View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by Elsevier - Publisher Connector

Available online at www.sciencedirect.com

SciVerse ScienceDirect

ELSEVIER

Procedia Environmental Sciences 18 (2013) 597 – 601

Procedia Environmental Sciences

2013 International Symposium on Environmental Science and Technology (2013 ISEST)

Trichloromethane formation potential in killing algae with chlorine dioxide

Shaoxiu Li [a,]*, Dejun Zhao[a], Shujie Hu[a], Zhihong Wang[a], Dongmei Li[a] , Xiuli Yuan[a], Baohong Xie[b]

[a]*Faculty of Civil and Traffic Engineering, Guangdong University of Technology, Guangzhou 510006, China*
[b]*Water Affair Project Construction and Management Center of Guangzhou, Guangzhou, Guangdong 510640, China*

Abstract

Trichloromethane was detected by gas chromatography-mass spectrum- selected ion monitoring system during killing algae with chlorine dioxide. After oxidized by chlorine dioxide, the algal solution was filtered to removed algae, the filtrate was cultured with chlorine, and the trichloromethane was also analyzed. The results showed that trichloromethane did not form during killing algae with chlorine dioxide，but the solution which was oxidized by chlorine dioxide and filtered to removed algae generated trichloromethane after cultured with chlorine. The concentration of trichloromethane formed was influenced by the dose of chlorine dioxide used to killing algae, initial algal number and chlorine concentration. When chlorine dioxide was below 3 $mg \cdot L^{-1}$, the trichloromethane concentration fast increased with the dose of chlorine dioxide increasing, while chlorine dioxide was above 3 $mg \cdot L^{-1}$, the trichloromethane concentration reached to a steady value. The trichloromethane concentration also increased with the increase of initial algal number and chlorine concentration. But even chlorine concentration was as high as 10 $mg \cdot L^{-1}$, the trichloromethane concentration was not over 28 $\mu g \cdot L^{-1}$, which was lower than the requirement for 0.06 $mg \cdot L^{-1}$ trichloromethane in China Standards for Drinking Water Quality (GB5749-2006).

© 2013 The Authors. Published by Elsevier B.V. Open access under CC BY-NC-ND license.
Selection and peer-review under responsibility of Beijing Institute of Technology.

Keywords: algae; chlorine dioxide; trichloromethane; formation potential

1. Introduction

Eutrophication of waters causes algae excessive growth. In certain condition, the occurrence of algae blooms threatens drinking water resources. Consequently, algae are increasingly considered in water treatment. It's urgent and necessary to research the efficient algae removal technology in water plants. As

* Corresponding author. Tel.: +86-13610306588; fax: +86-020-39322515.
E-mail address: water@gdut.edu.cn.

1878-0296 © 2013 The Authors. Published by Elsevier B.V. Open access under CC BY-NC-ND license.
Selection and peer-review under responsibility of Beijing Institute of Technology.
doi:10.1016/j.proenv.2013.04.081

a disinfectant, ClO_2 also has been found to be effective for killing algae [1,2]. But the security of organic toxicity of the technology of killing algae with ClO_2 has not been cleared. When ClO_2 reacts with organism, the organic by-products form [3]. It's known that trichloromethane is generated when the organism is chloridized[4]. While ClO_2 oxidizes organism, the inorganic by-products containing chlorine form, which further react with organism and trichloromethane is perhaps generated. Therefore, trichloromethane must be investigated to detect the security of the technology of killing algae with ClO_2. In addition, the precursor of trichloromethane may form during killing algae with ClO_2, thus, after oxidized by chlorine dioxide and filtered to remove algae, the filtrate is cultured with chlorine to study the formation of trichloromethane.

2. Experiment

2.1. Source of algae

The algae were *Cylindrospermopsis*. They were purchased from China Science Institute Wuhan freshwater algae species storehouse.

