CONTENTS

Aquatic environment

Advanced oxidation of bromide-containing drinking water: A balance between bromate and trihalomethane formation control
Yongjing Wang, Jianwei Yu, Po Han, Jing Sha, Tao Li, Wei An, Juan Liu, Min Yang .................................................. 2169

Effects on nano zero-valent iron reactivity of interactions between hardness, alkalinity, and natural organic matter
in reverse osmosis concentrate
Yuhoon Hwang, Hang-Sik Shin ................................................................. 2177

Environmental significance of biogenic elements in surface sediments of the Changjiang Estuary and its adjacent areas
Yu Yu, Jinming Song, Xuegang Li, Huamao Yuan, Ning Li, Liqin Duan .................................................. 2185

Environmental factors influencing cyanobacteria community structure in Dongping Lake, China
Xuetang Lu, Chang Tian, Haiyan Pei, Wengong Hu, Jun Xie ................................................................. 2196

Disinfection byproduct precursor removal by enhanced coagulation and their distribution in chemical fractions
Yanmei Zhao, Feng Xiao, Dongsheng Wang, Mingquan Yan, Zhe Bi .................................................. 2207

Evaluation of antioxidant enzymes activities and identification of intermediate products during phytoremediation
of an anionic dye (C.I. Acid Blue 92) by pennywort (Hydrocotyle vulgaris)
Fatemeh Vafaei, Ali Movafeghi, Ali Reza Khataee ................................................................. 2214

Decrease of NH$_4^+$-N by bacterioplankton accelerated the removal of cyanobacterial blooms in aerated aquatic ecosystem
Xi Yang, Ping Xie, Zhimei Ma, Qing Wang, Huahu Fan, Hong Shen .................................................. 2223

Spatial and seasonal variability of CO$_2$ flux at the air-water interface of the Three Gorges Reservoir
Le Yang, Fei Lu, Xiaoke Wang, Xiaonan Duan, Lei Tong, Zhiyun Ouyang, Heping Li .................................................. 2229

Atmospheric environment

Removal of nitric oxide from simulated flue gas via denitrification in a hollow-fiber membrane bioreactor
Xinyu Zhang, Ruofei Jin, Guanglei Liu, Xiuyong Dong, Jiti Zhou, Aijie Wang .................................................. 2239

Terrestrial environment

Comparison of a plant based natural surfactant with SDS for washing of As(V) from Fe rich soil

Environmental biology

Biodegradation of organochlorine pesticide endosulfan by bacterial strain Alcaligenes faecalis JBW4
Lingfen Kong, Shaoquan Zhu, Lusheng Zhou, Hui Xie, Kunchang Su, Tongxian Yan, Jun Wang, Jinhua Wang, Fenghua Wang, Fengxia Sun .................................................. 2257

Bioaugmentation with a pyridine-degrading bacterium in a membrane bioreactor treating pharmaceutical wastewater
Donghui Wen, Jing Zhang, Ruilin Xiong, Rui Liu, Lujun Chen .................................................. 2265

Absolute dominance of hydrogenotrophic methanogens in full-scale anaerobic sewage sludge digesters
Jaai Kim, Woong Kim, Changsoo Lee .................................................. 2272

Characterization and biodegradation kinetics of a new cold-adapted carbamazepine-degrading bacterium,
Pseudomonas sp. CBZ-4
Ang Li, Rui Cai, Di Cui, Tian Qiu, Changlong Pang, Jixian Yang, Fang Ma, Nanqi Ren .................................................. 2281

Environmental catalysis and materials

Effects of solution chemistry on arsenic(V) removal by low-cost adsorbents
Yuru Wang, Daniel C. W. Tsang .................................................. 2291

Synergistic photocatalytic degradation of pyridine using precious metal supported TiO$_2$ with KBrO$_3$
Fei Tian, Rongshu Zhu, Feng Ouyang .................................................. 2299
Simultaneous determination of brominated phenols in soils (Cover story)
Wei Han, Sen Wang, Honglin Huang, Lei Luo, Shuzhen Zhang
Simultaneous determination of ten taste and odor compounds in drinking water by solid-phase microextraction combined with gas chromatography-mass spectrometry
Xichao Chen, Qian Luo, Shengguang Yuan, Zi Wei, Hanwen Song, Donghong Wang, Zijian Wang
Benzene, toluene and xylenes levels in new and used vehicles of the same model
Joanna Faber, Krzysztof Brodzik, Anna Gola-Kopek, Damian Łomankiewicz
Preparation, characterization and application of thiosemicarbazide grafted multiwalled carbon nanotubes for solid-phase extraction of Cd(II), Cu(II) and Pb(II) in environmental samples
Jie Zhang
Determination of VOCs in groundwater at an industrial contamination site using a homemade low-density polyethylene passive diffusion sampler
Xu Ma, Zhiqiang Tan, Long Pang, Jingfu Liu
Quantification of changes in zero valent iron morphology using X-ray computed tomography
Ping Luo, Elizabeth H. Bailey, Sacha J. Mooney
Serial parameter: CN 11-2629/X*1989*m*183*en*P*22*2013-11
Advanced oxidation of bromide-containing drinking water: A balance between bromate and trihalomethane formation control

