

Control of Bromate and THM Precursors Using Ozonation Combined System¹

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Objective To investigate the feasibility of reducing THM precursors and controlling bromate taste and odor in drinking water taken from the Yellow River by an ozonation combined system. **Methods** The appropriate ozone dosage was determined, and then the changes of TOC, UV₂₅₄ and THM formation potential (THMFP) in the combined system were evaluated. **Results** One mg/L ozone could effectively remove taste and odor and meet the maximum allowable bromate level in drinking water. The pre-ozonation increased THMFP, but the conventional treatment system could effectively reduce the odor. The bio-ceramic filter could partly reduce CHCl₃FP, but sometimes might increase CHCl₂BrFP and CHClBr₂FP. The biological activated carbon (BAC) filter could effectively reduce CHCl₃FP and CHCl₂BrFP, but increase CHClBr₂FP. Compared with other filters, the fresh activated carbon (FAC) filter performed better in reducing THMFP and even reduced CHClBr₂FP. **Conclusion** The combined system can effectively reduce taste, odor, CHCl₃FP, and CHCl₂BrFP and also bring bromate under control.

Key words: Bromate; Ozonation; Disinfection by-products; Activated carbon

INTRODUCTION

There are offensive taste and odor, and possibly high level of carcinogenic trihalomethanes (THMs) in drinking water taken from the Yellow River. However, few studies have been conducted on reducing taste and odor and THM precursors in water from the Yellow River by advanced water treatment process. Ozone is widely used throughout the world due to its effectiveness in taste and odor control, especially in advanced countries. It has been used in some regions in China, such as Changzhou, Kunming, Shenzhen, and Guangzhou and may be extended and scaled up in this country in near future. However, ozonation of water containing bromide ion produces by-product bromate, a genotoxic carcinogen. Although bromide ion in the Yellow River is very high, unfortunately, there has been no report on bromate formation during ozonation or subsequent bromate reduction.

Ozone is used in disinfection, oxidation (e.g. taste and odor control, decoloration, elimination of

micropollutants, etc.), pre-oxidation and intermediate oxidation. Bromide occurs in drinking water due to natural anthropogenic sources including seawater intrusion, pesticide run-off, industrial wastewater, and impurities in road deicing salt^[1]. The maximum allowable bromate level of 25 µg/L is set according to WHO guidelines and 10 µg/L according to EU directives and US regulations^[2]. In China standard for urban drinking water quality issued in 2004 defines 10 µg/L as the maximum allowable bromate level in drinking water. However, few studies have been conducted in China to explore the minimizing bromate formation in order to effectively reduce it in drinking water. Pilot-drinking water studies have shown bromate formation in the range of 0-150 µg/L in normal water^[3]. Bromate formation is best achieved at high pH, initial bromide concentration, high alkalinity, and high ozone dose. On the other hand, increasing TOC and ammonia concentration decrease bromate formation^[4]. For the reduction of bromate two feasible techniques have been

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investigated. Siddiqui *et al.* reported that the reduction of bromate to bromide by the addition of ferrous iron as a reducing agent is feasible if ozonation treatment is followed by the coagulation process^[5]. It was reported that bench- and pilot-scale column can effectively remove bromate in the FAC filter^[2]. However, several studies have reported a poor reduction of bromate in the BAC filter^[3,5]. Unfortunately, up to date there is no report about the bromate formation and its subsequent reduction.

