



Effect of ozonation on trihalomethane formation potential and trihalomethane species in bromide-containing water

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ABSTRACT

The paper discussed the effects of ozonation on the trihalomethane formation potential (THMFP) and trihalomethane species in bromide-containing water, with humic acid as precursor of disinfection byproducts. The results demonstrated that higher concentration of bromide ions in raw water is favorable to increase of proportion of THMFP and brominated trihalomethanes (THMs-Br). However, once bromide-containing water was oxidized by ozone, part of bromide ions would be oxidized into bromate, and the incorporation of bromide to THM reduces thusly. The intermediate products of humic acid formed during oxidation are quite complex, which perhaps increases the yield of precursors of disinfection byproducts (DBPs) on the contrary. Only with higher ozone dosage, reduction of the total THMFP can be achieved. However, the bromate byproducts produced during oxidation were considered to be potential human carcinogens, which restricted the application of ozone in drinking water. The yield of bromate and THMFP would be reduced significantly as long as ammonia nitrogen is present in bromide-containing water during ozonation.

Keywords: water treatment, ozonation, trihalomethane formation potential; brominated trihalomethanes; bromate

INTRODUCTION

Chlorine, a traditional disinfectant, has found wide application in drinking water disinfection process due to its lower cost, higher oxidizing effect, and its capability of providing additional chlorine to prevent and control regrowth of microorganism in the water distribution system. However, the chlorine can also react with natural organic matter (NOM) and halides (e.g., Cl⁻ and Br⁻) to form chlorinated disinfection by-products (DBPs). Along with the innovation of disinfection methods and the increase of disinfectant varieties, more than 250 different DBPs have been identified including trihalomethanes (THMs), haloacetic acids (HAAs), halo ketones (HKs) and haloacetonitriles (HANs).

The precursors of THMs are categorized into macromolecular organic compounds like humic acid and fulvic acid and small organic molecules including phenolic compounds, aniline, benzene, ketone, 1, 3-cyclohexanedione and amino acids. Among those, humic acid and fulvic acid are the most common organics in water, accounting for 50% of the soluble organics in water, and they are one kind of precursors leading to mutagenesis of drinking water [1]. In the bromide-containing water, bromide ions would react with hydrochlorous acid (HOCl) to form the hypobromous acid (HOBr) or hypobromite, which could then react with organic matters to form the brominated DBP. It has been reported that THMs are easy to cause liver and kidney damage and give rise to renal, bowel, and other cancers and reproductive disorders; worse still, brominated trihalomethanes (THMs-Br) are suspected to be a much stronger carcinogen and mutagen than their chloride-containing analogues. Therefore, it is necessary to do research on the

formation of the total trihalomethanes (TTHMs) and the distribution of the individual species in bromide-containing water.

As an excellent disinfectant, ozone shows good degradation effect on persistent organic pollutants including drugs and endocrine disrupting chemicals harmful to the environment and it can even be used to inactivate microorganisms (e.g. protozoa) that are difficult to inactivate by ordinary chloric disinfectants, so it has found wide applications in water treatment. However, humic acid as the representative of NOM is difficult to be mineralized completely by ozone in water, instead, the structure and properties of it would be changed in the effect of ozone, imposing influence on morphology of disinfection by-products precursors. Bromate is an undesirable by-product formed during ozonation in bromide-containing water, which has been declared a potential carcinogen; worse still, it would be difficult to remove bromate from water once formed in conventional treatment process. However, some studies have shown that addition of ammonia to the bromide-containing water could reduce the yield of the bromate effectively and inhibit the formation of CBDPs.

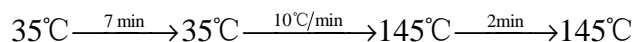
Trihalomethanes (THMs) byproducts by drinking water test fall into four categories: chloroform (CHCl_3), dichlorobromomethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl) and bromoform (CHBr_3). In the experiments, humic acid (HA) is used to provide the source of the precursors of DBPs. In combination with pH value range of local drinking water, this paper with humic acid as precursor studies the effect of ozonation on the trihalomethane formation potential (THMFP) and trihalomethane species in bromide-containing water.

EXPERIMENTAL SECTION

2.1 Detecting instruments and analytical methods

The ozonation experiments were performed in a three-liter glass reactor with an ozone generator (LF-20). Ozone dosage was adjusted by changing ozone flux fed into the reactor. To make ozone dissolved quickly, aerators with sand cores were arranged at the bottom inlet of the reactor. The tail gas was exhausted into the air after absorption by 2% KI solution.

