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Production of trihalomethanes, haloacetaldehydes and haloacetonitriles during chlorination of microcystin-LR and impacts of pre-oxidation on their formation

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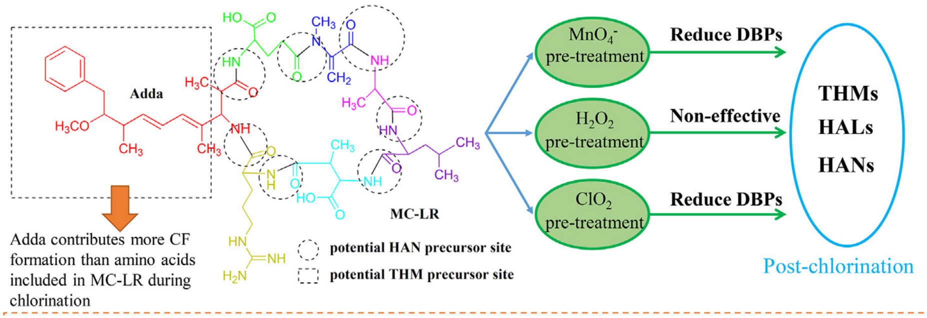
HIGHLIGHTS

- MC-LR formed more chloroform (CF) during chlorination than free amino acids.
- Peptide bonds in MC-LR contribute to dichloroacetonitrile (DCAN) formation.
- Higher pH favors CF and chloral hydrate (CH) formation, but restrains DCAN formation.
- Presence of bromide increased the formation of bromo-DBPs (e.g., TBAL) from MC-LR.
- ClO_2 or PM pre-treatment both reduced DBPs during chlorination, but not for H_2O_2.

GRAPHICAL ABSTRACT



Microcystin-LR (MC-LR) formed trihalomethanes (THMs), haloacetaldehydes (HALs) and haloacetonitriles (HANs) during chlorination, and ClO_2 and MnO_4^- (PM) pre-treatments both reduced their formation, but not for H_2O_2.

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ABSTRACT

Microcystins (MCs) in drinking water have gained much attention due to their adverse health effects. However, little is known about the impact of pre-oxidation in the formation of disinfection by-products (DBPs) during the downstream chlorination of MCs. The present study examined the formation of both carbonaceous and nitrogenous DBPs from chlorination of MC-LR (the most abundant MC species) and evaluated the impact of permanganate (PM), hydrogen peroxide (H_2O_2) and chlorine dioxide (ClO_2) pre-oxidation on the DBP formation in chlorination. Higher yields of chloroform (CF) (maximum 43.0%) were observed from chlorination of MC-LR than free amino acids which are included in MC-LR structure. Chloral hydrate (CH) and dichloroacetonitrile (DCAN) were also produced from the chlorination of MC-LR,

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Abbreviations: Adda, 3 amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid; Ala, alanine; Arg, arginine; Asp, aspartic acid; BCAN, bromochloroacetonitrile; BDCM, bromodichloromethane; BF, bromoform; BIF, bromide incorporation factor; BUF, bromide utilization factor; C-DBP, carbonaceous DBP; CH, chloral hydrate; ClO_2, chlorine dioxide; CF, chloroform; DBAN, dibromoacetonitrile; DBCM, dibromochloromethane; DCAN, dichloronitromethane; DBP, disinfection byproduct; DON, dissolved organic nitrogen; DWTP, drinking water treatment plant; GC/MS, gas chromatograph/mass spectrometry; H_2O_2, hydrogen peroxide; Glu, glutamic acid; Leu, leucine; HAL, haloacetaldehyde; HAN, haloacetonitrile; MC, microcystin; MeAsp, methyl-Asp; Mdha, N-methyl-dehydro-Ala; N-DBP, nitrogenous DBP; TBAL, tribromoacetaldehyde; TCAN, trichloroacetonitrile; THM, trihalomethane; PM, permanganate; PP1A, protein phosphatase type 1A; PP2A, protein phosphatase type 2A.

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Haloacetaldehydes
Permanganate
Hydrogen peroxide
Chlorine dioxide

and the latter one was formed probably due to the chlorination of peptide bonds. A high pH favored the production of CF and CH, but inhibited the formation of DCAN. In the presence of bromide, bromo-DBPs could be produced to pose a threat. For example, 0.58 μg/L of tribromoacetaldehyde was produced from the chlorination of MC-LR at $Br^- = 200$ μg/L. PM and ClO_2 pre-oxidation could both reduce the DBP formation from MC-LR. In contrast, H_2O_2 appeared not to significantly control the DBP formation.

1. Introduction

Outbreaks of cyanobacteria (blue-green algae) are a major environmental and public health concern over the world [1]. Most cyanobacterial bloom not only produces undesirable taste and odour compounds but also releases cyanotoxins [2]. As the most widespread cyanotoxin group, microcystins (MCs) can be produced by a large number of cyanobacteria genera such as Microcystis, Planktothrix (Oscillatoria), Anabaena, and Nostoc [3]. MCs are strongly hepatotoxic as they can cause both acute liver damage and chronic diseases. For example, they have a potential to promote the development of tumor through inhibiting activities of the protein phosphatase types 1 and 2A (PP1 and PP2A) [4]. Over 90 variants of MCs have been currently detected with a general structure of cyclo-Ala (D-alanine)- X- MeAsp (D-β-Me-isoaspartic acid)- Z- Adda (3-amino-9-methoxy-2,6,8-trimethyl-10- phenyldeca-4,6-dienoic acid)- Glu (D-glutamic acid)- Mdha (*N*-methyl-dehydro-Ala) in which X and Z represent two variable L-amino acids, respectively (Fig. SM1) [5,6].