Yongjing Wang1, Jianwei Yu1,*, Po Han2, Jing Sha2, Tao Li2, Wei An1, Juan Liu1, Min Yang1,*

1. State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: wild.trees@163.com
2. Zhengzhou Water Supply Investment Holdings Co. Ltd., Zhengzhou 450007, China

Received 07 January 2013; revised 08 March 2013; accepted 13 March 2013

Abstract

Addition of H2O2 has been employed to repress bromate formation during ozonation of bromide-containing source water. However, the addition of H2O2 will change the oxidation pathways of organic compounds due to the generation of abundant hydroxyl radicals, which could affect the removal efficacy of trihalomethane precursors via the combination of ozone and biological activated carbon (O3-BAC). In this study, we evaluated the effects of H2O2 addition on bromate formation and trihalomethane formation potential (THMFP) reduction during treatment of bromide-containing (97.6–129.1 μg/L) source water by the O3-BAC process. At an ozone dose of 4.2 mg/L, an H2O2/O3 (g/g) ratio of over 1.0 was required to maintain the bromate concentration below 10.0 μg/L, while a much lower H2O2/O3 ratio was sufficient for a lower ozone dose. An H2O2/O3 (g/g) ratio below 0.3 should be avoided since the bromate concentration will increase with increasing H2O2 dose below this ratio. However, the addition of H2O2 at an ozone dose of 3.2 mg/L and an H2O2/O3 ratio of 1.0 resulted in a 43% decrease in THMFP removal when compared with the O3-BAC process. The optimum H2O2/O3 (g/g) ratio for balancing bromate and trihalomethane control was about 0.7–1.0. Fractionation of organic materials showed that the addition of H2O2 decreased the removal efficacy of the hydrophilic matter fraction of DOC by ozonation and increased the reactivity of the hydrophobic fractions during formation of trihalomethane, which may be the two main reasons responsible for the decrease in THMFP reduction efficacy. Overall, this study clearly demonstrated that it is necessary to balance bromate reduction and THMFP control when adopting an H2O2 addition strategy.

Key words: bromate control; hydrogen peroxide addition; ozone-hydrogen peroxide; trihalomethane formation potential; ozone-biological activated carbon

DOI: 10.1016/S1001-0742(12)60280-0

Introduction

Ozone-biological activated carbon treatment (O3-BAC) has been widely applied for drinking water purification. O3-BAC is efficient at removal of chromaticity, taste and odor (Peter and von Gunten, 2007), as well as reducing dissolved organic carbon (DOC) and trihalomethane formation potentials (THMFP) (Xu et al., 2007). However, with the discovery of the formation of potentially carcinogenic bromate (BrO3−) during ozonation of bromide-containing source water (von Gunten and Hoigné, 1994), it is now becoming a great challenge to balance the requirements between improving drinking water quality and repressing bromate formation.

Several options for the suppression of BrO3− formation, including pH depression, ammonia addition or hydrogen peroxide (H2O2) addition, have been proposed (von Gunten and Pinkernell, 2000). Of these technologies, pH adjustment is normally difficult owing to its high cost and potentially corrosive effects toward related facilities (Sander et al., 1998), while ammonia addition only leads to a partial reduction of bromate (Pinkernell and von Gunten, 2001). Additionally, it has been reported that an H2O2/O3 (g/g) ratio of over 0.8 is required to control the bromate concentration below 10 μg/L (Mizuno et al., 2011). However, the suppression effects could vary among source waters because of disparities in parameters such as bromide, ammonia, background natural organic materials (NOM), and temperature (von Gunten and Oliveras, 1998; von Gunten and Hoigné, 1994).

* Corresponding author. E-mail: jwyu@rcees.ac.cn (Jianwei Yu); yangmin@rcees.ac.cn (Min Yang)
Conversely, the combination of \( \text{O}_3 \) and \( \text{H}_2\text{O}_2 \) (\( \text{O}_3\)-\( \text{H}_2\text{O}_2 \)), which is one of the most common advanced oxidation processes (AOP), would enhance the production of hydroxyl radicals (-OH) significantly. Unlike molecular \( \text{O}_3 \), which is likely to attack organic compounds with electron-rich moieties such as phenols, amines, olefins, amines and aromatic alcohols, hydroxyl radicals tend to react with almost all types of organic materials (Lee and von Gunten, 2010). Because of the differences in reaction pathways, it is likely that the reduction efficiency of THMFP by \( \text{O}_3 \)-BAC could be affected by \( \text{H}_2\text{O}_2 \) addition.