DOC was measured with a total organic carbon analyzer (TOC-VCPH, Shimadzu) and UV-absorbance was measured with a spectrophotometer (TU-1800). THMs was measured through gas chromatography (GC-2014C, Shimadzu) equipped with an ECD detector. Chromatographic column: HP-5(30m*0.32mm*0.25 μm), sample size: 1 μL , carrier flow: 1mL/min, temperature of injection port: 200 $^\circ\text{C}$, and temperature of detector: 280 $^\circ\text{C}$, splitless. Temperature rising procedure of the column:



Method for cultivation of THMFP: place 200mL water sample into a ground-glass bottle that has been preprocessed, adjust pH value of the water sample with hydrochloric acid to 7.0, and then take analytical pure NaOH of 11.7g and KH_2PO_4 of 68.1g to dissolve into high purity water. Finally, buffer solution is formed to maintain the pH value constant. Add the solution of 4mL to 200mL water sample, and add NaClO solution to water sample to make the chlorine dosage in water sample up to 20mg/L. Put the water sample in a biochemical incubator of 20 $^\circ\text{C}$ and save it in dark for 72 hours. Its own residual chlorine in water sample shall be maintained at 3-5mg/L, and finally terminate the reaction with sodium thiosulfate solution.

Method for water sample pretreatment: place 25mL water sample into a brown glass bottle with a polytetrafluoroethylene gasket, add 3mL MTBE and 10g extracted Na_2SO_4 , and then shake fiercely for 3min to make Na_2SO_4 unblocked. Then put it in a motionless state for 3-5min, and finally take upper organic solvent of 1 μL with a syringe for gas chromatograph analysis.

2.2 Water quality parameters

The humic acid stock solution (1mg/L): Take 1g humic acid and dissolve it into 1L distilled water, and then shake the mixture for 2h and then filtrate with 0.45 μm microfiltration. The solution after filtration is the humic acid stock solution of 1mg/L.

The water for the experiment: Maintain the concentration of humic acid solution to be 7mg/L by adding humic acid stock solution of 1mg/L to the distilled water, and then sodium hydroxide (NaOH) was used to adjust the pH value of humic acid solution to 7.5, finally, measure the water quality parameters listed in Table 1.

Table 1 Water quality parameters

| TOC/mg·L ⁻¹ | COD _{Mn} /mg·L ⁻¹ | UV ₂₅₄ | pH | Br ⁻ /mg·L ⁻¹ |
|------------------------|---------------------------------------|-------------------|-----|-------------------------------------|
| 2.01 | 3.72 | 0.238 | 7.5 | 0.1 |

This paper investigated four kinds of THMs, and they are CHCl₃, CHBrCl₂, CHBr₂Cl and CHBr₃. The incorporation of bromine to THMs is represented by incorporation factor *n* (Br), as shown in Formula 1.

$$n(\text{Br}) = \frac{C_{\text{CHBrCl}_2} + 2C_{\text{CHClBr}_2} + 3C_{\text{CHBr}_3}}{C_{\text{TTHM}}} \quad 0 \leq n \leq 3 \quad (1)$$

C_{CHBrCl_2} , C_{CHClBr_2} and C_{CHBr_3} are the molar concentrations (μmol/L) of CHBrCl₂, CHBr₂Cl and CHBr₃. C_{TTHM} is the total molar concentration (μmol/L) of THMs.

RESULTS AND DISCUSSION

3.1 Effect of bromide ions on the THMFP before ozonation

Five 250mL water samples were prepared for the experiment. The TOC in the water sample is 2.01mg/L, its pH value is 7.5, and the available chlorine dosing is 20mg/L. Firstly, adjust the concentrations of bromine ions in water samples to 0.04mg/L, 0.1mg/L, 0.3mg/L, 0.6mg/L, 0.8mg/L with KBr respectively. Then, sodium hypochlorite was added to the five water samples to maintain the available chlorine at 20mg/L. After incubated in a dark incubator at 20.0°C for 72h, terminate the reaction with sodium thiosulfate solution and measure the yield of THMs.

