

Preozonation of bromide-bearing source water in south China

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Abstract: The effectiveness of preozonation was evaluated on treating a bromide-bearing dam source water in south China through batch-scale experiments. Preozonation at ozone doses of 0.5–1.0 mg/L (at ozone consumption base) enhanced total organic carbon (TOC) removal through coagulation, and resulted in an almost linear reduction of ultraviolet absorbance at 254 nm (UV_{254}). The removals of TOC (after coagulation) and UV_{254} at the ozone dose of 1.0 mg/L were 36% and 70%, respectively. Preozonation at an ozone dose between 0.5 and 1.0 mg/L resulted in the removal of disinfection byproducts formation potential (DBFP) including trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP) for about 50%. The removals of THMFP and HAAFP decreased with the further increase of ozone dose. Ozonation of bromide-bearing water (bromide concentration, 34 $\mu\text{g/L}$) produced a bromate concentration under the detection limit (2 $\mu\text{g/L}$) at ozone doses <1.5 mg/L. However, bromate >10 $\mu\text{g/L}$ could be produced when the bromide concentration was increased to 96 $\mu\text{g/L}$.

Keywords: ozone; drinking water; preozonation; disinfection byproducts formation potential (DBFP); bromate formation

Introduction

Primary and secondary disinfections are usually performed with chlorine during drinking water treatment. The primary disinfection (prechlorination) is used mainly for the eradication of microorganisms present in raw water to ensure that the subsequent coagulation, sedimentation, and sand filtration will not be hindered by the excrescent microorganisms. The secondary disinfection is the use of a disinfectant residual in water distribution systems to prevent the re-growth of biological contaminants. Cl_2 (or hypochlorite) is still the most widely used disinfectant. It is nearly unrivaled in its potency as both a primary and secondary disinfectant (USEPA, 1996).

However, prechlorination produces a number of undesirable and potentially cancer-causing organic disinfection byproducts (DBPs). Among these, trihalomethanes (THMs) and haloacetic acids (HAAs) are the dominant species found in finished water (Rook, 1976). Because of health risks, U.S. Environmental Protection Agency (USEPA) began to regulate the levels of these DBPs in finished water by Stage 1 of disinfectants/disinfection by-products rule (D/DBPR), which established a maximum contaminant level of 80 g/L for total THMs and 60 g/L for five of HAAs (HAA5). To minimize the production of these compounds, preozonation was recommended rather than prechlorination in drinking water treatment (Amy *et al.*, 1991; Orren *et al.*, 2000).

Preozonation has been utilized in water works in some European countries because of its high oxidation potential (Lefebvre *et al.*, 1995; Böhme, 1999; Geering, 1999; Lowndes, 1999), and enhanced TOC removal through coagulation during preozonation has

been observed (Duguet *et al.*, 1986; Farvardin and Collins, 1989; Prados *et al.*, 1995; Orren *et al.*, 2000). Polymerization occurred during ozonation of simple phenolic compounds or humic substances-aided coagulation, resulting in the enhanced removals of natural organic matters (NOM), the principal precursor of chlorinated DBPs (Chrostowski *et al.*, 1983; Farvardin and Collins, 1989; Sudha *et al.*, 1995). However, some contradictory results regarding preozonation have been reported by different researchers (Becker and O'melia, 1995, 1996). It is speculated that the different preozonation results originated from different source water characteristics. For example, although preozonation has been widely utilized in European countries, no preozonation treatment has been adopted in Japan in spite of the wide use of post ozonation for drinking water treatment. Therefore, what kind of source water is suitable for preozonation remains an interesting topic for further exploration.

On the other hand, the formation of bromate (BrO_3^-), a major DBP generated from ozonation of bromide-containing source waters, should be considered when ozone is selected for drinking water treatment. Bromate as a carcinogen is currently regulated in treated drinking water under the Stage 1 D/DBP Rule of the Safe Drinking Water Act (2) at a maximum contaminant level (MCL) of 10 $\mu\text{g/L}$. There is currently no economically feasible technology to remove bromate once formed. So, clarifying the conditions of bromate formation will be helpful for the process selection.

