Pilot-scale O$_3$/BAC process for the advanced treatment of the Songhuajiang River, northeast China

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**ABSTRACT**

To increase the safety of drinking water supply for residents, the O$_3$/BAC (ozonation and biological activated carbon filtration) advanced treatment was investigated through a pilot-scale water plant in Harbin City. Results indicated that the raw water of the Songhuajiang River contained a high content of turbidity, chemical oxygen demand (COD$_{Mn}$), and NH$_3$–N, which resulted in substandard water quality via the conventional treatment. However, after treatment by the O$_3$/BAC process, the average removal rates of turbidity, COD$_{Mn}$, NH$_3$–N, UV$_{254}$, total organic carbon, and trihalomethane formation potential in effluent were 97.97%, 84.84%, 64.29%, 87.39%, 72.09%, and 78.67%, respectively. The combined effect of the pre-ozonation and O$_3$/BAC process also eliminated the precursors of disinfection by-products from water. The results indicate that the O$_3$/BAC process is effective and promising to treat water from the Songhuajiang River. Moreover, the stable operation of the system confirmed that it can meet the effluent requirements of the “Standards for drinking water quality” (GB5749-2006), and also ensure minimal fluctuations in the treated water.

**Keywords:** Pilot-scale study; O$_3$/BAC process; Stabilized operation; Songhuajiang River

1. Introduction

The quality of drinking water is closely related to human health [1,2]. Since the Songhuajiang River nitrobenzene pollution event in 2005, the Mopanshan Reservoir has been chosen as the only source of drinking water for the main urban area of Harbin City [3]. However, with the progress and development of human society, many problems have emerged for the Mopanshan Reservoir, including long-distance water diversion, eutrophication trend of the water quality, and a single main water source. These restraints significantly decrease the water supply safety in Harbin City and hinder the local economic growth and improvement of the investment environment. Thus, it is urgent to seek a new water source. This can not only help Harbin break the long-term restraint by the single water source of Mopanshan Reservoir for urban areas, but can also significantly improve the water supply safety.

The World Health Organization (WHO) asserts that 80% of human diseases are related to water pollution [4]. It is
necessary to evaluate the water quality to ensure the safety of drinking water. Until now, numerous countries have issued corresponding drinking water standards [5–7]. The main water quality indexes of China, America, Japan, and the European Union are presented in Table 1. The standards of some relevant water quality indexes of China are more stringent than those of developed countries. In this study, the “Standards for drinking water quality” (GB5749-2006) of China was utilized to appraise the water quality of the Songhuajiang River after the treatment.

The integrated ozone-activated carbon process suggested by Rivas et al. [8], has gradually attracted the attention of researchers and achieved good results in the field of water supply and drainage engineering [9,10]. This process has been proved effective for the elimination of recalcitrant organic pollutants. Li et al. [11] applied an integrated ozonation and biological activated carbon filtration (O3/BAC) process to remove sulfonamides. The content of sulfonamides decreased by 45% to 92% after treatment. The results indicated that BAC filtration was capable of overcoming the problem of increased formation of disinfection by-products caused by ozonation. The excellent effect of the O3/BAC process was also demonstrated by Östman et al. [12], Vatankhah et al. [13], and Liu et al. [14].

To ensure the drinking water safety with the Songhuajiang River as the water source, a pilot-scale test based on the O3/BAC process combined with pre-ozonation was implemented. The raw water quality was evaluated to identify the primary problems of the Songhuajiang River. Particular attention was paid to the removal efficiencies of chemical oxygen demand (CODMn), turbidity, NH3-N, UV254, total organic carbon (TOC), and trihalomethane formation potential (THMFP) in each treatment unit in the case of the O3/BAC process. The stable operation of the O3/BAC process was also analyzed to ensure the feasibility of the treatment process.

