Desalination xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Desalination

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

Advanced oxidation processes to remove cyanotoxins in water

Saad Y. Jasim *, Jayaprakash Saththasivam

Qatar Environment & Energy Research Institute, HBKU, QF, Doha, Qatar

HIGHLIGHTS

- Harmful Algal Blooms (HABs) are becoming a continuous challenge to the ecosystem and human health.
- Cyanotoxins are considered as a group of natural toxins, found to be hazardous to terrestrial mammals than aquatic biota.
- Cyanotoxins caused by cyanobacteria pose a risk to human health through the exposure or ingestion of contaminated water.
- Cyanotoxins can be eliminated from water by membrane, adsorption on activated carbon and ozonation.
- A study at QEERI will investigate the impact of Ozone Based Advanced oxidation on the removal of Cyanotoxins.

ARTICLE INFO

Article history:
Received 7 April 2016
Received in revised form 27 June 2016
Accepted 28 June 2016
Available online xxxx

Keywords:
Ozone
Advanced oxidation process
Cyanotoxins
Algal bloom

ABSTRACT

Investigation of source water quality is a key factor in selecting technologies to deal with certain water contaminants. Risk assessment and risk management are major tasks for drinking water systems engineers, managers and the regulatory agencies. Development of contingency plans are necessary to water systems, and having a multi barrier system is an approach started to become familiar to avoid any potential public exposure to water contamination that could have a serious impact on human health. Harmful Algal Blooms (HABs) are becoming a continuous challenge to the ecosystem and human health due to climate change, discharged nutrients from agriculture activities, improperly treated or untreated sewage effluents and others. Harmful Algal Blooms (HABs) are becoming a continuous challenge to the ecosystem and human health due to climate change, discharged nutrients from agriculture activities, improperly treated or untreated sewage effluents and others. The selection of certain technologies to deal with such challenge must take into consideration their impact on the sustainability of the water system. The successful applications of ozone and ozone based advanced oxidation process (AOP) gained major interest in mitigating challenges associated with cyanotoxins.

1. Introduction

Water system engineers, governing authorities and researchers have been continuously challenged with problems associated with Harmful Algal Blooms (HAB) for the past few decades, [1]. The public started to be concerned about the absence of proper solutions to these problems that could have serious impacts on human health. HABs are proliferations of microscopic algae that could harm the ecosystem by producing toxins that accumulate in certain species like fish. The Biomass accumulation may have negative impacts on other organisms and the food web [2]. Potential human illness and mortality following direct consumption or indirect exposure to toxic shellfish or toxins in the environment could result in illness or mortality for humans. Another serious impact is on the economic wellbeing and business survival for shoreline communities. Tourism and local seafood industry are some of the immediate visible impacts. Habitat degradation would cause the inability of the ecosystem to sustain some species. The HABs and the effect of cyanotoxins are cause for concern for potential impact on fish and other animals which could lead to serious economic impacts to shoreline communities, losses to aquaculture enterprises, and long-term ecosystem changes [1].

The cyanotoxins are a considered as a group of natural toxins, both from the chemical and the toxicological points of view where these toxins are found to be hazardous to terrestrial mammals than aquatic biota [3]. Cyanotoxins caused by Cyanobacteria blooms have been associated with the death of wildlife and domestic animals has posed risk to human health through the exposure to contaminated fresh water, ingestion of contaminated drinking water, or by the consumption of contaminated fish [4]. Major routes of human exposure are through ingestion of cyanotoxin contaminated drinking water, inhalation while showering, dietary intake via consumption of cyanotoxins in contaminated foods and algal dietary supplements. Adverse health outcomes from exposure to cyanotoxins range from mild skin rash to serious illness or death. Acute illnesses caused by exposure to cyanotoxins have been reported. Table 1 summarizes the health effects caused by the

* Corresponding author.
E-mail address: sjenvcons@gmail.com (S.Y. Jasim).

http://dx.doi.org/10.1016/j.desal.2016.06.031
0011-9164/

most common toxin producing Cyanobacteria. Table 2 shows the chemical structure of the common cyanotoxins namely microcystin-LR (*m*-LR), cylindrospermopsin and nodularin-R.

One of the most serious incidence occurred in 1996 at a hemodialysis clinic in Brazil when the deaths of over 50 patients receiving dialysis were attributed to exposure to microcyctins that was originating from clinic's water supply [7]. Recently, in August 2014, Harmful Algal Bloom (HAB) has contaminated the water in Lake Erie [8]. Microcystins were found to be the cause and public was advised not use water even by boiling as the toxin is completely unaffected by heat. The reason for the contamination was later found to be runoff water containing nitrates that triggered the cells growth which may lead to increase reproductive rate of cyanotoxins. In the Middle East region, seawater reverse osmosis desalination plants in Oman and United Arab Emirates were shut down or reduced operation due to excessive HAB [9].