Preozonation has been adopted for treating a bromide-bearing dam source water with a low specific ultraviolet (UV) absorbance, low hardness, and high

algae (6×10^6 – 3×10^7 cell/L) in one water works in south China since 2001. The suitability of preozonation on treating such kind of source water, however, had not been systematically investigated before. The objective of this research was to investigate the effects of preozonation on treating such a source water, and explore the feasibility and efficiency of using the preozonation process to remove the precursor of DBPs while controlling the formation of bromate. Variations of the disinfection by-product formation potential (DBFPF) were examined by the determination of THMFP and HAAFP during preozonation treatment. The effects of preozonation on removals of turbidity, particle numbers, TOC and UV_{254} were also followed.

1 Materials and methods

1.1 Experimental set-up

Fig.1 shows the schematic diagram of the batch-scale experimental set-up in this study. Two similar reactors in parallel (A and B) were adopted in experiment. Reactor A was used to treat raw water and reactor B to correctly measure ozone generated. The ozonation reactor was constructed of a glass contact column with an effective volume of 2.0 L (780 mm \times 70 mm i.d.). Ozone gas produced was introduced from the bottom through a perforated glass plate. A PSA (FY-3, Beijing Beichen Technology Co., China) was used for generating oxygen gas ($O_2 > 90\%$), and the gas flow rate supplied to the ozonizer (OS-IN, Mitsubishi Electric Co., Japan; rated ozone output, 1 g/h) was fixed at 18 L/h. The effluent gas was introduced into a KI absorption solution for measuring the ozone amount exhausted. The sampling outlet was installed on the bottom of the reactor. Following preozonation, coagulation was conducted in a jar-testor with a polyaluminium chloride (PAC; Al_2O_3 content, 10%) dose of 1.67 mg/L.

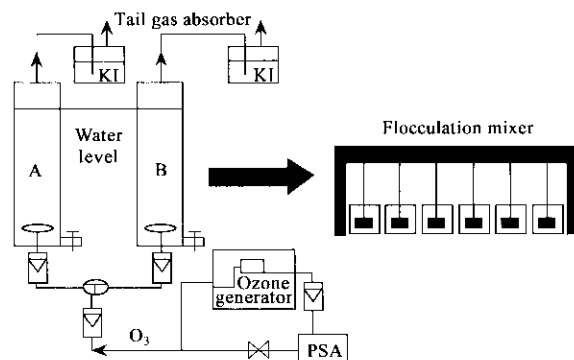


Fig.1 Schematic diagram of bench-scale experimental set-up

1.2 Analytical methods

All the analysis was conducted according to the fourth edition of The Standard Methods of Water and Wastewater Monitoring of China (EPB, 2002). The

TOC of liquid samples was analyzed by a TOC analyzer (Phoenix 8000, Tekmar Dohrmann, USA), and turbidity was measured by a portable turbidity meter (2100P, HACH Co., USA). UV absorbance was measured at 254 nm (UV_{254}) using a UV-visible spectrophotometer (Cary 100 UV-VIS, Varian Australia Pty., Mulgrave, Victoria, Australia). Prior to analysis, the samples were filtered through 0.45 μ m membrane filters. The particle number was measured by a particle number counter (IBR Inter Basic Resources Inc., USA). THMFP/HAAFP was analyzed with gas chromatography (Lin *et al.*, 2003). Bromate in the ozonated water was also determined by ion chromatography (ICS-1500 Ion Chromatography System, DIONEX, USA) with a minimum quantification limit of 2 μ g/L BrO_3^- (Liu and Shifen, 2004). Ozone measurement was performed using the iodometry method, and the ozone dose was calculated by deducting ozone amount in the effluent gas from that in the influent gas.