Humic substances in natural water have been shown to be especially reactive with a variety of oxidants and disinfectants that are used for the purification of drinking water, particularly chlorine. These substances react with chlorine to produce carcinogenic THMs, HAAs and other chlorination by-products (CBPs), a number of which have been shown to cause cancers in laboratory animals. However, chlorination of drinking water supplies is still widely used for disinfection, especially in China, which poses toxicological threat to the safety of drinking water. Therefore, the reduction of CBP precursors is usually necessary in minimizing the production of CBPs. The Yellow River is one of the largest drinking water sources in China but it is now faced with serious problems caused by pollution. However, the conventional drinking water treatment used in the Yellow River Basin consists of sedimentation, coagulation/flocculation, phase separation, rapid sand filtration, and disinfection. It cannot remove odor and taste, and CPB precursors effectively. Nowadays the tap water provide by most water supply systems cannot meet increasingly stringent drinking water quality criteria due to conventional drinking water treatment. The odor and taste of tap water are obviously offensive. Therefore, advanced water treatment has to be considered for the production of safer and cleaner drinking water. Unfortunately, few researches are available on the improvement of drinking water quality (especially reduction of THM precursors) by advanced water treatment process including biological pretreatment, ozonation and activated carbon filtration in the Yellow River Basin. To the authors' knowledge only our previous study has reported effective reduction of THM precursors by biological pretreatment^[6] and there is no report concerning reduction of THM precursors in the Yellow River. Moreover, about 200 µg/L bromide ion in the Yellow River is usually observed by Zhenzhou Water Supply Corporation. Amy *et al.* reported that under typical ozonation conditions about 20% of initial bromide ion could be converted to bromate^[7]. Therefore, bromate formation in Yellow River during ozonation may greatly exceed the bromate standards.

Therefore, the main objective of this study was

to investigate the feasibility of treating water from the Yellow River containing high bromide by using an ozonation combined system. Pre-ozonation was used because higher TOC and ammonia concentration in raw water might decrease bromate formation. Bromate formation during ozonation at different ozone dosages and subsequent reduction were investigated in this study. The reduction of bromate to bromide by the addition of ferrous iron as a reducing agent was investigated through bench-scale experiment instead of jar test experiment. The capacity of fresh carbon and old carbon attached with biofilm of reducing bromate was compared by column test. Moreover, changes of THM precursors in the combined process was also investigated. This study may provide useful and fundamental data for the design of safe water supply project taking water from the Yellow River, especially for the control of bromate and THM precursors.

MATERIALS AND METHODS

Experimental Setup

The schematic diagram of ozonation combined drinking water treatment system and the operating parameters of each unit are shown in Fig. 1 and Table 1 respectively. The combined system consists of pre-ozonation, biological pretreatment using bio-ceramic filter (BF), coagulation, phase separation, sand filtration, and advanced treatment unit using BAC filter or FAC filter.

The ozonation column (OC) is a cylinder made of stainless steel (3 m high and 0.35 m of inside diameter). Liquid and gas phases flow up through the filter in counter-current mode. The BF is a cylinder made of Plexiglas (3 m high and 0.5 m of inside diameter). The filter is filled with ceramic particles up to 2 m. The conventional treatment also consists of coagulation, sedimentation/phase separation and rapid sand filtration. The coagulation tank is a cuboid made of stainless steel (0.67 m high, 0.3 m long, and 0.3 m wide). The slanting-tube sedimentation tank has three zones including vertical sedimentation, slanting sedimentation, and settling zones. The slanting-tube sedimentation tank is also made of Plexiglas. The sand filter is a cylinder made of Plexiglas (3 m high with 0.7 m height of sand layer, and 0.35 m of inside diameter). The larger carbon filter is filled with old carbon attached by biofilm and the smaller carbon filter (FAC) is filled with fresh carbon. The two filters are operated in a parallel mode, namely most of sand filter effluent is pumped into the larger carbon filter but a small part of sand filter effluent is led into the smaller carbon filter. Before this study the BF and larger carbon filter were operated for about 1.5 years. Therefore, the larger carbon filter is actually a BAC filter.

