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Ozone-based advanced oxidation processes for the removal of harmful algal bloom (HAB) toxins: a review

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ABSTRACT

Cyanotoxin is one of the emerging water contaminants that pose serious health risks to humans. high performance liquid chromatography and liquid chromatography-mass spectrometry (LC-MS) are commonly used analytical tools for the detection and quantification of cyanotoxins. Recommended Environmental Protection Agency drinking water guidelines for majority of cyanotoxins is 1 µµg L and is followed by majority of drinking water treatment plants to ensure public health and safety. Ozone is an effective method for removing cyanotoxins present in water. Some stable cyanotoxin species can be removed by ozone-based advanced oxidation processes. UV irradiation and H_2O_2 when used along with ozone, and TiO_2 catalyzed ozonation can accelerate the cyanotoxin removal process in water. Water chemistry plays an important role in determining the efficiency of advanced oxidation processes. This paper summarizes the recent studies that are carried out targeting the removal of cyanotoxins in water, and evaluates benefits of ozonation as a pre- or post-oxidation process for drinking water desalination plants.

Keywords: Cyanobacteria; Blue-green algae; Cyanotoxins; Water treatment; ozone; Ozone-based advanced oxidation; Drinking water

1. Introduction

The occurrence and severity of harmful algal blooms (HABs) also known as blue-green algae have posed a serious threat of illness to humans. Cyanobacterial poisoning in humans and animals was first reported in literature by Hunter [1]. Many investigations were carried and confirmed cyanobacterial poisoning in humans, mammals and birds [2–5]. Cyanobacterial poisoning exists also in many other animals and plants [6–8]. Much attention was paid to cyanotoxins and clinical investigations related to hepatotoxicosis following the confirmed acute outbreaks of poisoning and human death in Brazil [9–11]. The main causes of poisoning were found to be haemodialysis and oral routes, and control measures were taken to eliminate cyanotoxins from the drinking water supply systems in many countries [12,13]. The direct contact with HABs can cause more serious health problems. 2-h exposure by direct contact with the bloom, which involved immersion, oral ingestion and inhalation in the water containing 48.6 µg/L of microcystin-LR (MC-LR), has caused gastrointestinal disorder (nausea, vomiting, fever, headache), followed by hepatotoxicosis and multiple organ failures [14–18]. Cyanobacterial toxins differ both in their chemical structure and properties. Some of the chemical structures of cyanobacterial toxins are cyclic peptides, alkaloids, lipopolysaccharides and organophosphates. Cyanobacterial toxins are primarily classified on the basis of their toxic effect on the organs, tissues and cells of organisms. MCs and cylindrospermopsin (CYN) of hepatotoxins group, Anatoxin-a and Saxitoxin of neurotoxin group are some important cyanotoxins that cause poisoning in humans. Concerns regarding the contamination by cyanotoxins of drinking water have stimulated the development of a range of detection methods for their identification and quantification [19–26]. Screening protocols included initial microscopic analysis of phytoplankton and evaluation of cyanobacterial cell density followed by toxin analysis for monitoring cyanotoxin risks efficiently [27]. In addition, many sen-

sors have been developed for the estimation of cyanobacterial abundance and even the estimation of toxic species [28,29]. Cyanotoxins can be eliminated from water by a variety of methods, for example, flocculation, membrane filtration, and adsorption on activated carbon, oxidation by permanganate, ozonation and chlorination [11,30–46]. However, the conventional treatment methods when used alone are unable to remove cyanotoxins completely. On the other hand, when different treatment methods are combined, toxin elimination becomes expensive process. The combination of flocculation by ferric chloride and slow sand filtration does cause cyanobacterial lysis leading to an increase in dissolved MC concentrations in drinking water [47]. Thus, they are effective methods for the removal of cell-bound toxins but not suitable for dissolved cyanotoxins. Combination of flocculation-filtration-chlorination demonstrated poor removal of MC. The methods that lead to cell lysis are not advisable because toxins are released from cells. Methods such as chlorination, activated carbon adsorption or ozonation can be applied to eliminate dissolved cyanotoxins. Flotation, filtration and pumping methods can be applied to reduce HABs. However, these methods are not suitable for open water columns where the floating algae are not thick enough and also because of high costs [48].Chlorination-based disinfection is widely used in the treatment of drinking water and reduces the concentration of cyanotoxins [49]. However, studies have shown that MC degradation is strongly dependent on chlorine doses, contact time and pH [50]. The conversion of various toxins to non-toxic compounds requires different conditions [49], and investigations have shown that the optimal conditions for the transformation of all toxins in the mixture cannot be achieved with chlorination process. The risk of toxin release from cells may also increase following chlorination [51]. Alternative process such as ozonation methods was proved to be efficient for the removal of MC [52,53]. The purpose of this article is to provide some background information on cyanotoxin detection and removal using ozone and ozone-based advanced oxidation processes (AOPs).

