oxides (MMO, IrO_2–Ta_2O_5/Ti) anode in different medium. In-situ electrogenerated oxidants including hydroxyl radical, active chlorine, and persulfate were confirmed in phosphate, chloride, and sulfate medium, respectively. Different from MMO anode, hydroxyl radical was observed to play a significant role in chlorine generation at BDD anode in chloride medium. Besides, BDD anode could activate sulfate electrochemically due to its high oxygen evolution potential, and MC-LR degradation rate increased with the decrease of solution pH. The effects of natural organic matters (NOM) and algal organic matters (AOM) on MC-LR degradation were evaluated and NOM presented stronger inhibition ability than AOM. Furthermore, the intermediates generated in MC-LR degradation in chloride and sulfate medium were identified by LC/MS/MS and possible degradation pathways were proposed based on the experiments results. Benzene ring and conjugated diene bonds of Adda group and double bonds of Mhda group were found to be the reactive sites of MC-LR. Overall, this study broadens the knowledge of electrochemical oxidation in removing microcystins in algae-laden water.

1. Introduction

In recent decades, cyanobacteria blooms frequently occurred in lakes and reservoirs around the world (Boyd et al., 2000; Yang et al., 2008; Li et al., 2012). During the blooms, large amount of algal cells,

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http://dx.doi.org/10.1016/j.chemosphere.2016.09.057
0045-6535/

as well as the cyanobacterial metabolites (such as microcystins, endotoxins and taste & odor compounds) pose a significant threat to water quality and human health (Henderson et al., 2008; Bogialli et al., 2012; Zhou et al., 2014). Among these metabolites, microcystins (MCs) have been paid more attention due to their stability and toxicity (Chang et al., 2014), with a lethal dose (LD_{50}) of 50–1200 mg kg^{-1} in mice (Rinehart et al., 1994). Around 40% of cyanobacteria could produce MCs and MCs can be released into surrounding water mainly through cell metabolic reactions or cell rupture (Repavich et al., 1990). It has been reported that approximate 90 kinds of MCs have been identified (Zhang et al., 2010), and can be divided as cytotoxins, neurotoxins, and hepatotoxins (Carmichael, 1992). Microcystin-LR (MC-LR), a hepatotoxin and a tumor promoter, is the most toxic and frequently found derivative (Carmichael, 1992). It could cause liver failure when people were exposed to high dose of MC-LR (Zhao et al., 2001). Therefore, World Health Organization (WHO) set a guideline value for MC-LR of 1.0 μg L^{-1} in drinking water (WHO, 1998).

Unfortunately, the conventional water treatment processes (such as coagulation, flocculation, sedimentation, and sand filtration) can poorly remove the extracellular MC-LR (Keijola et al., 1988; Zhang et al., 2016). Efforts have been paid to abate MC-LR using various technologies, including hydroxyl radical-based and sulfate radical-based advanced oxidation (Song et al., 2009; Antoniou et al., 2010), ozonation (Chang et al., 2014), chlorination (Zhang et al., 2016), ferrate (VI) (Jiang et al., 2014), photochemical (Yuan et al., 2006) and electrochemical oxidation (Liao et al., 2014). Among various kinds of processes, electrochemical oxidation is deemed as a potential technology in the future owing to the rapid development of electric power, which could be generated from wind and solar sources (Mook et al., 2014; Sirés et al., 2014; Martínez-Huitle et al., 2015). Besides, compared to conventional advanced oxidation process, electrochemical oxidation requires common electrolytes (e.g., NaCl, Na_2SO_4) instead of oxidants, and thus appears to be more safe and eco-friendly.

In electrochemical oxidation processes, anode materials and electrolytes are significant factors that influence the removal of contaminants (Jeong et al., 2009; Scialdone et al., 2009). Under most circumstances, anodes could be separated into two kinds: active anodes and non-active anodes (Comninellis, 1994). Active anodes (e.g., IrO_2, RuO_2) exhibited relatively low capability to directly degrade organic contaminants, while non-active anodes (e.g., PbO_2, SnO_2, boron-doped diamond (BDD)) usually have a higher overpotential for oxygen evolution and therefore show a higher ability to remove recalcitrant organics (Radjenovic and Sedlak, 2015). In this study, two different anodes: BDD anode (non-active) and mixed metal oxide anode (MMO, IrO_2–Ta_2O_5/Ti, active) were chosen to remove MC-LR.