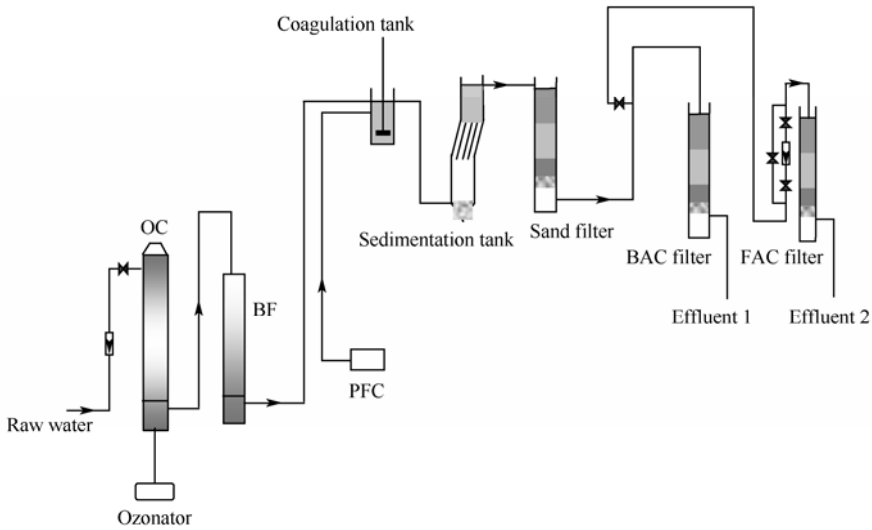


FIG. 1. Schematic diagram of the ozonation combined system for treatment of the Yellow River water.

TABLE 1

Operating Parameters of Each Unit in the Combined System

Reactor	Dimension (D×H mm ²)	Filter Layer Height (mm)	Filling Particle Size (mm)	Empty Bed Contact Time (min)
Ozonation Column	350×3000			17.3
Bio-ceramic Filter	500×3000	2000	2-5	23.6
Coagulation Tank	300×670			3.6
Slanting-tube Sedimentation Tank	400×2000*			19.2
Sand Filter	350×3000	700	1-1.5	4.7
BAC Filter	350×3000	1200	1-2	6.9
FAC Filter	100×2000	1000	1-2	6.9

Note. *The total height of vertical sedimentation zone and slanting sedimentation zone.

The study was performed in Shiyuan Water Works in Zhengzhou City. The combined system was fed with the Yellow River water after sedimentation for sand reduction. The influent flow was 1 m³/h. The pH value ranged 7.8-8.37 and water temperatures of raw water were 15°C and 20°C respectively. During this study, due to the high oxygen concentration in ozonated water (above 8 mg O₂/L), the BF was not aerated. The ozone dosage could be adjusted according to the experimental requirement. The coagulant applied in this study was FeSO₄ and the Fe²⁺ dosage was 20 mg/L.

Analysis

UV₂₅₄ was measured in a 1 cm quartz cell with a spectrophotometer (Shimadzu UV-1200) and TOC was determined using a TOC analyzer (Shimadzu TOC-5000). Dissolved oxygen (DO), pH and water

temperatures were determined using selective electrodes. Applied and utilized ozone concentrations were determined as previously described^[8].

Formation potential (FP) experiments for THMs in water were conducted with a 7-day incubation following introduction of the NaOCl solution and phosphate buffer (pH 7.0). The applied chlorine concentration for formation potential experiments was about 50 mg/L, which would provide free residual chlorine of at least 3 mg/L at the end of incubation. Analysis of residual chlorine was performed using DPD (N, N-diethyl-*p*-phenylene-diamine) ferrous titration method^[8]. THMs formed were extracted with *n*-pentane and the extract was then analyzed using a GC with a fused silica capillary column (DB-5, 30 m × 0.25 mm ID, 1.0 μm film thickness) and an electron capture detector. The

esterified extract was analyzed using the same GC setup. All the detailed analyses using the QA/QC programs^[8].

BrO_3^- , Br^- , Cl^- , and SO_4^{2-} concentrations were determined by ion chromatograph (Model 2000 I, Dionex, Sunnyvale) equipped with Ionpac AG12A guard/AS12A analytical columns and anion micromembrane suppressor. The effluent solutions were 20 mmol/L $\text{Na}_2\text{B}_4\text{O}_7$ and 18 mmol/L NaOH.