Many descriptions related to symptoms of Cyanobacteria poisoning in humans, mammals and birds were summarized by Chores and Barton [10], Stewart et al. [11] and Hunter [12]. Giannuzzi et al. [13] reported a clear, acute case of HAB poisoning following the accidental immersion of a man in a dam reservoir containing abundant bloom of Microcystis wesenbergii and Microcyctis aeruginosa. Two-hour exposure by direct contact with the bloom, which involved immersion, oral ingestion and inhalation in the water containing 48.6 μg/L of microcyctin-LR (MC-LR), has caused gastrointestinal disorder (nausea, vomiting, fever, headache), followed by hepatotoxicosis and multiple organ failures. 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 physiological effect on the organs, tissues and cells of organisms. Microcystins and cyclindrospermopsin of hepatotoxins group, Anatoxin-a and Saxitoxin of neurotoxin group are some important cyanotoxins that causes 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 [14]. Screening protocols included initial microscopic analysis of phytoplankton and evaluation of cyanobacterial cell density followed by toxin analysis for monitoring cyanotoxin risks efficiently [15]. Chlorophyll-a evaluation is found to be a rapid and low cost screening method for cyanotoxins, and correlations has been adopted as a criterion in the World Health Organization (WHO) guideline [16]. More detailed analytical techniques using HPLC, MS, MALDI-TOF-MS, capillary electrophoresis, bioassays, Elisa assay and next-generation sequencing (NGS) are also being used to detect and identify cyanotoxins.

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 [7]. 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 are effective methods for the removal of cell-bound toxins but not suitable for dissolved cyanotoxins [17]. Treatment methods that lead to cell lysis are not advisable because toxins are released from cells. 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 and uneconomical for open water columns where the floating algae are not thick enough [18]. Chlorination based disinfection is widely used in the treatment of drinking water and reduces the concentration of cyanotoxins. However, studies have shown that microcystin degradation is strongly dependent on chlorine doses, contact time and pH [19]. The conversion of various toxins to non-toxic compounds requires different conditions and investigations have shown that the optimal conditions for the transformation

Table 2
Chemical structures of microcystin-LR, cylindrospermopsin and nodularin-R [4].

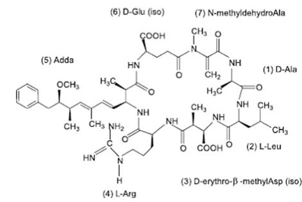
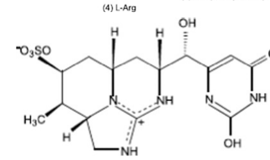
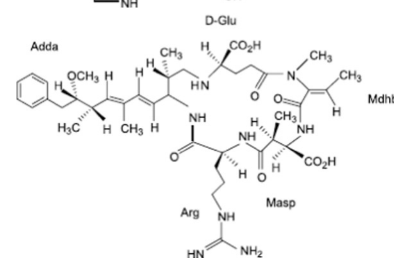
Cyanotoxin	Chemical structure
Microcystin-LR	
Cylindrospermopsin	
Nodularin-R	

Table 1
Cyanotoxins and health effects [5,6].

Cyanotoxins	Acute health effects in humans	Most common Cyanobacteria producing toxin
Microcystin-LR	Abdominal pain, headache, Vomiting and diarrhea, liver inflammation hemorrhage, acute pneumonia, acute dermatitis, kidney damage, potential tumor growth	Microcystis, Anabaena, Nodularia, Planktothrix, Fischerella, Nostoc, Oscillatoria, and Gloeotrichia
Cylindrospermopsin	Abdominal pain, headache, vomiting and diarrhea, liver inflammation hemorrhage, acute pneumonia, acute dermatitis, kidney damage, potential tumor growth	*Cylindrospermopsis raciborskii*, Aphanizomenon flos-aquae, Aphanizomenon gracile, Aphanizomenon ovalisporum, Umezakia natans, Anabaena bergii, *Anabaena lapponica*, *Anabaena planctonica*, Lyngbya wollei, Rhaphidiopsis curvata, and Rhaphidiopsis mediterranea
Anatoxin-a group	Tingling, burning, numbness, drowsiness, incoherent speech, salivation, respiratory paralysis leading to death[a]	Chrysosporum (Aphanizomenon) ovalisporum, Cuspidothrix, Cylindrospermopsis, Cylindrospermum, Dolichospermum, Microcystis, Oscillatoria, Planktothrix, Phormidium, *Anabaena flosaquae*, *A. lemmermannii* *Raphidiopsis mediterranea* (strain of Cylindrospermopsis raciborskii), Tychonema and Woronichinia

[a] Symptoms observed in animals.