2. Material and methods

2.1. Pilot-scale process setup

The pilot-scale plant, using the Songhuajiang River as the source of water, was located at a water purification plant in Harbin City. The conventional treatment process used in this work consisted of coagulation, precipitation, filtration, and sterilization. To improve the effluent water quality, an advanced treatment-O3/BAC process was utilized, with a pre-ozonation tank added before the coagulation tank and the main ozonation treatment unit attached after the sand filtration tank. The BAC filtration unit was behind the main ozone contact tank. The schematic process is illustrated in Fig. 1. The pilot plant scale was 5.0 t/h. Among these

<table>
<thead>
<tr>
<th>Index</th>
<th>Limiting value</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>China</td>
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<tr>
<td>pH</td>
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<td>Chromaticity (PCU)</td>
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<tr>
<td>CODMn (mg/L)</td>
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<tr>
<td>NH3–N (mg/L)</td>
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<tr>
<td>Trichloromethane (mg/L)</td>
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<tr>
<td>Chloral</td>
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</tr>
</tbody>
</table>

Table 1 Comparison of the partial water quality indexes of China, America, Japan and European Union

Fig. 1. Diagram of process flow.
processing units, composite aluminum ferric was used as a coagulant to strengthen the coagulation effect. The height, diameter, and valid volume of the two ozone contact tanks, which were made of stainless steel, were 2.5 m, 800 mm, and 2.0 m³, respectively. The hydraulic retention time of the pre-ozonation tank was 5 min, while it was 10 min for the main ozonation contact tank. For the two ozone schemes, the air was applied as the feed gas to produce ozone by an ozone generator (WH-H-Y3, Nanjing Wohuan Technology Co., China). Then, the ozone was bubbled into the contact tank by water ejector. The ozonation off-gas was recovered to increase the ozone absorption rate as well as the coagulation, reaction, and precipitation effect in the water.

Furthermore, the conventional filtration was based on quartz sand, while the BAC filtration mainly relied on the loaded microorganism, granular active carbon, and cobbler. The washing scheme of the conventional filtration was 2 min of air washing, 3 min of air-water backwashing, and 5 min of water washing with a washing intensity of 12.5 L/(m² s). The backwashing intensity of the BAC filtration (height 3.3 m, ID 1 m), which applied the air-water backwashing technique, was set as 11.5 L/(m² s) for 10 min.

### 2.2. Conventional water quality parameters

The Songhuajiang River, located in Northeastern China, undergoes a long frozen period from December to April. The annual mean temperature is about 3°C. Water samples were collected in triplicate by Teflon bottles from the outlet of each treatment unit during a month in 2017. Then the collected samples were transferred to the laboratory and stored at −20°C until further analysis. The turbidity was determined by a turbidimeter (TL23, HACH, America). Chromaticity was measured by a colorimeter (XZ-BS, Shanghai, China). The pH value was determined by portable pH meter (PHH-7200, OMEGA, America). Alkalinity was measured by the acid-base titration method. The COD₃₅₀ was determined by the oxidation of potassium permanganate. The ammonia-nitrogen (NH₃–N) content was measured by the salicylic acid-hypochlorite photometric method. UV₂₅₄ usually represents the aromatic character of the organic matter, which was determined by the specific UV absorption at 254 nm (DR6000, HACH, America). The THMFP and disinfection by-products (DBPs) were determined by a gas chromatography (TRACE™ 1310, Thermo Scientific™, USA) equipped with an electron capture detector [15–17]. TOC was measured by the nondispersive infrared absorption method using a TOC analyzer (model-VCSH, Shimadzu, Japan).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Monitoring mean value</th>
<th>Standard deviation</th>
<th>Parameter</th>
<th>Monitoring mean value</th>
<th>Standard deviation</th>
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<td>Turbidity, NTU</td>
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<td>Temperature, °C</td>
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<tr>
<td>COD₃₅₀, mg/L</td>
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<td>Alkalinity, mg/L as CaCO₃</td>
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<td>16.7</td>
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<td>UV₂₅₄, cm⁻¹</td>
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<td>0.011</td>
<td>Trihalomethane formation potential, μg/L</td>
<td>347</td>
<td>38.2</td>
</tr>
</tbody>
</table>