The impacts of \( \text{H}_2\text{O}_2 \) addition on THM precursors removal by ozonation have been investigated by some researchers. Duguet et al. (1985) found that the oxidation efficiencies of organic substances and THM precursors by \( \text{O}_3 \) were enhanced by \( \text{H}_2\text{O}_2 \) addition with the \( \text{O}_3 \) and \( \text{H}_2\text{O}_2 \) doses of 3.5 mg/L and 1.0 mg/L respectively, while Irabelli et al. (2008) found that \( \text{H}_2\text{O}_2 \) addition after ozonation produced an equal or higher THM concentration than that of ozonation alone under the \( \text{H}_2\text{O}_2/\text{O}_3 \) (g/g) ratios of 0.1, 0.2 and 0.35 in a pilot study. Mosteo et al. (2009) observed that 1.5 mg/L of \( \text{H}_2\text{O}_2 \) addition prior to ozonation generated a slightly negative effect on the control of THM precursors in treatment of a synthetic humic solution, compared to ozonation alone with a dosage of 3.0 mg/L. Tubić et al. (2011) also found that the addition of \( \text{H}_2\text{O}_2 \) led to slight increases in THMFP in ground water ozonation experiments at the \( \text{H}_2\text{O}_2/\text{O}_3 \) (g/g) ratios of 0.5 and 2.0, which was attributed to the scavenging effect of excessive amounts of \( \text{H}_2\text{O}_2 \) on hydroxyl radicals (Kleiser and Frimmel, 2000). However, the impacts of \( \text{H}_2\text{O}_2 \) addition on the removal of THM precursors by the combination of \( \text{O}_3 \) and BAC following conventional drinking water treatment have not yet been systematically studied and are not well understood.

In the present study, a pilot system treating bromide-containing source water taken from the downstream Yellow River was used to investigate: (1) the effects of \( \text{H}_2\text{O}_2 \) dose on \( \text{BrO}_3^- \) control under different ozonation conditions; (2) the effect of \( \text{H}_2\text{O}_2 \) addition on the removal of THM precursors and DOC by \( \text{O}_3 \)-BAC; and (3) the effect of \( \text{H}_2\text{O}_2 \) addition on the THM forming activity of each NOM fraction. This study will provide information enabling comprehensive understanding of the advantages and disadvantages of \( \text{H}_2\text{O}_2 \) addition, which is important for decision making in bromate control.

1 Materials and methods

1.1 Pilot system

A pilot system (500 L/hr) including successive coagulation-sedimentation, sand filtration (conventional treatment) and \( \text{O}_3 \)-BAC units (Fig. 1) was set up in a waterworks that received source water from the downstream Yellow River in North China through a sand-sedimentation reservoir. The \( \text{O}_3 \)-BAC pilot system was fed directly with the coagulation-sedimentation-sand filtration effluent water from another water treatment system since the study only focused on the \( \text{O}_3 \)-BAC treatment performance.

Coagulation was performed in a three-chamber mechanical flocculation subsystem under the following conditions: polyaluminium chloride (\( \text{Al}_2\text{O}_3 \) content, 11%) as coagulant, 3.2 mg/L; fast mixing (220 r/min), 1 min; slow mixing, 15 min (100 r/min and 5 min for the first stage, and 50 r/min and 10 min for the second stage). The sedimentation time was 40 min. Sand filtration was conducted in a polymethyl methacrylate column (height, 3000 mm; inner diameter, 300 mm; sand diameter, 0.95–1.35 mm; sand depth, 1100 mm) at a filtration velocity of 8.0 m/hr.

Ozonation reactors consisted of two stainless-steel con-
tact columns (column I: effective volume of 38.0 L with a height of 3000 mm; column II: effective volume of 82.8 L with a height of 2200 mm). The hydraulic retention times (HRT) for columns I and II were 4.6 min and 10.0 min, respectively. All tubing materials that came into contact with O$_2$ were made of Teflon or stainless steel. Ozone gas was regulated by a flow meter and then supplied into column I from a gas diffuser located on the bottom. Industrial grade H$_2$O$_2$ was added into the sand filtration effluent using a pump before ozonation.

The BAC filter was a polymethyl methacrylate column with an effective volume of 13.5 L and an inner diameter of 120 mm, which gave an empty bed contact time of 12.0 min. The BAC was taken from a full scale waterworks that had been in operation for 2 years in treating surface water.

The pilot experiments were performed from March to May in 2010, and the water quality varied during this period. The characteristics of raw water and sand filtration effluent water are given as ranges, as shown in Table 1. The samples of raw water were collected and analyzed once every two days and the samples of the sand filtration effluent water were collected daily. Before the experiment started, the pilot system was operated for four weeks until the parameters (turbidity, DOC etc.) of treated water become stable and the DOC reduction by BAC treatment was carried out after the post-ozone treatment was applied.

1.2 Sample collection

For each operational condition, the system was operated for at least 2 hr before effluents from the ozone columns and BAC filter were sampled, and each condition was replicated at least once. In addition, influent samples were collected once a day. The residual H$_2$O$_2$ and ozone were analyzed immediately after sample collection. Samples for bromate, bromide, DOC and THMFP analyses were passed through 0.45 µm membrane filters and stored at 4°C until analysis. The samples for natural organic matter (NOM) fractionation were transported back to the lab under cool conditions and the DOC and THMFP of each fraction were analyzed immediately following fractionation.