MC-LR (Fig. 1), consisting of five amino acids (glutamic acid, alanine, leucine [Leu], methyl-aspartic acid, arginine [Arg]), Adda and Mdha, is the most toxic and abundant MC, typically accounting for 46.0–99.8% of total MC concentration during a natural cyanobacterial bloom [7,8]. Because of its adverse health effects, the World Health Organization has set a provisional guideline level of 1 μg/L for MC-LR in drinking water [9]. The guideline level has been widely accepted by 18 countries and three U.S. states [10].

A conventional water treatment system including coagulation, flocculation, clarification (sedimentation or dissolved air flotation) and filtration is capable of effectively removing intact cells and the majority of intracellular toxins [11,12]. However, MCs can still be released after the death of algal cells or through lysis of the cells after physical/chemical treatments (e.g., application of pre-oxidation and algicides). The situation may be more serious during algal outbreaks [13,14]. Total MC concentration was reported to reach up to 19,000 μg/L (approx. 19 μM) in the water samples collected during a cyanobacterial bloom [5]. It is known that conventional water treatment trains poorly remove dissolved extracellular microcystins [10,15], so that they may contact with certain disinfectants (e.g., chlorine) to produce unwanted disinfection by-products (DBPs).

Over the last 40 years, most DBP studies have focused on the currently regulated carbonaceous DBPs (C-DBPs), especially trihalomethanes (THMs), which commonly occur in water at higher concentrations than the others [16]. However, in the past decade, nitrogen-containing DBPs (N-DBPs), such as haloacetonitriles (HANs), have increasingly received attention because of their significantly higher cytotoxicity and genotoxicity than regulated C-DBPs (e.g. THMs) [17]. Additionally, the presence of chloral hydrate (CH), the hydrated form of trichloroacetaldehyde (the most abundant one among the studied haloacetaldehydes [HALs]) in drinking water which has been investigated as a DBP since the late 1980s, has proven to be genotoxic in numerous prokaryotic and eukaryotic assay systems including mammalian cells, and mutagenic in vivo and in vitro [18–20]. And recent studies demonstrated that HALs were highly cytotoxic in comparison with other DBP chemical classes, including THMs and HANs [20,21], and tribromoacetaldehyde (TBAL) particularly exhibited the highest cytotoxicity in all chlorinated and brominated HALs [22].

A recent study reported that MC-LR could be transformed to chloroform (CF, the most abundant one in all studied THMs) after 24 h chlorination [23]. However, it is unknown whether other DBPs (e.g. HANs and HALs) can also be produced from the chlorination of MC-LR. In practices, considering that conventional drinking treatment processes are ineffective for the reduction of MCs, pre-oxidation is usually selected to improve the MC removal [24–26]. However, little information is available regarding the effect of pre-oxidation on the formation of DBPs from the downstream chlorination of MCs during disinfection. It is known that MCs are a class of typical combined acids, because they consist of a broad range of common free amino acids. Recent studies found that tyrosines in free and combined forms showed different N-DBP formation behaviors [27]. Therefore, it is of interest to compare the DBP formation from the chlorination of MCs and free amino acids included in MC molecular structure.

The objective of this study was to (1) investigate the formation of both C-DBPs (THMs and HALs) and N-DBPs (HANs) from MC-LR (a MC representative) during chlorination; (2) examine the influence of the commonly used pre-oxidation treatments (permanganate [PM], hydrogen peroxide [H_2O_2] and chlorine dioxide [ClO_2]) on the formation of these DBPs; and (3) compare the difference between the patterns of the C-DBP and N-DBP formation from MC-LR (as a combined acid) and free amino acid monomers included in MC-LR molecular structure. This study would provide essential information on the prediction and controlling of C-DBP and N-DBP formation at drinking water treatment plants (DWTPs) using algal-impacted water as their drinking water sources.

2. Materials and methods

2.1. Materials

Potassium permanganate (>99%), H_2O_2 (30 wt.%), and 10 DBP standards, including four THMs (CF, bromodichloromethane [BDCM], dibromochloromethane [DBCM] and bromoform [BF]), four HANs (dichloroacetonitrile [DCAN], trichloroacetonitrile [TCAN], bromochloroacetonitrile [BCAN], and dibromoacetonitrile [DBAN]) and two HALs (CH and TBAL) were obtained from Sigma–Aldrich (St Louis, Missouri, USA). MC-LR (≥97%) was purchased from Taiwan Algae Science Inc. (Taoyuan, Taiwan). All the other chemical reagents were at least analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) unless otherwise noted. Chlorine stock solution was prepared by diluting a 6% NaOCl solution with ultrapure water, and was daily standardized with a portable photometer (HACH Pocket Colorimeter™ II, USA) prior to use. ClO_2 solution was produced by the combination of two powder reagents of sodium chlorite and sodium bisulfate monohydrate and was daily standardized with a portable photometer (HACH Pocket Colorimeter™ II, USA) prior to use,