RESULTS

Determination of Appropriate Ozone Dosage for Effective Bromate Control

About 200 $\mu\text{g/L}$ bromide ion in the Yellow River was observed in this study. Typical changes of bromate in the combined system at different ozone dosages are shown in Table 2. No bromate was detected in raw water. The ozonation by-product bromate increased with the ozone dosage and the bromate level could exceed 10 $\mu\text{g/L}$ (the maximum allowable bromate level in drinking water regulated

in China) when the ozone dosage was 1 mg/L or more. The bromate formed in ozonation could be subsequently removed from the subsequent system. Therefore, when 1 mg/L ozone was used, bromate in effluent of the BAC filter or the FAC filter was below 10 $\mu\text{g/L}$ although the bromate formed in ozonation was above 10 $\mu\text{g/L}$. However, when 1.5-2 mg/L ozone was used, the bromate in the finished water of this combined system was still below 10 $\mu\text{g/L}$ using the FAC filter instead of the BAC filter. The bio-ceramic filter could partly reduce bromate. Moreover, the bromate reduced by the sand filter was also observed in this study.

The change of bromate in the combined system induced by 1 mg/L ozone during one-month operation is shown in Fig. 2. During this period of time, the FAC filter always performed better than the BAC filter in reducing bromate, although the activated carbon in FAC might be gradually transformed into biological active carbon. Therefore, chemical reduction of bromate was more effective than biological reduction in the FAC filter. Moreover, the bromate in the BAC filter effluent remained below 10 $\mu\text{g/L}$.

TABLE 2

Typical Change of Bromate in the Combined System at Different Ozone Dosages

BrO_3^- ($\mu\text{g/L}$) O_3 (mg/L)	Raw Water	Ozonation Column Effluent	Bio-ceramic Filter Effluent	Sedimentation Tank Effluent	Sand Filter Effluent	BAC Filter Effluent	FAC Filter Effluent
0.5	0	6.88	6.26	6.06	5.94	4.73	4.01
1	0	10.63	10.36	10.10	9.82	9.51	6.92
1.5	0	12.46	11.4	11.17	10.59	10.21	8.25
2	0	14.49	12.95	12.89	11.63	10.42	8.9

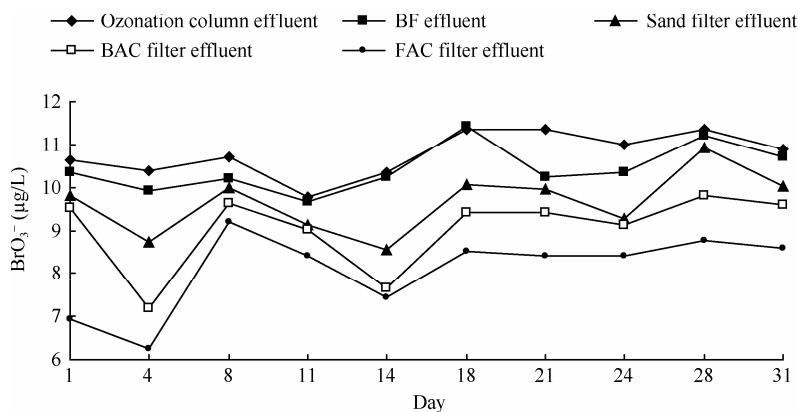


FIG. 2. Change of bromate in the combined system at 1 mg/L ozone.

In practical operation the FAC filter could turn into the BAC filter after several months. It is necessary to optimize ozonation conditions to minimize bromate formation while maintaining

effective removal of taste and odor. In this study there were still obvious taste and odor in ozonation column effluent and even in the finished water of the combined system at 0.5 mg/L ozone, but the taste and

odor were undetectable at 1-2 mg/L ozone. Therefore, 1 mg/L ozone could effectively remove taste and odor while meeting the maximum allowable bromate level in drinking water.

Change of TOC and UV₂₅₄ in the Combined System

The most common indicators for natural organic matters are TOC and UV₂₅₄. In regard to the prevention of THM generation, the TOC level is more important than the levels of easily biodegradable organic matters in water^[9]. The change of TOC in the combined system at 1 mg/L ozone during one-month operation is shown in Fig. 3. As shown in Fig. 3, the combined system using BAC filter or FAC filter could effectively reduce TOC.

