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Influencing factors of disinfection byproducts formation during chloramination of Cyclops metabolite solutions

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ABSTRACT

Effects of reaction time, chlorine dosage, pH and temperature on the formation of disinfection byproducts (DBPs), were investigated during the chloramination of Cyclops metabolite solutions. The results showed that some species of DBPs like trichloromethane (TCM), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) could accumulate to their respective stable values with a progressive elevation in reaction time and monochloramine concentration. And 1,1,1-2-trichloropropanone (1,1,1-TCP) content decreased correspondingly with a continuous increase of reaction time. The amounts of chloral hydrate (CH), chloropicrin (TCNM), 1,1,1-TCP and DCAA firstly increased and then decreased with increasing monochloramine doses. Higher temperature resulted in a decrease of CH, dichloroacetonitrile (DCAN), 1,1-dichloropropanone (1,1-DCP), 1,1,1-TCP, DCAA and TCAA concentration. pH affected the formation of the different DBPs distinctly. TCM accumulateded with the increase of pH under 9, and DCAA, TCAA, CH and 1,1-DCP decreased continuously with increasing pH from 5 to 10, and other DBPs had the maximum concentrations at pH 6–7.

Introduction

Cyclops of zooplankton excessively propagates in waters due to the eutrophication, especially in reservoirs and lakes for drinking water source in recent years. Cyclops overgrowth causes problems in drinking water treatment, such as clogging filters and easily penetrating sand filters. Cyclops also causes water quality problems in water supply, it may transmits disease as the host of pathogenic parasite, like schistosome and eelworm, to threaten human health (Cui et al., 2002; Lin et al., 2007).

Natural organic matter, defined as the complex matrix of naturally occurring organic materials present in natural waters, is usually considered to be a precursor of disinfection byproducts (DBPs) (Yang et al., 2007; Bougeard et al., 2010). Recent studies (Plummer and Edzwald, 2001; Zhang et al., 2009) otherwise revealed that, besides the humic acid and organic matter, certain bacteria and algae cells with their extracellular organic matter could also be the precursors of DBPs. Algal cells are known to be enriched in organic nitrogen in the forms of proteins, amino acids, and amines, and have established to the formation of carbonaceous and nitrogenous disinfection byproducts from the chlorination (Fang et al., 2010). It has been proved that trihalomethanes (THMs), haloacetonitriles (HANs) and chloral hydrate (CH) formation were detected after chlorination of the five kinds of bacteria cultures, and a great impact on the formation of HANs was bromide (Zhang et al., 2010). Compared to the algae, bacteria and other microorganisms, Cyclops is large in size, and it therefore suggests the contained biomass of amino acids, protein, fat and other organic matter, those all have a higher potential to form the DBPs (Liu and Fu, 2010). Therefore, it is interesting to find out how the metabolites produced by these organisms to affect the water safety and contribute to the production of DBPs.

Many factors have been extensively studied and reported to affect the formation of DBPs during disinfection, such as

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reaction time, pH, temperature, disinfectant concentration, and precursor properties. The formation of stable THMs and HAAs was increased with increasing reaction time and chlorine dosage (Fang et al., 2010). However, increasing in reaction time and chlorine dosage have little effect on the formation of unstable DBPs, such as HANs and haloketones (HKs). Higher pH led to an increase of THMs formation but a reduction of HAAs, dichloroacetonitrile (DCAN) and 1,1,1-trichloropropanone (1,1,1-TCP) (Reckhow et al., 2001; Yang et al., 2007).

Consistent efforts have been made to determine the identities and toxicities of various DBPs species and their groups, especially those of THMs, HAAs and HANs, and to model their formation and control their occurrence, but information about their relationship with chloramination of Cyclops metabolite solutions is unknown. The objective of this research is to evaluate the formation of selected DBPs during chloramination of Cyclops metabolite solutions under various conditions.