### 3. Results and discussion

#### 3.1. Raw water quality analysis of the Songhuajiang River

The relevant water quality parameters of the Songhuajiang River are listed in Table 2. The average contents of turbidity, COD₃₅₀, and NH₃–N were 57 NTU, 5.85 mg/L, and 1.07 mg/L, respectively. These values exceed the threshold value of “Standards for drinking water quality” (GB5749-2006), which states that their maximum values should be 1 NTU, 3 mg/L, and 0.5 mg/L, respectively. Thus, attention was mainly paid to the monthly monitoring of these three parameters in this study, as depicted in Fig. 2. It is interesting to note that the turbidity value of the Songhuajiang River was extremely high from April to November, while it sharply reduced from December to March. The turbidity in spring and summer was on average five-fold higher than that in autumn and winter. This is because the precipitation is plentiful from April to November in Harbin City, resulting in an increase in surface runoff and floating granules. In contrast, the river enters a frozen period from December to April, which is the main reason for low turbidity. Furthermore, the relatively high turbidity can directly influence the subsequent disinfection effect and increase the use of disinfectants. It can even increase the content of DBPs in water and decrease effluent safety.

For COD₃₅₀, all the monitored values were over the standard value. Especially, the COD₃₅₀ value reached a peak in May. This may be due to the surface runoff and sewage discharge from the circumjacent factories. However, the value for NH₃–N dramatically increased in the frozen period, which was primarily due to the following reasons: (1) the low precipitation resulting in the poor dilution capability for contaminants; (2) the high evaporation loss causing the high evaporated concentration of contaminants; (3) the low water temperature and dissolved oxygen leading to poor biological activity and purification ability; and (4) organic matter in the sediment reduced to NH₃–N and released into the water [18,19]. The high NH₃–N content can not only affect the subsequent disinfection effect and increase chlorine consumption but also generate mutagenic materials including chloramine (NH₂Cl). These matters can lead to the production of trihalomethanes (THMs) and other DBPs in disinfected water and further reduce drinking water safety [20,21]. Besides, the turbidity, COD₃₅₀ and NH₃–N values in the effluent treated by the traditional water purification process were 1.25 NTU, 3.08 mg/L, and 0.82 mg/L, respectively. The effluent quality of the traditional water purification process did not meet the drinking water standard.
The UV absorbance at 254 nm (UV\textsubscript{254}) is a useful indicator for the characteristics of dissolved organic matter [22]. As seen in Table 2, the UV\textsubscript{254} value was 0.13 cm\textsuperscript{-1}. It indicated that the Songhuajiang River possessed a high quantity of organic matter, which was similar to that of COD\textsubscript{Mn}. The content of THMFP in the raw water was also large with a value of 347 μg/L, which can enhance the productivity of DBPs for the utilization of liquid chlorine disinfection in the pilot-scale plant [23].

According to the raw water-quality monitoring of the Songhuajiang River, the water quality problems of this water plant mainly occurred during the frozen period in winter. Moreover, the Songhuajiang River is difficult to be treated by the traditional water purification process. Thus, it is necessary to adopt an advanced treatment process to treat the Songhuajiang River and ensure drinking water quality.

### 3.2. Analysis of ozone dosage

Ozone dosage is an important parameter for the O\textsubscript{3}/BAC process. In this study, concentration variations of COD\textsubscript{Mn} and NH\textsubscript{3}–N in the pre-ozonation tank and main ozone tank were detected by changing the ozone dosage, in order to determine the appropriate ozone dosage to oxidize organics and NH\textsubscript{3}–N in water. Ozone dosage was chosen as 0, 0.3, 0.4, 0.45, 0.5, 0.6, 1.0, and 1.5 mg/L, respectively. The relationship between ozone dosage and average removal rate of COD\textsubscript{Mn} and NH\textsubscript{3}–N is shown in Fig. 3.