Pre-ozonation in drinking water is mainly to improve the biodegradability of organic substances instead of completely mineralizing them at the prohibitive cost. Usually, there is only a slight reduction of TOC during ozonation. However, the BF could effectively reduce TOC in water. In this study,

the reduction rate of TOC in BF was 8.6%-15% (average 9.5%). The conventional treatment system (coagulation, phase separation, rapid sand filtration) could also effectively reduce TOC with a reduction rate of 8.8%-19.4% (average 12.4%). The FAC filter performed much better than the GAC filter in reducing TOC, although the BAC filter could effectively reduce TOC with a reduction rate of 11.5%-24.1% (average 17.9%) even after 1.5-year operation. Although the activated carbon in FAC might be gradually transformed into biological active carbon, its capacity of reducing did not obviously deteriorate.

UV₂₅₄ usually shows a good correlation with THM precursor and is thus regarded as a surrogate parameter of THM precursor although it is originally a general parameter^[10]. In this study, the change of UV₂₅₄ in the combined system at 1 mg/L ozone during one-month operation is shown in Fig. 4, indicating that the combined system using BAC filter or FAC filter could effectively reduce UV₂₅₄.

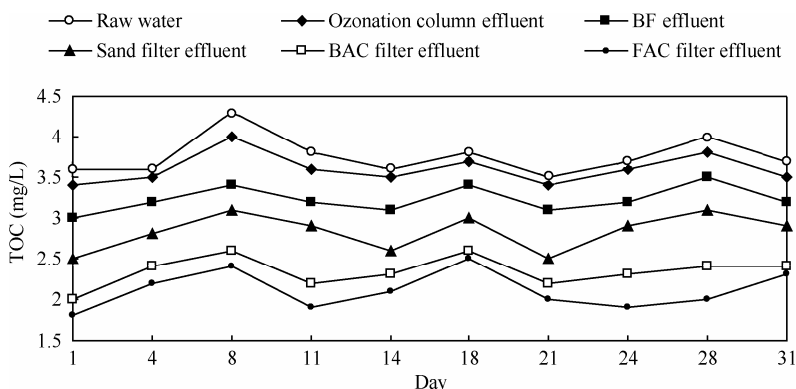


FIG. 3. Reduction of TOC in the combined system.

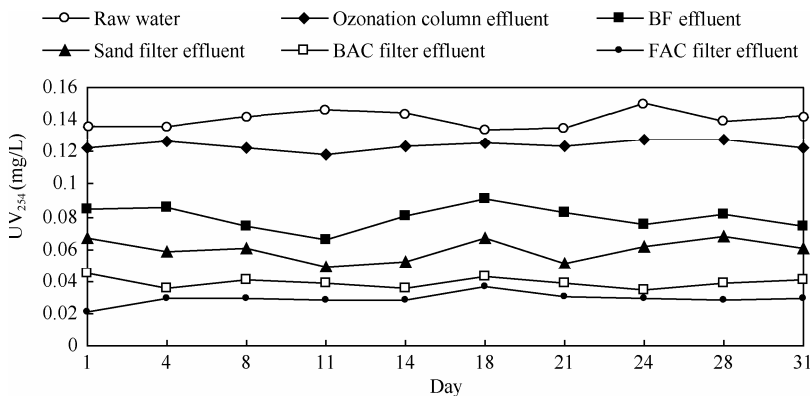


FIG. 4. Reduction of UV₂₅₄ in the combined system.