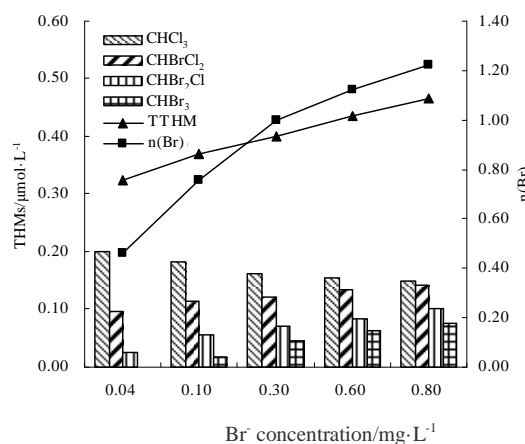


Fig. 1 Effect of bromide ions concentration on the THMFP

Fig.1 illustrates that TTHFP and *n*(Br) of bromide ions to THMs increase as bromide concentration increases, which was because the presence of bromide ions in water can make rapidly bromide oxidized into HOBr by HOCl, and the residual HOCl, along with HOBr, reacted with humic acid to produce THMs, as shown in the following equations:



From the study conducted by Symons [2], we can see that bromine reacts faster than chlorine with natural DOM and HOBr is a stronger oxidant and is 20 times of HOCl. This was why the water with high concentration of bromide ions tended to have higher level of TTHMFP. When the concentration of bromide ions was 0.03mg/L, the amount of HOCl in water is much higher than that of HOBr, and the formation of THMs-Cl was dominant. However, with the increase of bromide ion concentration, almost all of the bromide ions were oxidized into HOBr, and the formation of

THMs-Br was thusly inhibited and gradually shifted to brominated species including mixed chlorobromo species during chlorination. The proportion of brominated trihalomethanes was increased.

3.2 Effect of ozonation on the THMFP

In the process of ozonation of humic acid, the polarity and hydrophilic of humic acid was improved, the double bonds and aromatic were damaged, and the molecular weight was decreased, which effected the formation of hydroxyl, carbonyl, and carbonyl group of humic acid. The possible reaction of ozonation for humic acid were as follows: free or complex form of metal ions were oxidized to produce radical anion that further contributed to the ozone decomposition. Hydroxyl radical reacted with aromatic group of humic to produce hydroxy compound that is easy to react with O_3 . O_3 reacted with carbon-carbon double bonds of humic acid to produce peroxide intermediate initially, and then H_2O_2 and carbonylation.

When bromide-containing water was oxidized by ozone, Br^- and the intermediate oxidation states of Br^- were oxidized simultaneously or sequentially by both ozone and hydroxyl radical ($\cdot OH$) [3]. Firstly, Br^- was oxidized into BrO^- , which was conducive to the generation of the THMs-Br. However, as the O_3 dosage increases continually, BrO^- was further oxidized to BrO_3^- , which was difficult to produce more Br-THMs. Therefore, the morphology and yield of bromate produced during oxidation of Br^- with O_3 has imposed influence on formation of Br-THMs to some degree.

3.2.1 Effect of ozonation time on the THMFP

3L water sample with bromide ion concentration of 0.1mg/L was added to the glass reactor, and then pump in O_3 with ozone dosage of $4\text{mg}\cdot\text{L}^{-1}$ to the reactor. The exposure time to ozone is 5min, 10min, 15min, 25min, respectively. After that, 250ml water sample oxidized by O_3 was added to sodium hypochlorite to maintain the available chlorine at 20mg/L . After incubate in dark at 20.0°C for 72 h. after that, terminate the reaction with sodium thiosulfate solution and measure the yield of THMs in water.

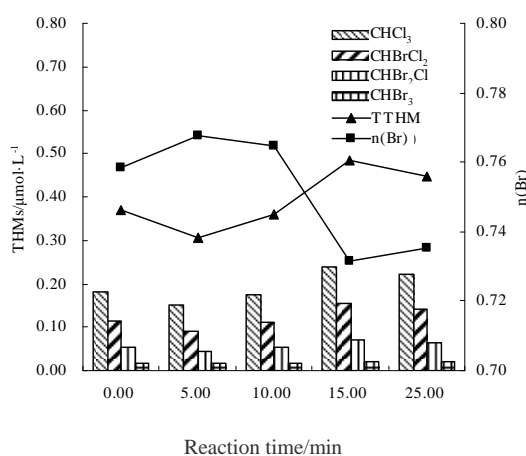


Fig. 2 Effect of reaction time on the THMFP with ozone dosage of $4\text{mg}\cdot\text{L}^{-1}$