As presented in Fig. 3, the removal of COD\textsubscript{Mn} and NH\textsubscript{3}–N treated by ozonation both improved with the increase in ozone dosage. The average removal rate of COD\textsubscript{Mn} in the main ozone contact tank was 69.57%, which was far higher than that in the pre-ozonation contact tank (9.43%). A similar phenomenon was observed for NH\textsubscript{3}–N. Furthermore, when the ozone dosage was more than 1.0 mg/L, the removal rates of COD\textsubscript{Mn} and NH\textsubscript{3}–N oxidized by the pre-ozonation process reached 20% and 10% and remained unchanged. However, the removal rate of the two indexes oxidized by the main ozonation process exceeded 60% when the ozone dosage was higher than 0.4 mg/L. Thus, the organics and NH\textsubscript{3}–N were primarily eliminated in the main ozonation contact tank, while the pre-ozonation process played an important role in the coagulation-supporting effect. This is in agreement with the previous studies, which indicated the coagulation-supporting effect of ozone [24,25]. Based on the above consideration, the ozone dosages in the pre-ozonation tank and the main ozonation tank were chosen as 1.0 and 0.4 mg/L, respectively.

The residual ozone was determined as 0.127 mg/L after the pre-ozonation process, reaching 87.30% of the ozone utilizing ratio. However, the residual ozone was measured as 0.116 mg/L after the main ozonation process, which was 71.00% of the ozone utilizing ratio. Although the excellent removal rate occurred in the main ozonation contact tank, the pre-ozonation process was more preferable to the main ozonation process for the ozonation utilizing ratio under the optimal dosage.

**Fig. 2. Variation of turbidity, COD\textsubscript{Mn} and NH\textsubscript{3}–N in the raw water and effluent.**

**Fig. 3. Effect of ozone dosage on the removal of COD\textsubscript{Mn} and NH\textsubscript{3}–N.**
3.3. Efficiency evaluation of each treatment process

3.3.1. Removal efficiency of turbidity

To evaluate the removal efficiency of the pre-ozonation and O3/BAC processes in the cold period, turbidity, COD$_{Mn}$, NH$_3$-N, pH, and alkalinity were selected to represent the physical and organic characteristics of the treated water. The water quality after the pre-ozonation and O3/BAC process is depicted in Fig. 4. The turbidity was reduced from 17.21 and 2.85 to 0.35 NTU, with a decrease of 83.44% after the pre-ozonation process and 87.72% after the O3/BAC process. It indicated that the pre-ozonation process promoted the elimination of turbidity. This is perhaps because it can increase the contents of organic substances with oxygen-containing functional groups (e.g., carboxylic acid) in water to form polymers with hydrolysate of metal salts and calcium salts. These polymers can lower the electrostatic interaction of natural organic matter (NOM) on the inorganic particle surface and trigger the polymerization of dissolved organic substances to form poly-electrolytes. These substances can serve as adsorption bridge and destabilize high-stability algae and produce co-precipitation [26,27]. The further treatment of the O3/BAC process resulted in the turbidity of treated water meeting the drinking water standard. Furthermore, compared with the raw water, the turbidity was completely removed with a value of 97.97%. This treatment not only reduced the suspended pollutants and the addition amount of coagulant but also increased the lifetime of the involved equipment.

3.3.2. Removal efficiency of COD$_{Mn}$ and NH$_3$-N

COD$_{Mn}$ usually represents the organic property of the studied water. As seen from Fig. 4, the value of COD$_{Mn}$ in raw water was 6.4 mg/L, which was evidently over the drinking water standard (<3 mg/L). However, the COD$_{Mn}$ reduced by 50.32% and 84.84% after the pre-ozonation and the O3/BAC process, respectively. Therefore, it is evident that organic matters are mainly degraded in the O3/BAC process. The COD$_{Mn}$ value reduced from 6.4 mg/L to 0.97 mg/L, indicating that COD$_{Mn}$ of the treated water could meet the current drinking water standard. In the advanced treatment process, the oxidation of O$_3$ plays an important role, which can produce ozone and hydroxyl radical (·OH). These oxidants can quickly degrade organic matter and oxidize them into small molecules.