Pre-ozonation played an obvious role in reducing UV₂₅₄ in this study. Humic substances were shown to have a large molecular structure, thus leading to the poor biodegradability. The reduction of UV₂₅₄ in

pre-ozonation is due to a reduction of aromatic structures and double bonds of the natural organic matters^[11]. In the BF, biological flocculation of biofilm could effectively absorb suspended matters

and colloids containing a large amount of humic substances, which play an important role in the reduction of humic substances or UV_{254} ^[6]. During this study the BF played a significant role in the reduction of UV_{254} and the reduction in the BF was 27.2%-44.5% (average 35.6%). One possible reason is that biological flocculation of biofilm could be improved without aeration. The conventional treatment system could also effectively reduce UV_{254} with a reduction rate of 18.2%-37.2% (average 25.0%). In the BAC filter biological flocculation of biofilm might play a more important role although the biological regeneration of carbon could occur through the biological degradation of organic matters absorbed into micro-pore and thus carbon could slightly adsorb excessive organic matters even after its saturation of adsorbing capacity^[12]. In the filter physico-chemical adsorption played a more important role. However, the FAC filter performed much better than the GAC filter in reducing UV_{254} . The reduction rate of UV_{254} in the FAC filter was 42.3%-69.4% (average 52.3%) in the FAC filter and 19.9%-43.6% (average 34.1%) in the BAC filter.

Change of Precursors of CBPs in the Combined System

The amount of precursors of CBPs in water is usually indirectly measured by formation potential (FP) in water research. In the present study, 3 CBP species, including chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$) and dibromochloromethane ($CHClBr_2$) were the major compounds detected in raw water after a 7-day incubation for the measurement of THMFP. The three THM species were all regulated as required by the China sanitary standard for drinking water quality.

The Change of $CHCl_3$ FP in the combined system at 1 mg/L ozone is shown in Fig. 5. $CHCl_3$ FP in raw water varied greatly, from 12.4 to 35.7 $\mu\text{g/L}$. The combined system using the BAC filter or the FAC filter could effectively reduce $CHCl_3$ FP. Pre-ozonation increased $CHCl_3$ FP in water. However, the BF could partly reduce $CHCl_3$ FP in ozonated water. The conventional treatment system could effectively reduce $CHCl_3$ FP, and a significant reduction was observed when $CHCl_3$ FP in BF effluent was relatively higher. The BAC filter could further reduce $CHCl_3$ FP and the FAC filter performed much better in reducing $CHCl_3$ FP. The reduction rate of $CHCl_3$ FP was 37.5%-68.5% (average 54%) in the FAC filter and 14%-46.8% (average 27.1%) in the BAC filter. In the FAC filter physico-chemical adsorption might play a major role in reducing precursors of chloroform, but in the BAC filter the role of biological flocculation of biofilm might be more important. Moreover, reduction of $CHCl_3$ FP in

the FAC filter did not obviously deteriorate, although the activated carbon in FAC might be gradually transformed into bio-active carbon.