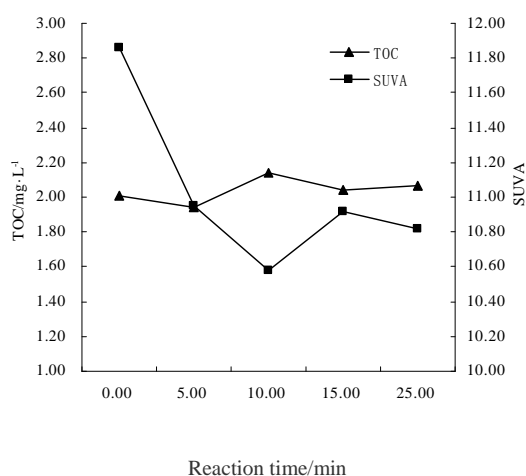


Fig. 3 Variation of TOC and SUVA with exposure time with ozone dosage of $4\text{mg}\cdot\text{L}^{-1}$

When water contains bromide ions, the yield of BrO_3^- is in proportion to $C \times t$ value gained from ozone exposure reaction [4]. It is found that the yield of BrO_3^- increases with exposure time extended, the rate increases rapidly in early period of continuous ozonation, and then tends to stay stable after 15min. The formation of BrO_3^- was not conducive to the formation of Br-THMs, matching with the trend of $n(Br)$ of bromine to THMs, as shown in Fig.2. Some authors attributed this primary production of bromate to the stronger oxidizing $\cdot OH$ pathway [5]. With the attenuation of ozone concentration and the weakening of the $\cdot OH$ oxidation in later stage, the rate of bromate formation slowed down, and the oxidation reaction tended to stay balanced. Ozekin [6] showed that $\cdot OH$ made a 70% contribution to the formation of BrO_3^- , while O_3 was only 30% in ultra-pure water system. As can be seen, $\cdot OH$ plays a dominant role in the formation of BrO_3^- .

As shown in Fig. 3, TOC concentration stays basically the same with oxidation time extended. Jin Pengkang [7] found that the purpose of ozonation was to change the characters and structures of the organic matters and reduce UV_{254} instead of reducing the total organic compounds in water. The specific UV absorbance (SUVA) of HA significantly decreased after oxidation of ozone, all of which was because the carbon-carbon double bonds, the aromatic ring structure as well as the portion of the metal ion were attacked by ozone, shifting the unsaturated bond to saturated bond[8].

3.2.2 Effect of ozone dosage on the THMFP

3L water sample with bromide ion concentration of 0.1mg/L was added to the glass reactor, and then pump in O_3 with ozone dosages of 2mg/L, 3mg/L, 4mg/L, 5mg/L and 6mg/L to the reactor. Exposure time to ozone is 25min. After that, 250ml water sample oxidized by O_3 was added to sodium hypochlorite to maintain the available chlorine at 20mg/L. After incubate in dark at 20.0°C for 72h, terminate the reaction with sodium thiosulfate solution and measure the yield of THMs in water.

According to Fig. 4, with the increase of ozone dosage, THMFP is tending down. When ozone dosage is 6mg/L, THMFP is lower than that of raw water. As can be seen, $n(Br)$ fluctuates slightly when ozone dosage is less than 5mg/L, and a significant increase in $n(Br)$ can be seen with the ozone dosage of 6mg/L, which presented an opposite trend to that of SUVA as shown in Fig.5. Because of the high SUVA experimental water, the amount of ozone consumed directly increases. What's more, the rates of reaction of O_3 with Br^- and with $HOBr/OBr^-$ are lower than those of O_3 with NOM and $HOBr/OBr^-$ with NOM [9], causing competition of ozone between humic acid and bromide ions for ozone. The trend lines of $n(Br)$ and SUVA are opposite.