NH$_3$-N is another important parameter used to appraise the degree of water pollution, which is primarily derived from the discharge of domestic sewage, industrial effluents, and agricultural wastewater [28]. It is usually difficult to fully eliminate from the water and a high concentration of NH$_3$-N tends to cause eutrophication [29]. As seen from Fig. 4, the removal efficiencies of NH$_3$-N were 9.80% and 64.29% after the precipitation and O3/BAC treatments, respectively. Compared with the O3/BAC process, the treatment effect of NH$_3$-N in the pre-ozonation process was poor with a difference of 54.49%. NH$_3$-N was mainly removed in the O3/BAC process. The content of NH$_3$-N in the effluent was 0.4 mg/L, which was less than the drinking water standard (<0.5 mg/L). Therefore, the Songhuajiang River water can reach the current drinking water standard through the upgraded treatment.

3.3.3. Removal efficiency of pH and alkalinity

Alkalinity and pH are also significant water quality parameters, which were monitored during the O3/BAC treatment process. Fig. 4 shows the variation of alkalinity and pH in the raw water, pre-ozonation, and O3/BAC units. Alkalinity and pH showed an evident downtrend after the pre-ozonation and O3/BAC treatments. The pH value was reduced from 7.53 to 6.8, while the alkalinity value was reduced from 65 to 52. This is because some organic acids are generated for the O$_3$ oxidation, which causes a decrease in the pH value. However, the ozonation capacity, organic pollutant properties, and even microbial activity are all related to the variation of pH and alkalinity. Their low values are not beneficial for the O3/BAC process. Accordingly, control of pH and alkalinity in the O3/BAC process also plays an important role in removing pollutants.

3.3.4. Removal efficiency of UV$_{254}$, THMFP and TOC

For deep purification of drinking water, much attention has been given to the removal of natural organic matter such as macro-molecule humic acid and fulvic acid, which can easily react with active chlorine to generate halogenated carcinogens [30,31]. UV$_{254}$ can be used as an alternative parameter for some indexes, such as TOC, dissolved organic carbon, and precursor of THMs [32]. It is an important parameter to measure organic substances in water. The UV$_{254}$ variation in each treatment unit is shown in Fig. 5.

As depicted in Fig. 5, the average UV$_{254}$ value of raw water was 0.119 cm$^{-1}$. After the O3/BAC process, the removal rate reached 87.39% with the UV$_{254}$ value decreasing to 0.015 cm$^{-1}$. The removal efficiency of UV$_{254}$ was 32.77% by the pre-ozonation process, 63.03% by the sand filtration process, and 87.39% by the O3/BAC process. In contrast to the pre-ozonation process, the removal efficiency of the
subsequent O_3/BAC process was higher than that of the pre-ozonation process with a difference of 54.62%. The UV_{254} can be drastically eliminated by the O_3/BAC process. Since UV_{254} represents organic substances with an aromatic ring structure or conjugated double bond, it can reflect the concentration of precursor of THMs. It is reported that ozone can easily react with C=C in organic substances [33]. It destroys the benzene ring and causes the aromatic property of organic matter to reduce or disappear. Therefore, the O_3/BAC process not only has high-efficiency for the removal of the trihalomethane precursor but also significantly reduces the content of organic matter in water.

DBPs have been a concern in the water supply and processing field. Especially, there is global concern regarding trihalomethane problems [34,35]. The components of NOM which can react with chlorine to generate THMs are identified as trihalomethane precursors. These precursors are usually determined by the THMFP to represent the content. The variation of THMFP in each treatment unit is shown in Fig. 6.

As illustrated in Fig. 6, the content of THMFP in raw water was 347 μg/L, which was eliminated by the pre-ozonation process with a removal rate of 38.9%. Although a part of THMFP can be removed by coagulation and precipitation, the elimination capacity is limited. For example, when the precipitation water passed through the filter tank, the concentration of THMFP increased with a removal rate of 36.6%. This may be attributed to the accumulation of algae and other organic matter in the filter material of the filter tank, since algae is also a kind of trihalomethane precursor [36,37]. Furthermore, the main ozonation process had a dominant removal effect on the THMFP. The removal rate reached 71.76% with the value reducing from 347 to 98 μg/L. However, the removal effect of activated carbon on the THMFP was also limited, because its removal by activated carbon mainly depends on its adsorption. The adsorption capacity of activated carbon decreases with long term use, resulting in poor removal efficiency. The THMFP showed an average decrease of 78.67% from raw water to the carbon-sand filter treated water. Thus, the trihalomethane precursors in raw water can be effectively eliminated by the O_3/BAC process.