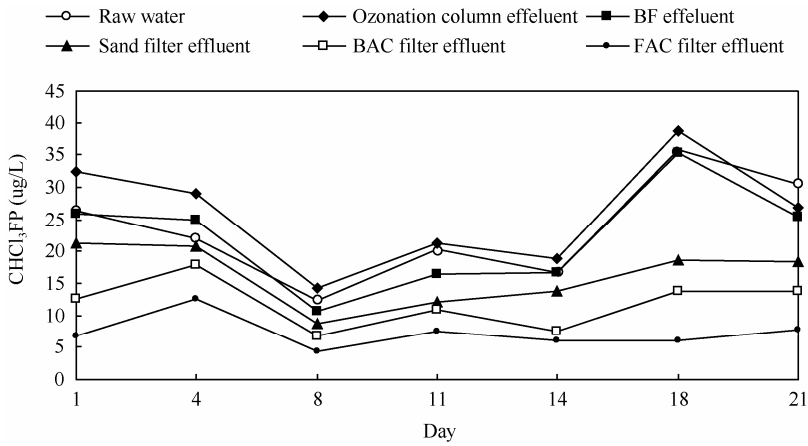
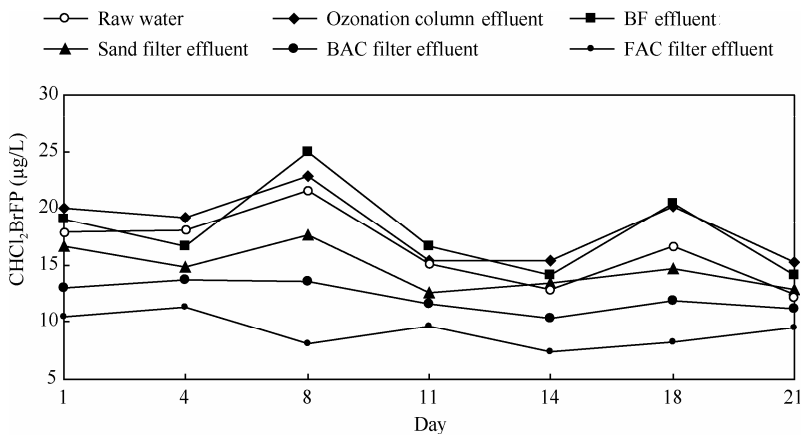
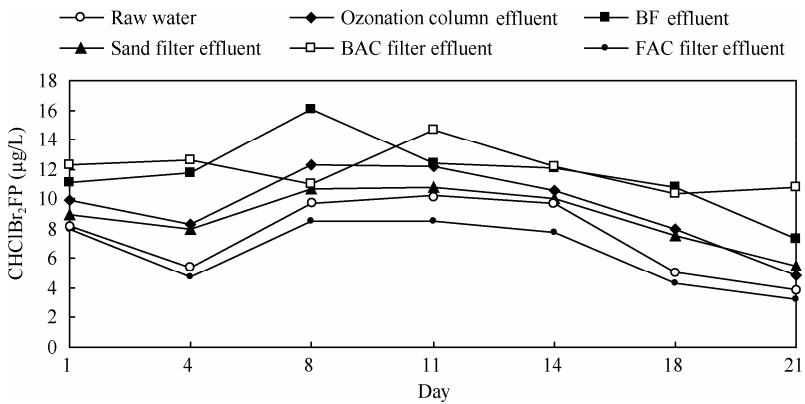
The Change of $CHCl_2Br$ FP in the combined system at 1 mg/L ozone is shown in Fig. 6. Pre-ozonation also increased $CHCl_2Br$ FP in water. However, the change of $CHCl_2Br$ FP in the BF was very complicated, and the decline and rise of $CHCl_2Br$ FP after biofiltration were both observed in this study. Therefore, after pre-ozonation and biofiltration $CHCl_2Br$ FP in water was usually increased. Similar to the reduction of $CHCl_3$ FP, the conventional treatment system could effectively reduce $CHCl_2Br$ FP, and a significant reduction was observed when $CHCl_2Br$ FP in BF effluent was relatively high.

The BAC filter could also further reduce $CHCl_2Br$ FP and the FAC filter performed much better in reducing $CHCl_2Br$ FP. The reduction rate of $CHCl_2Br$ FP was 23%-54.2% (average 36.1%) in the FAC filter and 7.4%-23.7% (average 16.5%) in the BAC filter. Similarly, in the FAC filter physico-chemical adsorption might play a major role in reducing precursors of dichlorobromomethane, whereas in the BAC filter the role of biological flocculation of biofilm might be more important. Moreover, the capacity of the FAC filter in reducing $CHCl_2Br$ FP did not obviously deteriorate, although the activated carbon in the FAC filter might gradually be transformed into bio-active carbon. In summary, the combined system using the BAC filter or the FAC filter could effectively reduce $CHCl_2Br$ FP.

The change of $CHClBr_2$ FP in the combined system at 1 mg/L ozone is shown in Fig. 7. The change of $CHClBr_2$ FP in raw water varied greatly, from 3.9 to 10.2 $\mu\text{g/L}$. Similarly, pre-ozonation increased $CHClBr_2$ FP in water. The change of $CHClBr_2$ FP in the BF was also very complicated, and the decline and rise of $CHClBr_2$ FP after biofiltration were also observed. In this study after pre-ozonation and biofiltration, the $CHClBr_2$ FP in water was always increased. The conventional treatment system could also effectively reduce $CHClBr_2$ FP, and a significant reduction was observed when $CHClBr_2$ FP in BF effluent was relatively high. After biofiltration using the BAC filter $CHClBr_2$ FP in water increased, although it could be further reduced by the FAC filter. The combined system using BAC filter always increased $CHClBr_2$ FP in water, but could lead to a limited reduction of $CHClBr_2$ FP when the FAC filter was used.