1.3 Analytical methods

All reagents applied in the experiment were of analytical grade, and all stock solutions were prepared with Milli-Q water (Millipore). The indigo method was employed to measure the aqueous ozone concentrations (Bader and Hoigné, 1981), and gaseous phase ozone was quantified by the iodometric method (APHA, 1995). Ozone consumption was defined as the difference between the influent and effluent gaseous ozone. Hydrogen peroxide was determined by the peroxidase-DPD method (Bader et al., 1988). The DOC was determined using a Shimadzu TOC analyzer (TOC-VcpH, Shimadzu, Japan). The ammonia and alkalinity were analyzed based on the Standard Method of Water and Waste Water Monitoring of China (Environment Protection Bureau, 2002). Bromate and bromide concentrations were analyzed by ion chromatography (Dionex 3000, USA) using an AC9-SC analytical column (Dionex) with a detection limit of 2.0 µg/L and 10.0 µg/L, respectively.

The THMFP analysis procedure was based on a previous study (Zhang et al., 2011). Briefly, the chlorine demand of each sample was determined according to the standard method (APHA, 1995), where 100 mL water samples were used for chlorination. HCl (0.1 mol/L) was applied to adjust the pH of the water samples to 7.0 ± 0.2 using 100 mL water samples. After a 4-hr period reaction at 25 ± 1°C, the residual chlorine was analyzed by the method of sodium hyposulfite titration (Environment Protection Bureau, 2002). For THM measurement, 10 mL of each water sample was placed in 10-mL borosilicate vials with sufficient chlorine to provide a free chlorine residual of 1.0 ± 0.4 mg/L after reaction at 25 ± 1°C for 24 ± 1 hr. The residual chlorine was quenched with sodium thiosulfate prior to analysis. Next, 8 mL chlorinated samples were extracted by 2 mL hexane and analyzed for THMs, including chloroform, bromochloromethane, dibromochloromethane and bromoform, using a gas chromatograph (Agilent 6890N, USA) equipped with a fused silica capillary column (HP-5, 30 m, 320 µm × 0.25 µm) and an electron capture detector. The analysis of THMs was conducted according to standard methods 5710B and 6232B (APHA, 1995).

1.4 DOM fractionation

The NOM of water samples was classified using macroporous resins DAX-8 and XAD-4 (Supelco Co., USA) to divide the samples into five fractions, including hydrophobic bases (HoB), the hydrophobic neutral fraction (HoN), hydrophobic acids (HoA), weakly hydrophobic acids (WHoA) and hydrophilic matter (HiM) (Wei et al., 2008). In this target source water, the DOC concentrations of HoB and HoN were relatively low; thus, they were combined as non-acid hydrophobic matter (NAHoM). The procedures for NOM fractionation were based on a previous study (Wei et al., 2008). Briefly, DAX-8 and XAD-4 were immersed in 0.10 mol/L NaOH for 24 hr, then cleaned with methanol by Soxhlet extraction for 48 hr. The resins were subsequently rinsed with 0.10 mol/L NaOH, pure water, 0.10 mol/L HCl and pure water sequentially.

| Table 1 Raw water and sand filtration effluent characteristics |
|-----------------|-----------------|
|                 | Raw water       | Sand filtration effluent |
| pH              | 8.18–8.24       | 7.85–8.03               |
| Turbidity (NTU) | 7.26–10.20      | 0.19–0.60               |
| Temperature (°C)| 9.5–18.3        | 9.3–19.5                |
| NH$_4^+$ (mg/L) | 0.19–0.84       | 0.0–0.65                |
| Alkalinity (mg/L)| 190.2–210.2  | 185.2–217.2            |
| DOC (mg/L)      | 3.25–3.78       | 1.93–2.73               |
| Bromide (µg/L) | 93.4–159.2      | 97.6–150.2              |
| THMFP (µg/L)    | 102.7–151.8     | 71.1–112.2              |
and then with 0.01 mol/L H₃PO₄ and pure water to remove the impurities until the DOC concentration of the effluent water was below 0.07 mg C/L.

1.5 Statistical analysis
Statistical analyses were performed using SPSS Base 18.0 software (SPSS, Japan). The correlations between the H₂O₂/O₃ (g/g) ratio and the THMFP residual rate in both ozonation and BAC process waters were investigated. An independent-samples T-test and paired-samples T-test were applied to analyze the significance of differences of data. Differences were considered to be significant if the 2-tailed significance < 0.05.

2 Results and discussion

2.1 Bromate formation potentials
As shown in Table 1, the source water contained 97.6–129.1 μg/L bromide and 0–0.65 mg/L ammonia. The concentrations of bromate formed under different ozone doses and ammonia contents are shown in Fig. 2. The bromate reached the maximum contaminant level (MCL) value of 10.0 μg/L at an ozone consumption dose of 2.0 mg/L when the ammonia concentration was below 0.05 mg/L (Test a). With the existence of ammonia at a level of 0.30–0.65 mg/L (Test b), the MCL value would be reached at an ozone dose of 2.4 mg/L, indicating that ammonia was partially effective at suppressing the formation of bromate (Pinkernell and von Gunten, 2001). As shown in Fig. S1 and S2, an ozone dose of 2.2–3.0 mg/L would be required for the effective reduction of DOC, particularly THMFP. Thus the balance between bromate control and THMFP reduction should be considered during treatment.