1 Materials and methods

1.1 Reagents and solutions

All chemical solutions were prepared from reagent grade chemicals or stock solutions. Methanol, acetone and methyl-tert-butyl ether were all HPLC grade. The monochloramine solution (500 mg/L) was freshly prepared by mixing a free chlorine solution with an ammonium chloride (NH_4Cl) solution at an initial Cl/N mass ratio of 4/1 and measured by DPD/FAS titration (APHA Standard Methods 4500-Cl). Phosphate buffers (0.2 mol/L) at pH 5, 6, 7, 8, 9 and 10 were prepared with 0.2 mol/L NaH_2PO_4 and 0.2 mol/L Na_2HPO_4. Standard samples for THMs, HAAs, HANs, HKs, CH and chloropicrin (TCNM) analyses were obtained from Supelco.

1.2 Sample preparations

Cyclops, initially collected from the vicinity of Mopanshan reservoir in Harbin, and Mopanshan reservoir is an important drinking water sources for Harbin. Cyclops was cultured in an aerated 25 L glass aquaria filled with raw water from reservoir. Aquaria were kept at a constant temperature (15°C) and exposed to a consistent photoperiod (12 hr light/12 hr dark). Cyclops cultured for 10 days under this condition. Large numbers of Cyclops were added in a 1 L beaker with deionized water. Cyclops was removed after 24 hr, and Cyclops suspensions were filtered by a 0.45 μm membrane to eliminate suspended solids and stored in the dark at 4°C, to minimize changes in the constituents, and analyzed within one week. The total organic carbon (TOC) concentration was measured. Standards were prepared by diluting reagents to 4 mg/L.

1.3 Analytical methods

The chloramine concentration was measured by DPD/FAS titration (APHA Standard Methods 4500-Cl). Analyses of THMs, HAAs, HANs, HKs, CH and TCNM were carried out on a gas chromatograph (GC) (Agilent 7890) with an electron capture detector (ECD) (US EPA, 1995, 2003). The THMs, HANs, HKs, CH and TCNM concentrations were measured by liquid-liquid extraction procedure by methyl tert-butyl ether and acid methanol according to US EPA Method 551.1. The column used was an HP-5 fused silica capillary column (30 mm × 0.25 mm I.D. with 0.25 mm film thickness). The GC-ECD operating conditions were: detector, 290°C; injector, 200°C; injection volume 1 mL; and temperature program, 35°C for 5 min, ramped to 75°C at 10°C/min, held for 5 min, then ramped to 100°C at 10°C/min, and then held for 2 min. For DCAA and TCAA analysis, the samples were pretreated with extraction/derivatization procedure by methyl tert-butyl ether and acid methanol according to US EPA Method 552.3. The column used was an HP-5 fused silica capillary column (30 mm × 0.25 mm I.D. with 0.25 mm film thickness). The injector, ECD and GC oven temperature programs for compounds other than HAA_9 were: injector of 200°C; ECD of 290°C; oven of an initial temperature of 35°C for 9 min, ramping to 40°C at 2°C/min and holding for 8 min, ramping to 80°C at 20°C/min, ramping to 160°C at 40°C/min and holding for 4 min; and those for HAAs were: injector of 210°C; ECD of 290°C; oven of an initial temperature of 30°C for 20 min, ramping to 40°C at 1°C/min, ramping to 205°C at 20°C/min and holding for 4 min.

1.4 Experimental procedures

The stock solution with Cyclops metabolite solutions was diluted with deionized water to make testing solutions of 4 mg/L as TOC. A monochloramine concentration of 10 mg/L was applied to Cyclops metabolite solutions buffered at pH 7.5 with deionized water in the 250 mL glass bottles, and incubated at 20 ± 1°C after 48 hr. Under the baseline conditions, the influencing factors of reaction time (2, 4, 6, 12, 24, 36, 48, 72 hr), monochloramine concentration (1, 2, 4, 6, 8, 10, 20 mg/L), pH (5, 6, 7, 8, 9, 10) and temperature (10°C, 20°C, 30°C) were investigated during the monochloramination of Cyclops metabolite solutions. After the reaction of monochloramination, solutions were quenched with sodium sulfite and extracted for subsequent DBPs analyses. For comparison, a study using deionized water was also conducted in the same manner under the baseline condition, and the following experimental results have been subtracted the blank. The DBPs detected in the present study were originated from the Cyclops metabolite solutions.