Separation and Purification Technology 117 (2013) 53–58

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

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

Removal efficiency and possible pathway of odor compounds (2-methylisoborneol and geosmin) by ozonation

Baoling Yuan [a,*], Dongmei Xu [a], Fei Li [a], Ming-Lai Fu [b,*]

[a] Institute of Municipal and Environmental Engineering, College of Civil Engineering, Huaqiao University, Xiamen, Fujian 361021, PR China
[b] Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, PR China

ARTICLE INFO

Article history:
Received 4 December 2012
Received in revised form 11 April 2013
Accepted 18 April 2013
Available online 26 April 2013

Keywords:
Ozone
MIB
GSM
Lyngbya kuetzingii
Degradation pathway

ABSTRACT

2-Methylisoborneol (MIB) and geosmin (GSM) are taste and odor compounds produced as secondary metabolites by some cyanobacteria and actinomycetes, and thus they can be present in some drinking water sources. The removal efficiency, intermediate by-products, and degradation pathway of MIB and GSM in synthetic water by ozonation were studied. The results show that ozone is efficient in removing MIB and GSM from an aqueous solution, depending on pH and the initial MIB and GSM concentration. Ozonation of algal suspension was also studied and the removal efficiency of GSM mainly produced by *Lyngbya kuetzingii* can reach 99.91% although the ozonation could damage the algal cells and release the intracellular organic compounds. The degradation by-products of MIB or GSM were identified by gas chromatography–mass spectrometry and dehydration and open ring compounds are the main by-products. Possible degradation pathways for the ozonation of MIB and GSM were proposed.

1. Introduction

In recent years, with the aggravation of eutrophication in surface waters, cyanobacterial blooms occur frequently [1,2]. 2-methylisoborneol (2-MIB) and geosmin (1,2,7,7-tetramethyl-2-norborneol) (GSM) are semi-volatile compounds, which are usually produced as the secondary metabolites by some actinomycetes, planktonic and epiphytic cyanobacteria [3–6]. These two compounds impart earthy–musty taste and odor to water at very low odor thresholds concentration of less than 15 ng L^{-1} [7,8]. In China, the threshold odor concentrations of these odor compounds in drinking water are 10 ng L^{-1} according to the China Standards for Drinking Water Quality (GB5749-2006).

Conventional water treatment processes (pre-chlorination, coagulation, sedimentation, and filtration) cannot remove these two odor compounds efficiently [9–11]. These secondary metabolites can serve as precursors to form disinfection by-products (DBPs) during pre-chlorination [12,13], producing potential health risks [14–16]. Only the adsorption on activated carbon has been applied successfully to reduce the concentration below the threshold odor concentration [17]. In the past few years, the research on the removal of taste and odor compounds has been greatly focused on oxidative techniques and advanced oxidation processes (AOPs) [18–21]. In advanced drinking water treatment practices, ozonation is the process most commonly employed to remove or decompose these taste and odor compounds (T&Os) as well as precursors of triharomethane because of its strong oxidation potential [22–24]. Westerhoff et al. [24] conducted batch ozonation experiments to study the effect of ozone oxidation parameters on the removal of MIB and GSM. Liang et al. [25] found that pH is a significant factor affecting oxidation of MIB by ozonation and the presence of natural organic matters did not have a significant effect on ozonation of MIB and GSM.

Removal of MIB and GSM by ozonation is dependent on reaction parameters such as pH, ozone dosage, reaction time, water quality parameters, temperature and initial concentrations. This paper not only investigates the correlation between ozonation and water quality parameters, but also presents a detailed investigation of MIB and GSM degradation in an attempt to gain more insight into the underlying reaction mechanisms by ozonation. The intermediate by-products were particularly focused and the possible pathway during the ozonation reaction was proposed.