2.2. Experimental method

Algae solution was prepared by diluting algae with distilled water. Chlorine dioxide was added into the algae solution, which was fast mixed to make chlorine dioxide and algae react enough. Algae solution was filtered after the reaction of chlorine dioxide and algae. Then some of the filtrate was analyzed to detect thetrichloromethane.

Another 200ml of the filtrate was taken into a ground glass bottle. pH of the filtrate was adjusted to 7 with 1M diluted HCl solution. 4mL of phosphate buffer(0.29MNaOH+0.5M KH_2PO4) was added into 200 mL of the filtrate. After addition of sodium hypochlorite solution, the bottle containing filtrate was capped and stored in a Biochemical incubator in darkness at（20 ± 0.5）℃for 72 hours. After that, 50ml of the bottle's solution was taken out and ascorbic acid was added in to remove the excess chlorine for trichloromethane analysis.

2.3. Analysis method

Trichloromethane concentration was analyzed by the method of gas chromatography-mass spectrum-selected ion monitoring（GC-MS-SIM）. Sample for analysis was injected on a 30m×0.25mm×0.25µm column purchased from Thermo Electron Corporation. Column temperature was set at 40℃for 10 minutes, then rose with a rate of 5℃ per minute until 200℃. The sample was injected to the column by auto-headspace method, then trichloromethane concentration was measured by GC-MS-SIM.

3. Results

3.1. Trichloromethane formation potential after killing algae with ClO_2

Experiments of killing algae with ClO_2 were carried out while the dosage of chlorine dioxide was 2, 4, 8, 10 $mg \cdot L^{-1}$respectively under pH 6.5, 7.0 and 7.5 respectively. Algae concentration of the water samples was 1.8×10^8cells per litre. The contact time between algae and ClO_2 was 10 minutes, temperature of reaction was at 25°C. Trichloromethane was not found in the algae solutions after reaction. It means that trichloromethane does not form during oxidizing algae by ClO_2. Because the grade of purity of ClO_2 used in killing algae is more than 99%, there is not chlorine to react with algae generating trichloromethane.

3.2.Trichloromethane formation potential after culturing with chlorine

Although trichloromethane doesn't directly form during the reaction between ClO_2 and algae, some intermediate unsaturated organisms perhaps form. Once these organisms react with chlorine, which proceeds in later cholorination disinfectation in drinking water treatment, trichloromethane will form. Thus, it is necessary to study the trichloromethane formation potential. The trichloromethane formation potential refers to the amount of forming trichloromethane in water cultured with chlorine under high dose of chlorine and long reaction time. The factors of influencing the trichloromethane formation were studied.

3.1.1. Effect of chlorine dioxide dose on the trichloromethane formation potential

The experiments of killing algae by ClO_2 under different dose of ClO_2 were carried out, then the algae solutions were filtered, the filtrate were cultured with chlorine, 72 hours later, trichloromethane was measured by GC-MS-SIM system. The results are shown in Fig. 1, which reflects that the dose of ClO_2 influences the formation of trichloromethane in later chlorination. When the dosage of ClO_2 is less than 3mg·L^{-1}, the trichloromethane concentration increases with the dosage of ClO_2 increasing, but when the dosage of ClO_2 is more than 3mg·L^{-1}, the trichloromethane concentration almost keep unchanging. But even though the dosage of ClO_2 is high up to 10 mg·L^{-1}, the trichloromethane concentration doesn't exceed 16 μg·L^{-1}. These experiments illustrate the precursors of trichloromethane form during killing algae with ClO_2. The more dose of ClO_2, the more precursors of trichloromethane.So the trichloromethane concentration increases with the increase of ClO_2 dosage.

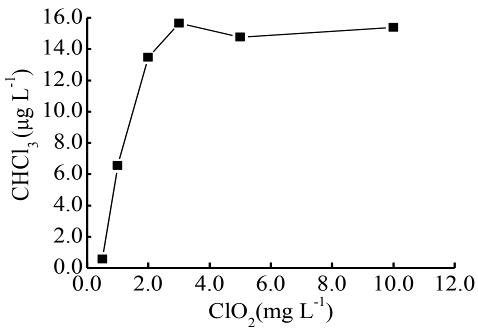

Fig. 1. Effect of ClO_2 dose on the formation of trichloromethane.