2.2 Conditions for suppressing bromate formation by H₂O₂ addition
Figure 3 shows the concentration of bromate as a function of the H₂O₂/O₃ ratio under different ozone doses during treatment of sand filtration effluents with an ammonia concentration of 0.44 mg/L. As the H₂O₂/O₃ ratio increased, the bromate production first increased, and then decreased when the H₂O₂/O₃ ratio was over 0.5. At low H₂O₂/O₃ ratio, the decomposition rate of molecular ozone was lower than that for higher H₂O₂/O₃ ratios, so the molecular ozone persisted for a longer time (von Gunten and Oliveras, 1998) (Fig. S3). As a result, the synergistic effect of molecular ozone and hydroxyl radicals formed may have led to enhancement of bromate formation (von Gunten and Hoigné, 1994; Mizuno et al., 2011). The maximum bromate formation was observed at an H₂O₂/O₃ ratio of 0.1–0.3, which was lower than those (0.4–1.0) reported in other studies (von Gunten and Hoigné, 1994; Mizuno et al., 2011). This discrepancy may have originated from the difference in bromide concentrations in the raw water (500–1000 μg/L in other studies) and/or the treatment systems adopted (batch tests in 1 L-flasks) (von Gunten and Hoigné, 1994).

The H₂O₂/O₃ ratio required for suppression of bromate formation increased as the ozone doses increased. At an ozone dose of 4.2 mg/L, H₂O₂/O₃ of over 0.1 was required to control the bromate concentration below 10.0 μg/L, while for an ozone dose of 3.2 mg/L, an H₂O₂/O₃ ratio of 0.7 was sufficient. Mizuno et al. (2011) reported that bromate production could be controlled below 10.0 μg/L with an H₂O₂/O₃ ratio of 0.5–0.8 for treatment of bromide-containing source water (200 μg/L) under an ozone dose of 2.0 mg/L. However, much higher H₂O₂ levels would be needed when the bromide concentration increased to 500

![Fig 2](image1.png)

Fig. 2 Bromate formation as a function of ozone consumption with NH₄⁺ and without NH₄⁺. Test a: Br⁻ 97.6–129.1 μg/L, temperature 9.3–11.8°C, NH₄⁺ 0.30–0.65 mg/L, pH 7.85–8.03, alkalinity 192.5–217.2 mg/L, DOC 2.26–2.73 mg/L. Test b: Br⁻ 100.8–127.2 μg/L, temperature 18.5–19.0°C, NH₄⁺ 0–0.05 mg/L, pH 7.93–8.01, alkalinity 185.2–210.2 mg/L, DOC 1.93–2.65 mg/L.

![Fig 3](image2.png)

Fig. 3 Bromate formation as a function of the H₂O₂/O₃ (g/g) ratio in O₢-/ H₂O₂ reaction system. Conditions: Br⁻ 109.9–132.1 mg/L, temperature 9.5–11.5°C, NH₄⁺ 0.30–0.53 mg/L, pH 7.85–8.03, alkalinity 192.5–217.2 mg/L, DOC 2.36–2.70 mg/L.
µg/L. Similar results were reported by von Gunten and Oliveras (1998), who found that bromate production was still higher than 150 µg/L when the H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} ratio was as high as 3.0 for source water containing 1000 µg/L bromide. Although the bromate formation and suppression efficacy by H\textsubscript{2}O\textsubscript{2} may vary with the bromide, DOC and ammonia concentrations, an H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} (g/g) ratio of 1.0 was sufficient to control the bromate to less than 10.0 µg/L in this study. However, further studies are required to understand the mechanism of the impact of bromide, NOM and ammonia concentrations on bromate control by H\textsubscript{2}O\textsubscript{2} addition.

As shown in Fig. S4, the percentage of H\textsubscript{2}O\textsubscript{2} consumed decreased rapidly as H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} increased until it reached a value of 1.0, where 70% H\textsubscript{2}O\textsubscript{2} remained in the treated water, regardless of ozone dose, and no residual ozone was detected in the effluents (Fig. S3). Previous studies showed that over 75% and 90% of H\textsubscript{2}O\textsubscript{2} remained in treated water at H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} of 0.8 and 3.0, respectively (Mizuno et al., 2011; von Gunten and Oliveras, 1998). When abundant H\textsubscript{2}O\textsubscript{2} is present, hypobromous acid (HOBr)/hypobromite (OBr\textsuperscript{-}), a requisite intermediate in bromate formation, can be rapidly reduced to bromide with a second-order rate constant (von Gunten and Oliveras, 1997). Indeed, this process is considered to be primarily responsible for hindering bromate formation (von Gunten and Oliveras, 1998).