Furthermore, THMFP is also related to the variation of TOC after the ozonation oxidation. The change in TOC can reflect the state of THMFP to some extent since some dissolved organic matters are the primary components of the trihalomethane precursors. The content variation of TOC in each treatment unit is presented in Fig. 7. The elimination of TOC exhibited a steady increase with a removal rate of 18.6% after the pre-ozonation process and 72.09% after the O_3/BAC process. Moreover, the content of THMFP accounted for 8.07% of the TOC, while the proportion was reduced to 6.17%. This result indicated that a portion of trihalomethane precursors had indeed been eliminated from the water after the O_3/BAC process.

The detectable DBPs in the effluent are listed in Table 3. These detectable DBPs all reached the requirement of “Standards for drinking water quality” (GB5749-2006). Among them, the content of the high-profile trichloroacetic aldehyde was 0.004 mg/L, which reduced by 60% in comparison with the drinking water standard (0.01 mg/L). Moreover, the contents of common trichloromethane, trichloroacetic acid, and dichloroacetic acid also decreased by 91.67%, 93%, and 74%, respectively. The other DBPs, especially those containing bromine atoms generated by the ozonation oxidation, were all below the detection limit. The production of DBPs was under good control through the treatment of the O_3/BAC process. To sum up, the precursors of DBPs can be effectively eliminated by the O_3/BAC process in the Songhuajiang River water, and also the content of the DBPs meets the national drinking water standard.

3.4. Stable operation of O_3/BAC process

As mentioned above, the water quality deterioration of the Songhuajiang River usually occurred in the frozen period, increasing the treatment difficulty. The upgraded
O3/BAC process can significantly alleviate this problem. The turbidity, variation of the organic matter and even the content of trihalomethane precursors in the cold period can all be effectively removed through the upgraded O3/BAC process, and the effluent quality can meet the domestic drinking water standard. To evaluate the stable operation effect of the O3/BAC process, stable running of the pilot-scale test for about three months (October 2018–March 2019) was investigated during the frozen period of the water plant (Figs. 8–11). In this section, the parameters of turbidity, chromaticity, CODMn, and NH₃–N were selected to appraise the water quality.

The turbidity variation during the stable operation is illustrated in Fig. 8. It can be seen from Fig. 8 that the turbidity of raw water and pre-ozonation effluent both fluctuated in waveform during the frozen period, while the effluent turbidity was stable after the subsequent treatments. In particular, the turbidity value remained unchanged for the carbon filter effluent. The removal rate of turbidity after the upgraded O3/BAC process was more than 95%. The effluent turbidity was about 0.2 NTU, indicating that the effluent met the threshold limit value (1 NTU) of “Standards for drinking water quality” (GB5749-2006).

Chromaticity is caused by the water-soluble humus, organic or inorganic substances, and reflects the apparent pollution status of water. The chromaticity variation during the stable operation is depicted in Fig. 9, which was evidently similar to the turbidity variation. The chromaticity was mainly removed in the sand filtration process and the O3/BAC process with a decrease of 71.05% and 93.16%, while the treatment efficiency of the pre-ozonation process was poor with a removal rate of only 7.89%. Chromaticity was primarily eliminated in the O3/BAC process. Moreover, the effluent chromaticity was stable, with an average value of 3 PCU during the operation of the system. This satisfactorily meets the threshold limit value (15) of “Standards for drinking water quality” (GB5749-2006).