3.1.2. Effect of algae number on the trichloromethane formation potential

The effect of algae number on the trichloromethane formation is shown in Table 1, which demonstrates that when algae number is1.8×10^6 cells·L^{-1}, the trichloromethane concentration is low, only 2.31μg·L^{-1}, but the trichloromethane concentration subsequently increases with the increase of algae number. Large algae number causes more precursors of trichloromethane to form, thus, higher concentration of trichloromethane were gained.

Table 1. Effect of algae number on the trichloromethane formation.

Algea number (×10^8 cells·L^{-1})	$CHCl_3$(μg·L^{-1})
0.018	2.31
0.18	8.14
1.8	17.36
9	20.54

3.1.3. Effect of chlorine dose on the trichloromethane formation potential

The concentration of chlorine theoretically influences the trichloromethane formation. Fig. 2 is the result that the effect of chlorine dose on the trichloromethane formation potential. It shows that when chlorine concentration is below 2 mg·L^{-1}, the trichloromethane concentration increases fast with the increase of chlorine concentration, but when the chlorine concentration is above 2 mg·L^{-1}, the trichloromethane concentration slow increases. When the chlorine concentration is up to 10 mg·L^{-1}, the trichloromethane concentration is not exceed 28 μg·L^{-1}.

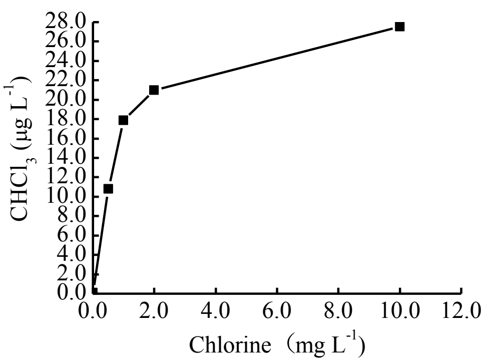

Fig. 2. Effect of ClO2 dose on the formation of trichloromethane.

4. Conclussions

Trichloromethane doesn't form during killing algae by chlorine dioxide, but forms after chlorine is added into the water in which algae have been removed. The concentration of trichloromethane formed is relevant to the dose of ClO_2 used to killing algae, initial algal number and chlorine concentration. When ClO_2 is below 3 mg·L^{-1}, the trichloromethane concentration fast increases with the dose of ClO_2 increasing, while ClO_2 is above 3 mg·L^{-1}, the trichloromethane concentration reaches to a steady value. The trichloromethane concentration increases with the increase of initial algal number and chlorine concentration. Even chlorine concentration is high to 10 mg·L^{-1}, the trichloromethane concentration is not over 28 μg·L^{-1}, which is lower than the requirement for 0.06 mg·L^{-1} trichloromethane in China Standards for Drinking Water Quality (GB5749-2006). In fact, the dosage of chlorine is lower in the process of disinfection after killing algae with ClO_2, so trichloromethane does not affect the safety of killing algae with ClO_2 in drinking water.

Acknowledgements

This work was financially supported by Water Affair Science and Technology Project of Guangzhou City in 2011.

References

[1] Li SX, Xia Zhao DJ, Yuan XL, Wang ZH, Li DM, et al. Killing Cylindrospermopsis with Chlorine Dioxide. *Chinese journal of environmental engineering*, 2012;10(6):51–9. (in Chinese)

[2] Ji Y, Fu J, Huang JL. Removal efficiency of microcystis in water by chlorine dioxide. *Chemical Engineer*, 2008;148（1）：17-20.(in Chinese)

[3] Dabrowska A, Swietlik J, Nawrocki J. Formation of aldehydes upon ClO2 disinfection. *Water Research*, 2003;37: 1161–1169.

[4] Cynthia MMB, Emma HG, Bruce J, Simon AP.Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. *Water Research*, 2010;44(3):729-740.