2.3 Effect of H\textsubscript{2}O\textsubscript{2} addition on the reduction of DOC and THMFP

The effect of H\textsubscript{2}O\textsubscript{2} addition on the reduction of THMFP was assessed under an ozone dose of 3.2 mg/L (Fig. 4). A paired-samples T test indicated that the impact of H\textsubscript{2}O\textsubscript{2} addition on DOC removal by O\textsubscript{3}-BAC was not significant (2-tailed significance 0.252–0.592) (Fig. 4a), which was in accordance with the results of a previous study (Sidiqui et al., 1997). However, it is clear that the THMFP reduction efficacy decreased as the H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} increased (Fig. 4b). As shown in Supplementary Information Table S1, the correlations between the H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} and the THMFP/THMFP\textsubscript{0} (the ratio of THMFP with O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2}-BAC treatment to that with conventional treatment) in both the ozonation effluents and BAC effluents were significant (SPSS 18.0; 2-tailed significance 0.000–0.001). When compared with the O\textsubscript{3}-alone treatment, increases of THMFP at the H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} ratios of 1.0 and 1.5 were significant (2-tailed significance p < 0.05), as shown in Fig. 4b. The O\textsubscript{3}-BAC process reduced 48% of THMFP, but this decreased to 27% and 17% when H\textsubscript{2}O\textsubscript{2} was added at an H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} ratio of 1.0 and 1.5, respectively. These results showed that the impact of H\textsubscript{2}O\textsubscript{2} addition on THMFP reduction by O\textsubscript{3}-BAC cannot be neglected, especially when control of DBPs is an important target.

As shown in Fig. 3, depending on the ozone dosages, the H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} (g/g) ratio should be higher than 1.0 to suppress the bromate concentration to less than 10.0 µg/L. Since the THMFP in the BAC treated water will increase with the increase of the H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} (g/g) ratio, the optimum H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} ratio to balance the bromate and THMs control should be a value between 0.7 and 1.0.

A decrease in THMFP reduction efficacy accompanying H\textsubscript{2}O\textsubscript{2} addition has been found by several researchers. Specifically, O\textsubscript{3}-H\textsubscript{2}O\textsubscript{2} treatment has been shown to allow up to 20% higher THMFP than treatment with ozone-alone (Frimmel et al., 2000; Irabelli et al., 2008). To explore the possible mechanisms of this phenomenon, the impact of H\textsubscript{2}O\textsubscript{2} addition on the removal of different fractions (HiM, WHoA, HoA and NAHoM) of NOM by O\textsubscript{3} was investigated (Fig. 5).

As shown in Fig. 5a, the HiM fraction was found to be the most abundant (60% of the total DOC) in the...
sand filtration effluent ($O_3 = 0 \text{ mg/L, } H_2O_2 = 0 \text{ mg/L}$), which was likely because this fraction is more difficult to remove by conventional water treatment processes than hydrophobic materials (Chae and Kim, 2000). HoA and WHoA, which primarily consisted of hydrophobic materials, were the other two main fractions of NOM in the target source water. Ozonation could remove part of the HiM fraction (34%) and a large part of the HoA fraction (45%), while the DOC of the WHoA fraction increased from 0.29 to 0.47 mg/L. Some researchers also found a high reactivity of HoA with $O_3$ (Westerhoff et al., 1999a). This may have occurred because HoA was the most abundant hydrophobic fraction, and it is rich in aromatic structures, which are prone to being attacked by $O_3$ (Westerhoff et al., 1999b). The destruction of aromatic moieties and carbon-carbon double bonds in the ozonation process has been shown to lead to an increase of carboxyl organic matter with low molecular weight and few hydrophobic compounds (Westerhoff et al., 1999a), which could be the main reason for the increase in the WHoA fraction.

$H_2O_2$ addition markedly reduced removal of the HiM and HoA fractions by ozonation, and led to a lower concentration of WHoA DOC (Fig. 5a). It is well known that the $O_3$-$H_2O_2$ process is characterized by a high efficiency for generating hydroxyl radicals, which are more active than molecular ozone and thus more easily consumed by coexisting radical scavengers (Lee and von Gunten, 2010). Kleiser and Frimmel (2000) attributed that the decreased reduction of THMFP caused by $H_2O_2$ addition to the scavenging of excessive amounts of $H_2O_2$. Conversely, the alkalinity of the target source water was as high as 185.2–217.2 mg/L (as CaCO$_3$), and the pH was 7.85–8.03, resulting in a high bicomponent concentration (3.7–4.3 mmol/L) (Environment Protection Bureau, 2002). Bicarbonate with a high OH radical consumption rate (reaction constant, $8.5 \times 10^9$ mol/(L·sec); Buxton and Elliot, 1986) may be one of the main factors leading to the reduced oxidation of NOM in the $O_3$-$H_2O_2$ process.

Figure 5b shows that ozonation reduced the THMFP of four fractions of NOM. However, $H_2O_2$ addition reduced the removal efficacy of THM precursors by the ozonation process. The THMFP of the HiM fraction increased from 33.2 to 48.2 μg/L after $H_2O_2$ addition. A paired-samples $t$ test indicated that the decrease of THMFP reduction caused by $H_2O_2$ addition was significant (2-tailed significance $p = 0.043$). The reactivity of each organic fraction during the formation of THM (THMFP/DOC) was also determined (Fig. 5c). HoA exhibited the highest activity (75.5 μg/mg), followed by HoA (44.6 μg/mg). These fractions have been reported to contain electron-rich moieties such as aromatic compounds, which are susceptible to chlorine (Bond et al., 2009). Ozonation decreased the reactivities of all the three fractions, particularly HoA and WHoA. Humic substances such as THM precursors are known to be prone to be oxidized by ozone (Singer et al., 1999).