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Table 3
List of detectable DBPs in the effluent

<table>
<thead>
<tr>
<th>Disinfection by-products</th>
<th>Structural formula</th>
<th>Content (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloromethane</td>
<td><img src="image" alt="Trichloromethane" /></td>
<td>0.005</td>
</tr>
<tr>
<td>Trichloroacetic aldehyde</td>
<td><img src="image" alt="Trichloroacetic aldehyde" /></td>
<td>0.004</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td><img src="image" alt="Trichloroacetic acid" /></td>
<td>0.007</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td><img src="image" alt="Dichloroacetic acid" /></td>
<td>0.013</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td><img src="image" alt="Bromodichloromethane" /></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td><img src="image" alt="Dichloromethane" /></td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Tribromomethane</td>
<td><img src="image" alt="Tribromomethane" /></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td><img src="image" alt="Dibromochloromethane" /></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Cyanochloride</td>
<td><img src="image" alt="Cyanochloride" /></td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>2,4,6-Trichlorophenol</td>
<td><img src="image" alt="2,4,6-Trichlorophenol" /></td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>
the frozen period. The average concentration of COD$_{mn}$ in raw water was 5.71 mg/L, while the removal efficiency reached 4.03% after the pre-ozonation, 50.09% after the main ozonation, and 88.27% after the O$_3$/BAC process. Although the COD$_{mn}$ exhibited a large fluctuation at some point, the COD$_{mn}$ of the effluent remained stable. The average COD$_{mn}$ value was 0.67 mg/L in the effluent, which meets the threshold limit value (3 mg/L) of “Standards for drinking water quality” (GB5749-2006). In other words, the modified process has a good removal effect on the organic matter in water.

The NH$_3$–N variation during the stable operation is presented in Fig. 11. As seen from Fig. 11, the fluctuation of NH$_3$–N in each treatment unit was severe, especially in the initial stage of the system. The average concentration of NH$_3$–N was 1.58 mg/L in raw water. However, the value increased by 13.29% after the pre-ozonation process. This is because the organic nitrogen was oxidized into NH$_3$–N via O$_3$, which further caused the increase in NH$_3$–N content after treatment by the pre-ozonation process. Through the subsequent O$_3$/BAC process, the NH$_3$–N content was drastically reduced by an average of 72.78%, especially by activated carbon filtration. This was mainly due to the combination of activated carbon adsorption and microbial degradation. Furthermore, the biological activated carbon column also had a strong impact load resistance for the NH$_3$–N removal, which was similar to the previous report [38]. As seen from Fig. 11, the variation of NH$_3$–N in the effluent was gentle with an average value of 0.43 mg/L, indicating that NH$_3$–N content was also in accordance with the threshold limit value (0.5 mg/L) “Standards for drinking water quality” (GB5749-2006).

In summary, the water quality of the Songhua River can meet the current drinking water standard through the upgraded O$_3$/BAC treatment. The major water

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**Fig. 8. Turbidity variation during stable operation.**

**Fig. 9. Chromaticity variation during stable operation.**

**Fig. 10. COD$_{mn}$ variation during stable operation.**

**Fig. 11. NH$_3$–N variation during stable operation.**
quality indexes also showed no great fluctuations after the modified system ran stably for about three months.

4. Conclusions
In the pilot-scale study, the upgraded O3/BAC process was utilized to evaluate the raw and treated water quality of the Songhuajiang River in a water plant in Harbin City. The results showed that the Songhuajiang River water exhibited a high content of turbidity, COD$_{Mn}$, and NH$_3$–N, especially in the frozen period. This resulted in standard water quality via conventional treatment. However, the O3/BAC process was demonstrated as an appropriate technology for the removal of these pollutants from treated water. The optimal ozone dosage in pre-ozonation was 1.0 mg/L with ozonation utilizing ratio of 87.30%, while the optimal ozone dosage of the main ozonation was 0.4 mg/L with ozonation utilizing ratio of 71.00%. Moreover, the average removal rates of turbidity, COD$_{Mn}$, NH$_3$–N, UV$_{254}$, TOC and THMFP in the effluent after the O3/BAC process were 97.97%, 84.84%, 64.29%, 87.39%, 72.09% and 78.67%, respectively. Importantly, the deuterogenic DBPs in the effluent were all under good control after treatment by the O3/BAC process. These typical indexes in the effluent all reached the current required standard for drinking water quality (GB5749-2006).

Furthermore, after the stable operation of the system for about three months, the whole treatment still maintained a good purification effect for the Songhuajiang River water. The effluent met the current drinking water standard. Moreover, the system showed no great fluctuations throughout the stable running period.

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References