DISCUSSION

It was reported that bromate could be effectively

FIG. 5. Change of CHCl_3FP in the combined system.FIG. 6. Change of CHCl_2BrFP in the combined system.FIG. 7. Change of CHClBr_2FP in the combined system.

removed by the FAC filter^[2]. Mary *et al.* reported that more than 60% of bromate could be removed by the FAC filter^[13]. However, in this study bromate was not significantly reduced in the FAC filter. The presence

of Br^- , Cl^- , and SO_4^{2-} could decrease bromate in the FAC filter^[14]. In this study Br^- , Cl^- , and SO_4^{2-} in water were approximately 200 mg/L, 60-70 mg/L, 100-150 mg/L respectively, suggesting that bromate

reduction in the FAC filter might be greatly limited by the high level of Br^- , Cl^- , and SO_4^{2-} .

Siddiqui *et al.* reported that bromate can be reduced by the addition of ferrous iron as a reducing agent during coagulation process^[7]. However, only a slight reduction of bromate during the coagulation process at normal empty bed contact time (EBCT) was observed during this pilot-scale experiment, suggesting that using ferrous iron to reduce bromate is questionable.

Pre-ozonation in the treatment of the Yellow River water has two-edged effects. It could obviously eliminate offensive taste and odor in water. However, bromate formation during pre-ozonation could not be neglected because there is about 200 $\mu\text{g/L}$ bromide ion in the Yellow River. Fortunately, in this study the actual bromate formed during pre-ozonation was much lower than 40 $\mu\text{g/L}$ (expected value), although Amy *et al.* reported that under typical ozonation conditions about 20% of the initial bromide ions could be converted to bromate^[7]. Relatively higher TOC and ammonia concentration in raw water might decrease bromate formation because pre-ozonation is directly applied to raw water. However, once bromate is formed during ozonation, subsequent reduction is limited. Reducing bromate formation in accordance with ozonation (mainly removal of taste and odor in this study) could be an effective measure for reducing bromate in the drinking water.

Pre-ozonation is often applied to reducing THM precursors^[15]. However, in this study THMFP in water increased after pre-ozonation. An increase in the dissolved organic carbon content in the algal suspension caused by pre-ozonation might be responsible for the increase of THMFP in water^[16]. Algae are also important THM precursors^[10]. In order to minimize bromate formation while removing taste and odor, 1 mg/L ozone was low in this study, so pre-ozonation might only increase in the dissolved organic carbon content in the algal suspension by breaking up the algal cells, instead of completely mineralizing them in raw water.

It was reported that there is a poor or even no reduction of THMFP in the BAC filter or the FAC filter^[17-18]. However, in this study the BAC filter could further reduce CHCl_3FP and CHCl_2BrFP , and the FAC filter performed much better in reducing them. One possible reason is that pre-ozonation increased the biodegradability or/and absorbability of precursors of chloroform and dichlorobromomethane by destroying their original structure. However, after the treatment of biofiltration using the BAC filter CHClBr_2FP in waters increased. Therefore, in the BAC filter the biological action on the change of CHClBr_2FP was different from that on the change of

CHCl_3FP and CHCl_2BrFP .

UV_{254} usually shows a good correlation with THM precursor and is thus regarded as a surrogate parameter of THM precursor, although it is originally a general parameter^[10]. However, in this study pre-ozonation obviously reduced UV_{254} in water but increased CHCl_3FP , CHCl_2BrFP , and CHClBr_2FP . In the BF and BAC filter, changes of UV_{254} , CHCl_3FP , CHCl_2BrFP , and CHClBr_2FP were different, suggesting that UV_{254} is not an appropriate surrogate parameter of THMFP. When UV_{254} reduction can be used to predict THM precursors or THMFP reduction in pre-ozonation or other treatment processes.

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