Conversely, the addition of $H_2O_2$ decreased the efficiency of ozonation in reducing the THM formation potential of each fraction, particularly the WHoA fraction, which was even higher than that before oxidation. It is well known that hydroxyl radicals, having much less reaction selectivity than molecular ozone, are less efficient at transforming NOM containing electron-rich moieties (Lee and von Gunten, 2010). In addition, when compared with molecular ozone, the high oxidation ability of hydroxyl radicals could lead to the formation of phenolic moieties or ketones, which easily react with chlorine and form THMs (von Sonntag, 1996; Leenheer et al., 2001).

As shown in Fig. 5c, the reactivity of the HiM fraction in forming THMs was quite low when compared with the other fractions. The low molecular weight compounds in this fraction, such as short-chain aliphatic amines, aldehydes and $< C_5$ aliphatic carboxylic acids, have been found to have low reactivity for the formation of THM (Leenher, 2004). Ozonation and $O_3$-$H_2O_2$ treatment led to a slight increase in the reactivity of this fraction from the original 21.0 to 29.7 and 32.3 μg/mg, respectively.

Thus the decrease of the THMFP reduction caused by $H_2O_2$ addition could be a result of the combined effects of the reduction in oxidation efficiencies of some fractions.
(e.g., the decrease in HiM removal) and the increase in THM-forming reactivity of some fractions (e.g., the increase in the THM-forming activity of WHoA), as observed in Fig. 5b. Although the HiM fraction exhibited the lowest THM-forming activity among the four groups (Fig. 5c), its contribution to THMFP was the highest because of its abundance in the source water. As shown in Fig. 5b, the increase in THMFP from this fraction due to H₂O₂ addition could not be neglected. Electrospray ionization coupled to Fourier transform ion cyclotron resonance mass spectrometry may be an effective tool for exploring the differences between direct ozonation and O₃-H₂O₂ by analyzing the detailed oxidation products (Zhang et al., 2012).

3 Conclusions

This study investigated the effects of H₂O₂ addition on the bromate formation and the DOC and THMFP reduction of organic fractions by ozonation. The following conclusions were obtained: (1) To effectively suppress the formation of bromate, an H₂O₂/O₃ (g/g) ratio of 1.1 or higher was desirable for the studied source water. An H₂O₂/O₃ ratio below 0.3 should be avoided since the bromate concentration will increase as the H₂O₂ dose increases. (2) H₂O₂ addition prior to ozonation may lead to a decrease of THMFP reduction efficacy by the O₃-BAC processes. The O₃-BAC process could reduce 48% of THMFP, but this decreased to 27% when H₂O₂ was added at an H₂O₂/O₃ ratio of 1.0. The optimum H₂O₂/O₃ (g/g) ratio for bromate and THM control was 0.7–1.0 under different ozone dosages. (3) The decrease in the THMFP reduction caused by H₂O₂ addition could be a result of the combined effects of the reduction in oxidation efficiencies of some fractions (e.g., the decrease in HiM removal) and the increase in THM-forming reactivity of some fractions (e.g., the increase in the THM forming activity of WHoA).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 50938007), the Funds for Major Science and Technology Program for Water Pollution Control and Treatment (No. 2012ZX07403-002-02), and the Special Co-construction Project of the Beijing Municipal Commission of Education. The authors would like to express their gratitude towards the testing center of Zhengzhou Water Supply Investment Holdings Co. Ltd. and the laboratory department of the Shiyuan Water Plant for their help in analysis.

Supporting materials

Supplementary data associated with this article can be found in the online version.

References


Mizuno T, Ohara S, Nishimura F, Tsuno H, 2011. O₃/H₂O₂ process for both removal of odorous algal-derived compounds and control of bromate ion formation. Ozone: Science and


**Supporting materials**

This supplementary information provides the effectiveness of O₃-BAC treatment on organic matter removal. The molecular ozone and H₂O₂ residual in the ozonated water are also presented.

**Removal of organics by O₃-BAC treatment**

The DOC residual ratios (DOC/DOC₀) of both ozonation and BAC treatment effluent water, as compared to sand filtration effluent water, are displayed in Fig. S1. For both waters, the residual ratio decreased and then increased slightly as the ozone consumption doses increased. At an ozone dose of 2.2 mg/L, the DOC residual ratio in BAC effluent became the lowest, at 68%, which may have resulted from ozonation transforming refractory NOM into biodegradable organic carbon (BDOC), which could be used by the bacteria in BAC (Goel et al., 1995; Siddiqui et al., 1997). When the ozone doses were above 2.2 mg/L, DOC residual ratio became a little higher. Since the ability of ozone to mineralize BDOC is much higher than the ability to convert refractory organics to BDOC (Chiang et al., 2002), additional BDOC formation cannot be expected at relatively high ozone consumption doses.