1.3 Experimental methods

Two litre raw water was injected into a single glass contact column, and the reaction was initiated by feeding ozone gas of different ozone concentrations through the perforated plate. After ozonation for 4 min, oxygen gas from the PSA was introduced into the reactor to purge the remaining ozone into KI absorption container for 15 min. After sampling, 1 L of the treated water was transferred into a 1.5 L glass beaker, treated with polyaluminium chloride (PAC; Al_2O_3 content, 10%) on a jar-testor under the following conditions: PAC dose, 1.67 mg/L (Al_2O_3 content); fast mixing (200 r/min), 1 min; slow mixing, 15 min (the first stage, 150 r/min, 5 min; the second stage, 100 r/min, 5 min; and the third stage, 50 r/min, 5 min). Supernatants were taken following a sedimentation time of 35 min.

To investigate bromate formation at different bromide concentrations, sodium bromide was spiked into the source water to prepare solutions containing bromide varying from 34 μ g/L (raw water) to 298 μ g/L.

All samples were refrigerated at 4°C until analysis, and the samples were analyzed within one week after reception.

2 Results and discussion

2.1 Raw water characteristics

Table 1 shows the average parameters of source water during the experiment. Raw water was taken from a dam in Guangdong Province, China. Water temperature during the experiment varied between 19 and 22°C. The dam water had a relatively low TOC content, alkalinity, hardness, and UV_{254} . The turbidity was generally low and stable, and the algae content was at a medium level (9×10^6 cell/L). The ammonium

concentration was not so high, indicating that the source water was not heavily polluted from municipal wastewater. It should be noted that the water contained 18–35 µg/L bromide ions.

Table 1 Parameters of raw water

Parameter	Range	Mean
pH	6.8–7.1	6.9
Turbidity, NTU	3.48–14.26	8.5
Alkalinity, mgCaO/L	13.04–15.81	13.8
Ammonium, mg/L	0.32–3.61	1.85
Hardness, mg CaCO ₃ /L	31.7–43.6	38.5
TOC, mg/L	1.95–2.62	2.3
COD, mg/L	1.48–5.23	2.8
UV ₂₅₄ , cm ⁻¹	0.01–0.05	0.03
Br, µg/L	18–35	34
Algae, cell/L	6 × 10 ⁶ –3 × 10 ⁷	9 × 10 ⁶

2.2 Algae removal

The effect of ozone dose on the removal of algae after sedimentation is shown in Fig.2. The removal of algae increased with ozone dose when the dose was below 1.0 mg/L. Further increase of ozone did not have much effect on the removal of algae because most of algae were already removed at an ozone dose of 1.0 mg/L.

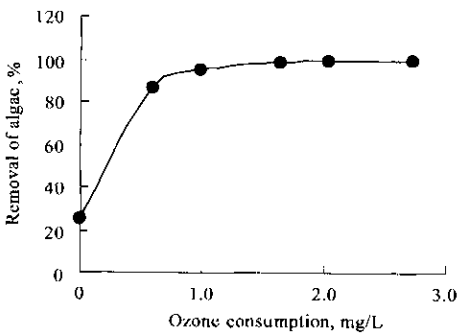


Fig.2 Algae profile under different ozone doses

2.3 Turbidity and particulate removals

The effects of preozonation on turbidity removal by coagulation were investigated, and the results are shown in Fig.3. Raw water with different turbidity (sample 1#, 1.56 NTU; sample 2#, 4.51 NTU; sample 3#, 7.27 NTU; and sample 4#, 13.58 NTU) was used for the tests. The turbidity increased slightly with the increase of ozone dose in most cases, especially when the ozone dose was over 1 mg/L. According to previous studies (Chang and Singer, 1991; Chandrakanth *et al.*, 1996), enhanced turbidity removal through coagulation during preozonation easily occurred in waters with hardness-to-TOC ratios >25 mg CaCO₃/mgTOC. It is speculated that organic compounds became more easily associated with a