2. Cyanotoxin detection and quantification

Detection of cyanotoxin at very low concentrations is required for potable water applications. For such low concentration measurements, toxicity-based bioassays are impractical in terms of pre-concentration of water samples. Sensitivity of enzyme-linked immunosorbent assay (ELISA) and Phosphatase assay methods are very high; however, cross-reactivity was found to be a major problem which causes overestimation or underestimation of toxin concentrations. ELISA and Phosphatase assay methods are useful qualitative screening tools but not suitable for cyanotoxin quantification [9,54]. For monitoring the potential hazard of cyanotoxins in water, some qualitative methods can be employed. After sampling, identification and quantification of cyanotoxins can be precisely carried out by the various analytical techniques in the laboratory (Table 1).

High-performance liquid chromatography (HPLC) is a commonly used analytical procedure for the determination of cyanotoxins. Separation of toxins have been successfully carried out using a reverse phase C18 packed column, amide C16 column, internal surface reverse phase column or ion exchange column, and with an aqueous mobile phase containing methanol or acetonitrile. For accurate quantification of cyanotoxins, good resolution and separation of peaks are required; the mobile phase determines whether toxins are resolved from each other and from co-extracted compounds. MC-LR and MC-YR co-elute with acetonitrile/ammonium acetate as mobile phase. However, good separation and resolution can be obtained with methanol-based mobile phases. UV absorbance is one of the commonly employed techniques for detecting these toxins following chromatographic separation. Most MCs have a UV absorption maximum at 238 nm; however, MC-LW that contains aromatic amino acid constituents has absorbance maxima at lower wavelengths (222 nm). One of the drawbacks of UV detector is the interference from co-eluting components in the sample extract and their effects on the quantification of toxins. A photo-diode array (PDA) detector records both UV response and the spectrum of a separated analyte. It provides better evidence of the presence of a specific cyanotoxin than using single wavelength

Table 1
List of analytical techniques used for the removal of cyanotoxins

Analytical techniques	Sensitivity range	Measurements
HPLC-MS [55–59]	0.01–2.64 µg L	Measures individual toxin. May assist in identification of particular toxins. Quantification still depends on available standards.
HPLC-PDA [60–63]	0.02 µg L	Measures individual toxins, subject to availability of standards
HPLC-UV [64]	0.02 µg L	Measures individual toxins, subject to availability of standards
MALDI-TOF-MS [65]	<7 µg L	Measures individual toxins, lack of available and versatile internal standards has limited its use
NMR [66, 67]	Sub-µg levels	Measures individual toxins, subject to availability of standards
Electrochemical-based biosensors [68–71]	<1 µg L	Extremely specific and highly sensitive method
Capillary electrophoresis (CE, CE-MS) [68]	–	Measures individual toxins, subject to availability of standards