**Table 1** shows that the THMFP of raw water varied from 102.7 to 151.8 g/L, and for the sand filtration effluent water it varied from 71.1 to 112.2 g/L. The conventional water treatment removed 21%–33% of the THMFP of raw water. Figure S2 displays the THMFP residual ratio of ozonation and BAC effluent water as compared to sand-filtered water. When ozone was not used, 83% of THMFP was residual in the BAC effluent water. This shows that the THMFP residual ratio (THMFP/THMFP₀) of ozonated and BAC treated water decreased as the ozone doses increased from 0 to 3.2 mg/L, with 61% and 55% remaining in the two waters respectively. This effect of increasing ozone doses on THMFP reduction were also found by other researchers (Chiang et al., 2002; Georgeson et al., 1988; Kim et al., 2005), but no further reduction was obtained at higher ozone doses.

**Residual ozone in ozonated water**

The molecular ozone residual in ozonated water is shown in Fig. S3. As the H₂O₂/O₃ (g/g) ratio increased, the decomposition of ozone was accelerated. The residual ozone in effluent water decreased notably. As the ratio increased to 0.5 or higher, the residual ozone after HRT of 4.6 and 10.0 min was almost undetectable.
Advanced oxidation of bromide-containing drinking water: A balance between bromate and trihalomethane formation control

Table S1 Correlations between the THMFP residual in ozone or BAC treated water and the H$_2$O$_2$/O$_3$ (g/g) THMFP residual in Post-ozonation effluent THMFP residual in BAC effluent

<table>
<thead>
<tr>
<th></th>
<th>Pearson</th>
<th>Correlation Sig. (2-tailed)</th>
<th>N</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$/O$_3$ (g/g)</td>
<td>1</td>
<td>0.795**</td>
<td>13</td>
<td>001</td>
<td>0.000</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed).  

Fig. S4 H$_2$O$_2$ consumption ratio as a function of H$_2$O$_2$/O$_3$ for varying ozone doses. Conditions: temperature 10.3°C, pH 7.89, alkalinity 210.2 mg/L, Br$^-$ 115.4 µg/L, NH$_4^+$ 0.44 mg/L.

Consumption rate of H$_2$O$_2$ in ozonated water  
As shown in Fig. S4, the consumed H$_2$O$_2$ ratio decreased rapidly with the increase of H$_2$O$_2$/O$_3$ ratio until the ratio reached a value of 1.0. At an H$_2$O$_2$/O$_3$ ratio of 1.0 or higher, over 60% H$_2$O$_2$ remained in the treated water.

References


Editorial Board of Journal of Environmental Sciences

Editor-in-Chief
Hongxiao Tang
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Associate Editors-in-Chief
Jiuhui Qu
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Shu Tao
Peking University, China
Nigel Bell
Imperial College London, United Kingdom
Po-Keung Wong
The Chinese University of Hong Kong, Hong Kong, China

Editorial Board

Aquatic environment
Baoyu Gao
Shandong University, China
Maoshong Fan
University of Wyoming, USA
Chihpin Huang
National Chiao Tung University, Taiwan, China
Ng Wun Jern
Nanyang Environment & Water Research Institute, Singapore
Clark C. K. Liu
University of Hawaii at Manoa, USA
Hokyong Shon
University of Technology, Sydney, Australia
Zijian Wang
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Zhizhong Wang
The Ohio State University, USA
Yuxiang Wang
Queen’s University, Canada
Min Yang
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Environmental toxicology and health
Jingwen Chen
Dalian University of Technology, China
Jianying Hu
Peking University, China
Guibin Jiang
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Sijin Liu
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Tsuyoshi Nakanishi
Gifu Pharmaceutical University, Japan
Willie Peijnenburg
University of Leiden, The Netherlands
Bingsheng Zhou
Institute of Hydrobiology, Chinese Academy of Sciences, China

Atmospheric environment
Jiajia Chen
Fudan University, China
Abdelwahid Mellouki
Centre National de la Recherche Scientifique, France
Yujing Mu
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Min Shao
Peking University, China
James Jay Schauer
University of Wisconsin-Madison, USA
Yuesi Wang
Institute of Atmospheric Physics, Chinese Academy of Sciences, China
Xin Yang
University of Cambridge, UK

Environmental catalysis and materials
Zongwei Cai
Hong Kong Baptist University, Hong Kong, China
Jiping Chen
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China
Minghui Zheng
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Environmental analysis and method
Zongwei Cai
Hong Kong Baptist University, Hong Kong, China
Jiating Chen
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

Municipal solid waste and green chemistry
Pinjing He
Tongji University, China

Environmental biology
Yong Cai
Florida International University, USA
Henner Holbert
RWTH Aachen University, Germany
Jae-Seong Lee
Hanyang University, South Korea
Christopher Rensing
University of Copenhagen, Denmark

Environmental ecology
Zongwei Cai
Hong Kong Baptist University, Hong Kong, China
Rusong Wang
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Editorial office staff
Managing editor
Qingcai Feng

Editors
Zixuan Wang
Suqin Liu
Zhengang Mao

English editor
Catherine Rice (USA)
Aims and scope

Journal of Environmental Sciences is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via http://www.elsevier.com/locate/jes.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of a manuscript implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at http://www.jesc.ac.cn. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@263.net, jesc@rcees.ac.cn. Instruction to authors is available at http://www.jesc.ac.cn.