2. Materials and methods

2.1. Algae culturing and preparation

2.1.1. Algal culturing

Planktonic blue–green algae *Lyngbya kuetzingii* (FACHB 388) was obtained from the Institute of the Freshwater Algae Culture Collection of the Institute of Hydrobiology (FACHB-Collection), Chinese Academy of Sciences. *L. kuetzingii* was cultivated in batch cultures in BG-11 medium under a cool-white fluorescent lamp with

* Corresponding authors. Tel.: +86 592 616 2780; fax: +86 592 6190762.
E-mail addresses: yuanbl@hotmail.com (B. Yuan), mlfu@iue.ac.cn (M.-L. Fu).

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http://dx.doi.org/10.1016/j.seppur.2013.04.029

the light intensity 2000 lx in a light/dark (L/D) 12 h/12 h cycles at an ambient temperature of 25 ± 1 °C and the algal solutions were shaken for several times every day for avoiding the aggregation. Culture was harvested in the log growth phase after 15 days.

2.1.2. Preparation of the algae suspensions

Algae cell concentration in suspensions solution was determined by the concentration of chlorophyll a (Chl-a). Stock culture of *L. kuetzingii* ($2–8 \times 10^{11}$ cells L^{-1}) was collected by centrifugation at 5000 rpm for 10 min. The supernatant was used for the measurement of extracellular GSM. The cells separated during the centrifugation were washed three times and then re-suspended in deionized water. The cells were then subjected to three freeze/thawing cycles, and then ultrasonic treatments (5–5 s pulse, 300 W, 10 min), before filtered through 0.45 μm cellulose acetate membranes. The organic matters in the filtrate were referred as intracellular GSM.

2.2. Ozonation

Ozone was generated by a corona discharge ozone generator (Model CF-YG5, China). A batch method was used for the ozonation of synthetic waters (containing MIB and GSM) or algal suspensions. The volume of Millli-Q purified water sample was 500 mL and an ozone solution (4.19 mg L^{-1}) was obtained by bubbling ozone gas into Millli-Q purified water at 4 °C constantly. MIB and GSM standard mixture was added into the vessel with the continued stirring. The ozone gas was kept entering into the vessel for 30 min. Ozonation was quenched with 0.1 mol L^{-1} sodium thiosulfate solution. The samples were prepared for analysis. All ozonation experiments were conducted at 25 ± 1 °C and pH of 7.3. Each experiment was performed in triplicate. O_3 concentrations were measured using the standard methods for drinking water (GB/T 5750-2006). Fig. 1 shows a schematic diagram of the experimental procedure for the decomposition of MIB and GSM.

2.3. Analytical methods

2.3.1. MIB and GSM exaction in synthetic water by Purge-Trap (PT)

MIB and GSM were purchased from Sigma–Aldrich (USA) as solutions of 100 mg L^{-1} in methanol. Internal standards of (+/−)-d_5-geosmin (d_5-GSM) and (−)-2-methylisoborneol-d_3 (d_3-MIB) were also obtained from Sigma–Aldrich (USA). Five milligrams of d_3-MIB and d_5-GSM were dissolved in methanol to make a mixed stock solution at an approximate concentration of 500 mg L^{-1} for each. The synthetic water containing MIB and GSM was kept at 4 °C after filtering through a membrane of 0.45 μm and then determined within 14 days. PT was performed by Eclipse 4660 Purge and Trap Sample Concentrator, with 4551A autosampler (OI Analytical Company, USA), a #10 trap (OI Analytical Company, USA), and a 25 mL purge tube. An OI-Analytical Eclipse 4660 with Tenax-Silica Gel-Charcoal sorbent was used. PT was programmed as follows: a 25 mL of water sample (containing 5 g NaCl) with internal standards was drawn by a sample loop of autosampler and transferred to the purge tube. Target compounds were purged from the sample by high-purity nitrogen, with a flow rate of 40 mL min^{-1} at 60 °C for 13 min, and trapped on Tenax-Silica Gel-Charcoal sorbent. Subsequently, the trap was heated to 200 °C and the trapped components were desorbed by helium for 0.5 min, and then transferred directly to the GC system. Meanwhile, the sampling needle, loop and purge tube were washed with HPLC water three times, and the trap was baked at 240 °C for 10 min. These processes are enough to clean the purge system.