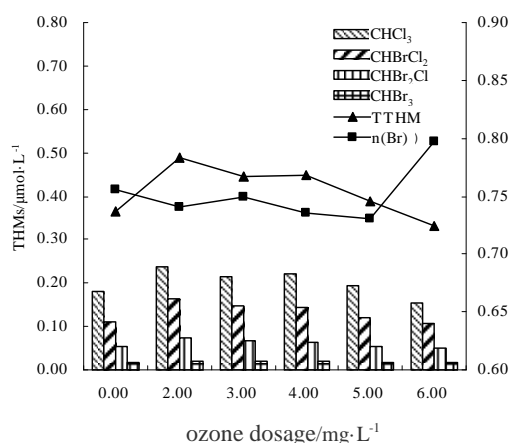


Fig. 4 Effect of ozone dose on the THMFP

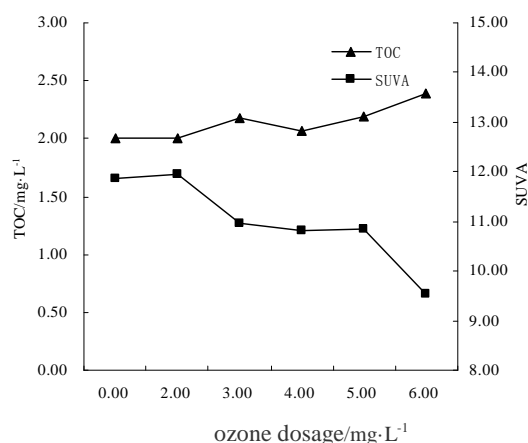


Fig. 5 Variation of TOC and SUVA with exposure time

Although ozone is an attractive disinfectant with strong oxidization capability, it is difficult to mineralize humic acid completely. Studies have found that the small molecular aldehydes formed by oxidation of ozone were precursors of THMs-Br [10]. Although the unsaturated bond-containing precursors of DBPs could be oxidized by ozone rapidly, newly formed precursors of DBPs like aldehyde could cause a higher level of THMFP with the increase of O_3 dosage. Thus, the ozonation intermediate products of humic acid are quite complicated. Only in the early stage of formation of intermediate products or in the stage where the organic matters treated by ozonation have been decomposed to final products, they could inhibit the formation of THMs.

3.3 Effect of ammonia nitrogen on the THMFP and bromate

In the presence of ammonia, $HOCl$ would react with ammonia to produce monochloramine, and its rate was faster than that of oxidation of bromide ions. The formation of monochloramine consumes a large quantity of $HOCl$, leading to a lower yield of the THMs. Owing to the competition between ammonia and bromide ions for available chlorine during chlorination, the bromine incorporation changed. On the one hand, the reaction of ammonia nitrogen with chlorine could reduce THMs products; on the other hand, the reaction of bromide ions with chlorine increases the proportion of THMs-Br. Therefore, with the increase of ammonia concentration, the proportion of THMs-Cl would reduce while proportion of THMs-Br increases. In addition, inorganic bromochloramine can be formed from reaction of monochloramine with bromide ions. Besides, it is also known that it can react with organic precursors to form THMs-Br, which further increases the yield of THMs-Br.

Adding ammonia to bromide-containing water, HOBr would react very quickly with ammonia to produce NH₂Br, and then, NH₂Br was oxidized to NO₃⁻ and Br⁻. When most of the ammonia is reacted, the residual HOBr/BrO⁻ was further oxidized to BrO₃⁻ by O₃. Therefore, ammonia could delay or partially inhibit bromate formation [11]. Another study suggested that ammonia could remove ·OH, and NH₃ can react with ·OH rapidly, which controls formation of BrO₃⁻. However, the reaction that NH₃ reacts with HOBr to produce NH₂Br is reversible, leading to a higher NH₃ concentration to meet demands [12]. Adding ammonia to bromide-containing water also favors the formation of nitrogenous disinfection byproducts, which was supposed to be a stronger toxicity than carbonaceous DBPs according to a newly launched study [13].

CONCLUSION

The total THMFP and the proportion of THMs-Br increase significantly with the increase in concentration of bromide ions in bromide-containing water. However, once bromide-containing water is treated with ozonation, the incorporation of bromide ions to formation of THM reduces. Humic acid was difficult to be mineralized completely with ozonation, instead, the structure and properties of it can be changed, and its intermediate products are very complicated. Only higher ozone dosage can reduce the total THMFP. Although bromide ions could be removed by oxidation to further reduce the formation of brominated disinfection byproducts, the yield of bromate increases, which could reduce the safety of drinking water. However, the addition of ammonia to the bromide-containing water during ozonation could lower the THMFP and the yield of bromate significantly.

Acknowledgements

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