complexing agent (e.g. calcium) because of more ligand sites (such as oxalic acid) formed upon ozonation. This process resulted in the adsorption of organic matter onto particles, thereby leading to a reduction in particle stability through surface charge reduction (Camel and Bermond, 1998). In this study, however, the ratio of hardness via TOC was less than 16, which might be a reason why coagulation-enhancing effects were not observed. Adverse effects of preozonation on coagulation were probably also related to the existence of algae (9 × 10⁶ cell/L in most cases). It was speculated that cytoplasm released by algae under the attack of ozone interfered with the coagulation reactions through complexation between organic and Al ions. The details, however, remain to be explored.

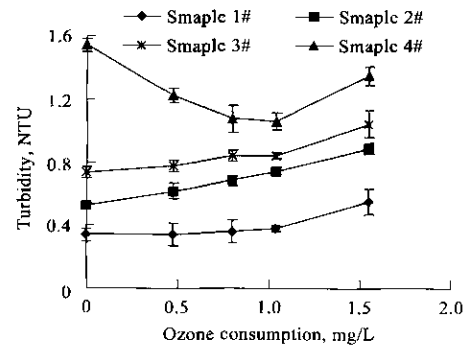


Fig.3 Effects of ozone dose on turbidity removal

Fig.4 shows the effect of ozonation on particulate counts after sedimentation (particulate size, >2 µm). The turbidity of the 3 raw water samples were similar (1#, 7.4 NTU; 2#, 8.1 NTU; 3#, 7.8 NTU). It is clear that the particulate counts in samples treated with ozone were significantly lower than those without ozonation. It is possible that some particles (like algae) were destroyed by ozone. However, further studies are required to investigate if more smaller particles, which could be not detected by the monitor, were formed on ozonation.

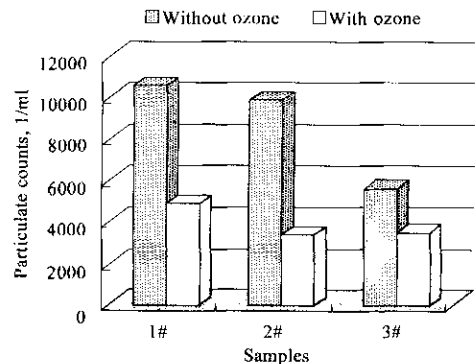


Fig.4 Effect of ozonation on particulate counts (ozone dose, 0.5 mg/L)

2.4 TOC removal

The effects of ozone on TOC removal are shown in Fig.5. It is clear that preozonation did not directly

result in the perceptible reduction of TOC. The removal of TOC by direct ozonation was roughly 0.1 mg TOC removed per mg ozone consumed. This is reasonable because of the low ozone dose and high selectivity of ozonation at neutral pH. However, the TOC after coagulation decreased with the increase of ozone dose, indicating that preozonation enhanced the removal of TOC through coagulation. Some studies have shown that the coagulation process could effectively remove hydrophobic organics (Collins *et al.*, 1986). However, this does not explain the enhanced removal of TOC in this study since ozonation generally reduces the hydrophobicity of organics in water. Polymerization of NOMs might be the main reason for the enhanced removal of TOC (Chrostowski *et al.*, 1983; Farvardin *et al.*, 1989; Sudha *et al.*, 1995).

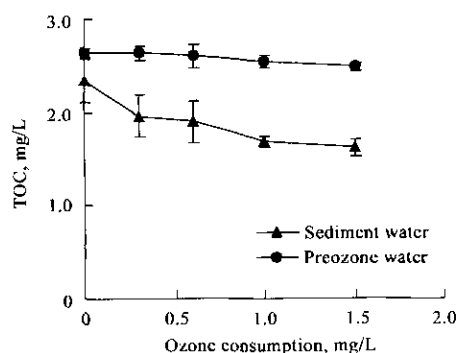


Fig.5 Removal of TOC

The TOC removal reached 36% under an ozone dose of 1.0 mg/L. However, TOC removal did not increase with the further increase of ozone dose. So, an ozone dose of 0.5–1.0 mg/L is enough for enhancing TOC removal through coagulation.