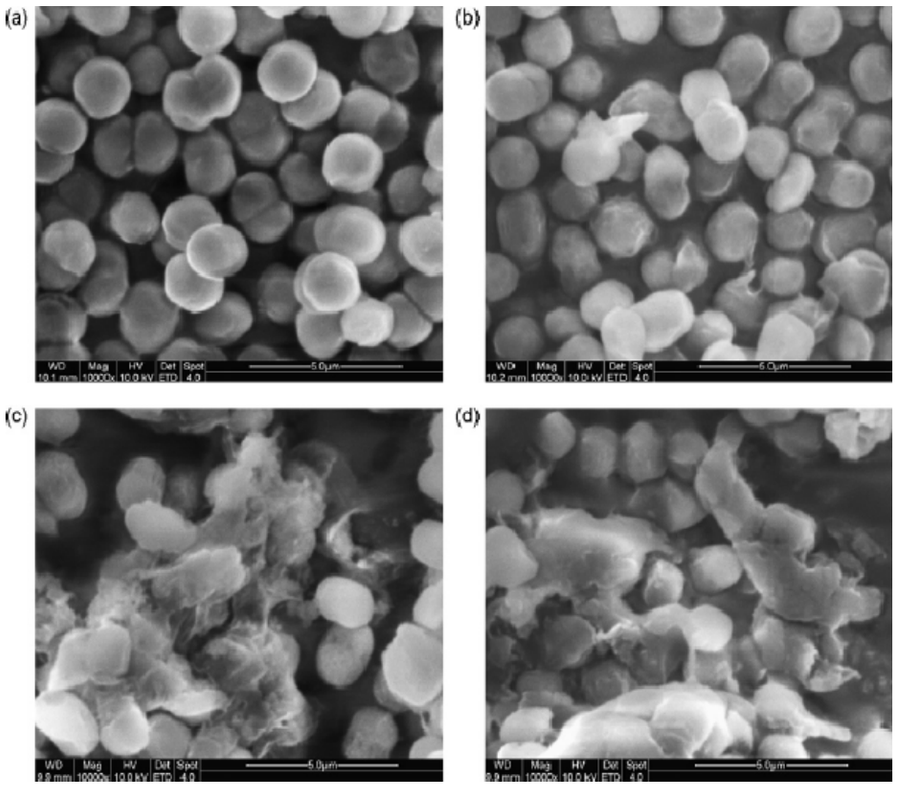

Fig. 1. SEM image of cyanotoxin before and after ozonation: (a) No ozone, (b) 1 ppm ozone, (c) 3 ppm ozone, and (d) 5 ppm ozone [73].[AQ17]

detection. However, when the concentrations of cyanotoxins are low and spectra are not well defined, the identification of peaks is difficult and depends on the experience of the analyst. Concentrations of cyanotoxins can be obtained by quantification of peaks relative to a standard. Mass spectrometry detection following HPLC separation is a better method for identification of individual cyanotoxins as long as a mass spectrum of an authentic standard is available. MS/MS detections offer better resolution where the fragmentation pattern can be used to greatly assist in determining the identities of unknown cyanotoxins. matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry has also been successfully used as a detection method following chromatographic separation. Capillary electrophoresis can be employed to separate and quantify cyanotoxins; however, this method is less sensitive when compared with HPLC method. Nevertheless, the above-mentioned instrumental methods require expensive equipment, skilled personnel, time consuming and less suitable for routine and field analysis. Biosensors are attractive and valuable tools for routine analysis and quick monitoring of cyanotoxins in water. Optical, enzyme-based, immune sensors, nanomaterials (gold, silver, carbon nanoparticles) have been successfully applied in biosensors for the detection of cyanotoxins.

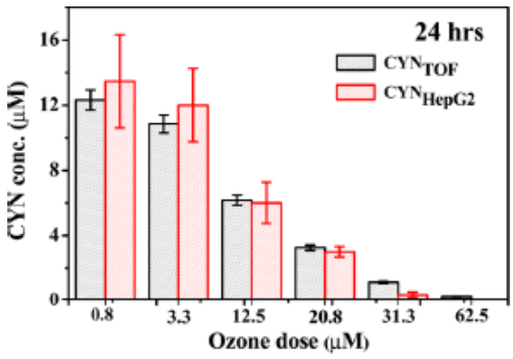

Fig 2. Chart illustrating degradation of cylindrospermopsin at various ozone doses. Concentrations of cylindrospermopsin measured by LC-MS method are shown in black; concentrations calculated out of cytotoxicity assessment are shown in red [76].