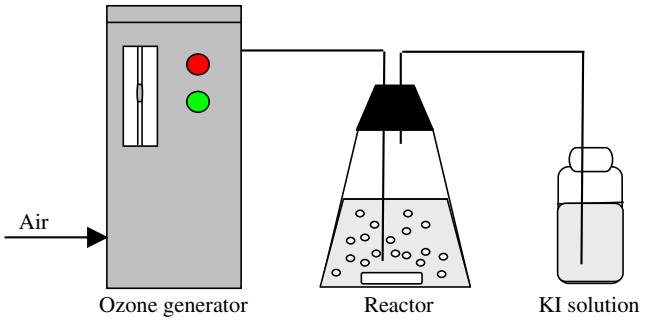

Fig. 1. Experimental setup of ozonation of MIB and GSM.

2.3.2. MIB and GSM extraction in algal suspension by Solid Phase Micro-Extraction (SPME)

One hundred and fifty milliliters of water samples were placed into a 250 mL vial containing a magnetic stirrer. After addition of 45 g of NaCl and 150 μL of mixed internal standard stock solution (500 mg L^{-1}), the vial was sealed with a silicon-Teflon septum cap. The sealed vial was placed in a water-bath at 60 °C for 30 min and stirred at 800 rpm of the stirring rate.

Odor organic compounds derived from algae or formed during ozonation in solution were extracted by using SPME manual devices (Supelco, USA). After pre-heating, 50/30 μm Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fiber was used to penetrate the septum and the fiber extended into the headspace for extraction. After exposures for 40 min, the fiber was immediately inserted into the GC injection port for desorption.

2.3.3. Detection of MIB, GSM and by-products by GC/MS method

The injector temperature was set at 280 °C in the split mode (split ratio: 20:1) for PT. The injection temperature was set at 230 °C in the splitless mode and desorption time was 3 min for SPME. Analyses were carried out with an Agilent 6890 series GC system coupled with a 5973i series mass spectral detector. High-purity helium (99.9999%) with a constant flow rate of 1 mL min^{-1} was used as the carrier gas. The oven temperature was programmed from an initial temperature of 50 °C held for 2 min, then ramped to 160 °C at 5 °C min^{-1}, finally ramped to 280 °C at 20 °C min^{-1} and held for 8 min, and the total run time was 38 min. The GC–MS transfer line temperature was maintained at 300 °C. The electron impact (EI) ion source of the mass spectrometer and the quadrupole temperature was set at 230 °C and 150 °C, respectively. The EI ionization mode was used with an electron energy of 70 eV. The mass spectra were obtained at a mass-to-charge ratio scan ranging from 45 to 200 amu to determine appropriate masses for selected ion monitoring (SIM). Mass spectral quantitative ions were *m/z* 107, 138, 112, and 114 for MIB, d_3-MIB, GSM and d_5-GSM, respectively [26]. Identification of by-products by ozonation was also carried out by mass-spectra.

3. Results and discussion

3.1. Ozonation of MIB and GSM

The ozonation of MIB and GSM were conducted at 4.19 mg L^{-1} of ozone concentration for 20 min of reaction time. Concentrations of MIB and GSM were determined using PT-GC/MS analyses of the solutions at different reaction times. Control experiments confirm that the concentrations of MIB and GSM remain constant throughout the experimental process without ultrasonic irradiation (no loss due to evaporation or adsorption). Upon ozonation, MIB and GSM (100 ng L^{-1}) are readily degraded and the removal rates within 5 min are more than 60%, as showed in Fig. 2. After ozonation for 20 min, over 90% of both compounds were degraded. As Waterhoff