2.5 Reduction in UV absorbance

Ozone is known to cleave the aromatic carbon structures of NOM that are responsible for absorption of UV radiation at 254 nm (Paralkar and Edzwald, 1996). Fig.6 shows the effects of preozonation and coagulation on the reduction of UV₂₅₄. The removal of UV₂₅₄ mainly occurred during ozonation. The reduction of UV₂₅₄ increased almost linearly with the in-

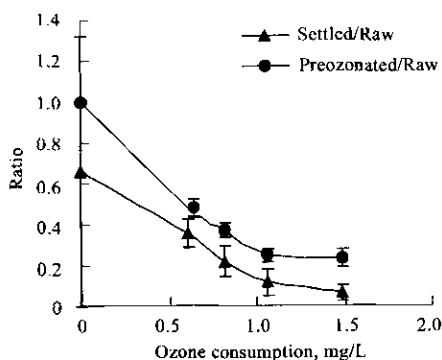


Fig.6 Removal of UV₂₅₄

crease of ozone dose because of direct destruction of UV absorbed structures by ozone. However, the reduction of UV₂₅₄ became much slower after ozone dose reached 1.0 mg/L. For reducing UV absorbance, a proper ozone dose is 1.0 mg/L.

2.6 Removal of THMFP and HAAFP

Since preozonation resulted in the reduction of UV absorption and enhanced TOC removal through coagulation, it is easy to speculate that ozonation might also be effective for enhancing the removal of the chlorinated DBPFPs, namely THMFP and HAAFP. Fig.7 shows the profiles of THMFP and HAAFP under different ozone doses. The average THMFP for raw water ranged between 181 to 190 μg/L and the average HAAFP was between 281 to 295 μg/L. The THMFP and HAAFP after coagulation decreased with the increase of ozone dose, and reached the lowest levels at an ozone dose of 0.6–1.0 mg/L. The highest removals for THMFP and HAAFP were 54% and 52%, respectively. It should be noted that both the THMFP and HAAFP increased when the ozone dose was increased from 1.0 mg/L to 1.5 mg/L, which was not observed in the profiles of TOC and UV₂₅₄. Ozonation may produce some new THMFP while destroying the original THMFP (Dore *et al.*, 1978). It seemed that the ozonation by-products produced at an ozone dose higher than 1.0 mg/L had a higher potential to form THM and HAA with chlorines.

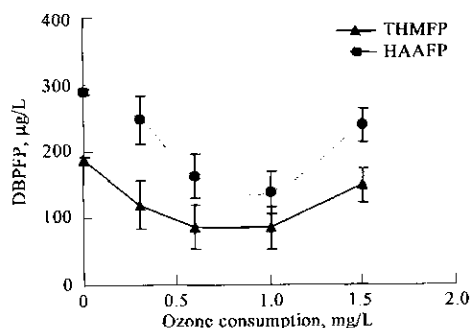


Fig.7 Removal of DBPFP

2.7 Bromate formation

Since the source water contained bromide, the possibility of bromate formation had to be considered before that an ozone process was adopted (von Gunten and Hoigne, 1992, 1994). Considering the bromide concentration in the source water might be affected by seawater, bromide concentration varied from 34 μg/L (raw water) to 291 μg/L by spiking bromide. Bromate formation profiles under different bromide concentrations are shown in Fig.8. 1 μg/L was adopted in Fig.8 when the bromate concentration was below the detection limit (2 μg/L). It is clear that bromate was under the detection limit in an ozone dose range between 0 and 1.7 mg/L when raw water was ozonated, indicating that preozonation of the source