3. Ozonation process and cyanotoxin removal in water

Ozone is a powerful oxidant for the removal of some classes of cyanotoxins. Cyanotoxins such as Anatoxins-a, CYN, MC and nodulain in water can be successfully removed by ozonation process. Oxidation of MC-LR and nodulain in pure water appears to be complete within few minutes. Saxitoxin is the least susceptible to ozone-based destruction. To ensure cyanotoxin removal, ozone must be applied and dissolved at the required residual concentration in water. Water quality parameters such as pH and dissolved organic carbon (DOC) strongly influence required ozone dosage levels and contact time. In general, ozone residual dose of 0.2 mg L with a contact time of 5 min will be required for destruction of cyanotoxins [72]. Reaction kinetics will not be favorable for oxidation of cyanotoxins when organic material is present in

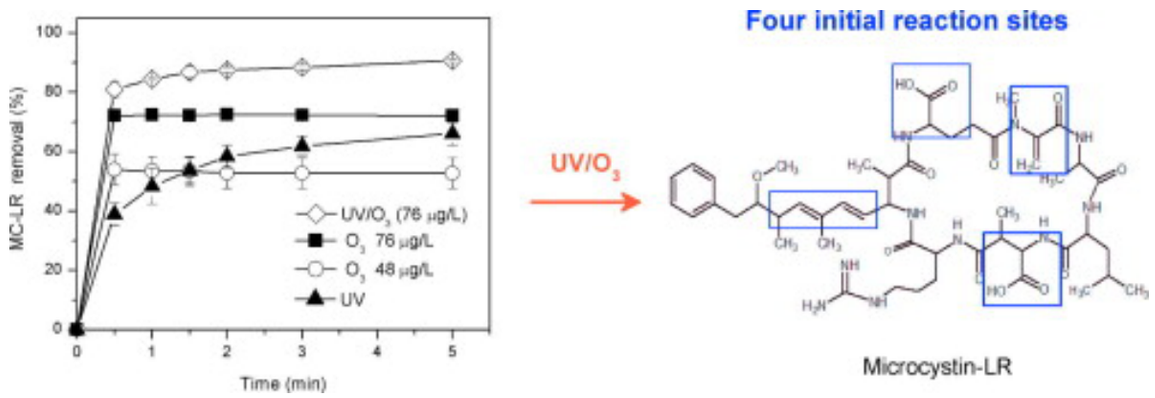

Fig. 3. Degradation of microcystin-LR with UV/O_3 process and the representation of reaction sites of microcystin-LR [79].

raw water. Studies have shown that the ozonation when applied in early phase of water treatment process is prone to destroy cyanobacterial cells (as seen in Fig. 1.), increases DOC and eventually results in increase in cyanotoxin concentrations in water [73–75]. Effect of ozonation on the cellular morphology of *Microcystis aeruginosa* is shown in Fig. 3. When the concentration of Ozone dose increased during treatment; cell wall gets damaged; and cellular cytoplasm gets released from the cells, which in turn increased DOC concentrations in water. Performance of ozone process was found to be different for the cells from natural bloom conditions when compared with laboratory cultured cells. In addition, the cyanobacterial biomass and the initial MC concentration are factors affecting the effectiveness of the oxidation process. O_3/DOC and alkalinities are some of the factors which would define the inter-bloom reactivity and describe the differences in ozone decay. Studies have also demonstrated that during direct ozonation of toxin cells from natural blooms, MCs were resistant with least complete cell lysis and lowest lysis rate [74].

Reactivity of ozone varies dramatically with different organic functional groups. Reaction of CYN with ozone is strongly pH dependent, and the detailed reaction pathways

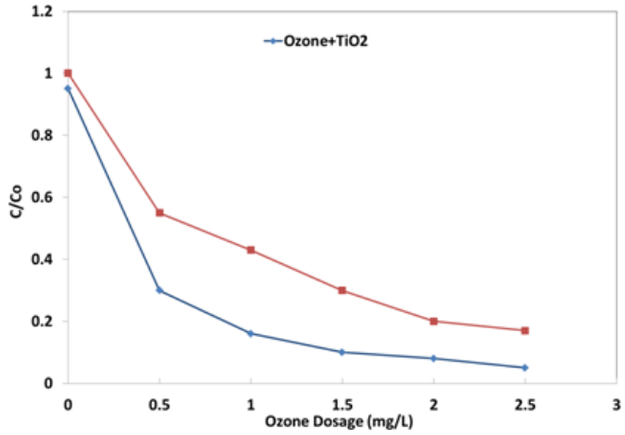

Fig 4. Degradation of CYN present in lake water, Taiwan, by ozonation and catalytic ozonation. Experiments were performed at pH 7.5 at 20°C. HPLC-MS analytical tool was used for CYN quantification [79].

of ozonation process have been recently reported by Yan et al. [76]. Common ozone reaction mechanisms include double bond cleavage, electron transfer, hydroxyl radical oxidation and oxygen atom transfer. The degradation begins with carbon-carbon double bond cleavage of the toxic uracil moiety of CYN, and complete degradation occurs as the ozone dose is increased (Fig. 2). Cytotoxicity measurements have confirmed that ozone-based oxidation is an effective and practical method for the removal of CYN in drinking water [76].