Besides, different oxidants would be produced when different electrolytes were employed. The generation of ozone, ferrate, chlorine and other peroxosalts ($S_2O_8^{2-}$, $C_2O_6^{2-}$) have been reported by many other researchers (Sirés et al., 2014; Radjenovic and Sedlak, 2015). In this study, three kinds of common electrolytes were used, including phosphate, chloride, and sulfate medium. The possible reactions that may occur during the process have been listed in Table 1 (M means anodes).

Unfortunately, the information regarding the comparison of MC-LR removal using BDD and MMO electrodes with different electrolytes is limited until now. Hence, the objectives of this study were as follows: (1) to investigate MC-LR removal efficiency in phosphate, chloride, and sulfate medium with BDD and MMO electrodes; (2) to evaluate the relationship between MC-LR removal and oxidants generation; (3) to propose possible pathways of MC-LR degradation in different medium.

Table 1
Reactions occurred in the electrochemical oxidation.

No.	Reactions
1	$M + H_2O - e^- \rightarrow M(\cdot OH) + H^+$
2	$H_2O - 2e^- \rightarrow 2H^+ + \frac{1}{2}O_2$
3	$2Cl^- - 2e^- \rightarrow Cl_2$
4	$Cl_2 + H_2O \leftrightarrow HClO + HCl$
5	$2HSO_4^- - 2e^- \xrightarrow{BDD} S_2O_8^{2-} + 2H^+$
6	$2SO_4^{2-} - 2e^- \xrightarrow{BDD} S_2O_8^{2-}$
7	$OH^{\cdot} + Cl^- \rightarrow ClOH^{\cdot -}$
8	$ClOH^{\cdot -} \rightarrow HClO + e^-$

2. Materials and methods

2.1. Materials

HPLC-grade acetonitrile and formic acid were obtained from Sigma-Aldrich (USA). DPD (N, N-diethyl-p-phenylenediamine) free chlorine reagents were supplied by Hach (USA). MC-LR (>95%) isolated from *Microcystis aeruginosa* was purchased from Alexis biochemicals (Switzerland). Sodium sulfate, sodium chloride, disodium hydrogen phosphate, nitrate acid, potassium iodide, sodium bicarbonate, humic acid, and isopropyl alcohol were supplied by Sinopharm Chemical Reagent Co. (China). BDD/Nb electrodes were purchased from NeoCoat (Switzerland). MMO electrodes (IrO_2–Ta_2O_5/Ti) were supplied by 3 N International (USA). Glass microfiber filters (GF/F) were obtained from Whatman (UK). All solutions were prepared with ultrapure water, unless otherwise specified.

2.2. Experimental procedures

Batch experiments were conducted open to the air and in a borosilicate glass jar containing 50 mL solution. The BDD (or MMO) anode and stainless steel cathode with dimensions of 5 cm × 2.5 cm were set in parallel at a distance of 2.0 cm (Fig. SM-1 in the Supplementary Material). The total submerged area of electrodes was 10 cm^2 in the electrolytic cell. A direct current source was used to supply power to the system. The initial concentration of MC-LR was fixed at 0.2 μM. To determine the generation of chlorine and persulfate with time, a set of experiments were conducted without

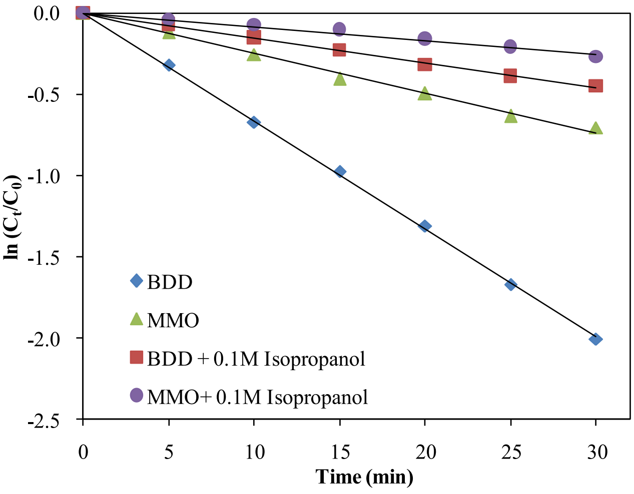

Fig. 1. MC-LR degradation in phosphate medium using BDD and MMO anodes. Experimental conditions: Current density = 5.0 mA cm^{-2}, $[MC\text{-}LR]_0$ = 0.2 μM, Electrolyte: $[NaH_2PO_4]_0$ = 30 mM, pH = 7.0, reaction time = 30 min.