Arid countries are increasingly reliant on seawater desalination for drinking water and industrial purposes. An emerging threat to public health is due to unpredicted rapid growth of HABs/cyanotoxins in seawater. Contributors to the growth of blooms are anthropogenic inputs from industrial and agricultural waste stream disposal into sea, and also climate change. For the effective removal of cyanotoxins and to avoid lysis in source water, ozonation process should be applied at the later phase of water treatment/desalination process for potable water applications.

4. Ozone-based advanced oxidation

Ozone-based AOP produces hydroxyl radicals which can react with and destroy a wide range of cyanotoxins. The effectiveness of an AOP relies on its ability to generate hydroxyl radicals. Ozone-H_2O_2, and UV are some of AOPs employed for cyanotoxin removal. The addition of hydrogen peroxide facilitates the decomposition of ozone leading to the formation of hydroxyl radicals. Once the hydroxyl radicals are formed, the propagation of chain reaction happens while destructing target contaminants. The efficiency of MC destruction was enhanced by the ozone-H_2O_2 process when compared with ozone alone. With the H_2O_2:O_3 ratio of 0.5, 1 mg L of MC-LR was completely destroyed within 30 min [52]. Effectiveness of toxin removal can be improved by UV irradiation along with consequent ozonation process. MC degradation was found to be more efficient when UV/O_3 processes applied sequentially. Similar to hydrogen peroxide, UV irradiation helps to promote the decomposition of ozone to generate strong hydroxyl radicals. With 5 min of UV irradiation (intensity 1.9 mW cm²) and consequent 5 min of ozonation at 0.5 mg L, 90% of MC removal can be achieved for the waters loaded with 1 mg L MC concentrations [77]. Process efficiencies of ozone, UV and UV/O_3 for MC removal

with elucidation of reaction pathways and possible mechanisms were recently reported by Chang et al. [78].

The study confirmed that high pH and DOC in water inhibited the degradation of the toxin for UV/O_3 process [78]. The degradation of MC-LR initially occurred at four sites as pointed out by Chang et al. as shown in Fig. 3.

One of the common and stable cyanotoxin present in drinking water is CYN ($C15H21N5O7S$). USEPA drinking water guidelines state that CYN concentration must be less than 1 µg L to avoid any kind of health risks to humans. As an AOP, heterogeneous catalytic ozonation accomplishes both O_3 and the adsorptive and oxidative properties of solid-phase metal oxide catalysts. Wu et al. has recently demonstrated TiO_2-based catalytic ozonation to remove CYN at room temperature [79].

The study carried by Wu et al. demonstrated that TiO_2 facilitates the decomposition of O_3 in the oxidation of CYN by forming radicals and increased the rate of oxidation reaction (Fig. 4).

5. Conclusion

Cyanotoxins is one of the emerging water contaminants that pose serious health risks to humans. Several monitoring and detection tools are available to date for qualitative screening and quantification of cyanotoxins. HPLC-MS/MS technique can detect even trace amount of cyanotoxin present in water. Biosensors are best suited for routine monitoring of cyanotoxins. Studies have demonstrated that ozonation is an effective and safe method for removal of cyanotoxins. AOP when used with ozone accelerates the decomposition of ozone, and increases cyanotoxin removal efficiency. During AOP/ozonation, water quality parameters such as pH, DOC are some of the factors to be taken into account for the successful removal of cyanotoxins. Drinking water treatment plants while targeting cyanotoxin removal, it is essential and important to use ozone and ozone-based AOP in the later phase as a final polishing process. Around the world, there are wide variety of cyanotoxin species present in lakes, river and in sea. It is worthwhile to perform a region specific study to identify and target the right cyanobacterial species for ensuring public health and safety.

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