Comparison of $O_3 +$ GAC, $O_3 + H_2O_2 +$ GAC, and GAC unit operation on natural organic matter and taste and odor causing compounds removal using a pilot plant study

Hanbai Park, Tae-Yul Kim, Dalsik Woo and Yong-Sik Cho

ABSTRACT

Removal of natural organic matter (NOM) and taste and odor problems in drinking water are a sensitive issue in municipal water treatment plants. This study investigated the effectiveness of ozone ($O_3$) + granular activated carbon (GAC), $O_3 +$ hydroperoxide ($H_2O_2$) + GAC, and GAC processes using a pilot scale plant to remove NOM and geosmin ($50 - 1,000$ ng/L), and 2-methylisoborneol (2-MIB: $50 - 300$ ng/L). In the $O_3 +$ GAC process, NOM-related parameters showed an average of 52% dissolved organic carbon (DOC) removal from 2 mg/L DOC influent, 99.3% haloacetic acids (HAAs) removal from 0.097 mg/L HAAs influent, and 100% removal from 0.05 mg/L bromide influent. Taste and odor removal rates were 94–100% for geosmin and 87–100% for 2-MIB. The $O_3 + H_2O_2 +$ GAC process removed an average of 55% DOC, 99.7% HAAs, 100% bromate, 94–100% geosmin, and 93–100% 2-MIB. The GAC process removed 46% DOC, 98.3% HAAs, 100% bromate, 83–100% geosmin, and 81–100% 2-MIB. Based on a comparison of the efficiencies and an economic analysis, the $O_3 + H_2O_2 +$ GAC process was determined to be the optimal system for removing NOM and taste and odor compounds.

Key words | advanced oxidation processes (AOPs), GAC, geosmin, hydrogen peroxide, NOM, 2-MIB

INTRODUCTION

Natural organic matter (NOM) and taste and odor problems in municipal water treatment plants have been significant issues over the past few decades. While conventional water treatment processes can control the majority of water contaminants, such as organic chemical and heavy metals, water contaminants such as pharmaceutical residue, cyanotoxins, geosmin and 2-methylisoborneol (MIB) from blue algae, and water pathogens cannot be completely removed by these processes. Westerhoff et al. (2005) conducted a survey of more than 800 water utilities in the United States and Canada and found that 16% of utilities experienced serious taste and odor problems, and that these utilities spent approximately 4.5% of their total budget in attempts to control these problems. In South Korea, algae blooms usually occur during the summer to fall; in August, 2014, during the algae bloom in Paldang Dam, the geosmin concentration reached 1,131 ng/L (Lee & Kim 2014).

Lalezary et al. (1986) reported that conventional water treatment technologies, consisting of breakpoint pre-chlorination, coagulation, sedimentation, and post-chlorination, are not effective in removing geosmin and MIB from potable water to below its odor threshold of 10 ng/L. Common technologies used to remove taste and odor compounds (TOCs) include activated carbon, advanced oxidation processes (AOPs), chlorination, and biofiltration (Lundgren et al. 1988; Westerhoff et al. 2006; Srinivasan & Sorial, 2011). A standard system is to use activated carbon treatments for taste and odor events (Srinivasan & Sorial, 2011); however, due to the difficulty of removing TOCs, activated carbon cannot completely remove them.

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Previous studies have suggested that ozonation could reduce the formation potential of hazardous chlorination by-products such as trihalomethanes (THMs), and haloacetic acids (HAAs), by oxidizing their precursor compounds (Kim et al. 1997; Collivignarelli & Sorlini 2004; Ham et al. 2012). Nalinakumari (2004) reported a 2-MIB removal of 70–90% at an ozone dose of 1.5 mg/L, with geosmin oxidation being on average 15% higher than 2-MIB oxidation. Liang et al. (2007) reported removal rates of 61.1, 94.9, and 99.9% at respective pH values of 5, 7, and 9 after 20 min for geosmin at 400 ng/L and ozone at 0.35 mg/L.

Currently, the use of O3, combined with technologies such as H2O2 and UV light, is known to be effective. Collivignarelli & Sorlini (2004) proved that supplying 1.5–3 mg O3/L using a low-pressure lamp (5,000–6,000 J/m2) completely removed geosmin and MIB. Rosenfeldt et al. (2008) then conducted experiments using 7.2 mg H2O2/L supplied with low and medium-pressure lamps (1,000 J/m2) and obtained more than a 70% removal of geosmin and MIB, with better removal found with the medium-pressure lamps. Since activated carbon filtration and oxidation filtration are effective methods for removing geosmin and 2-MIB, the combination of these two should be effective for improving the removal performance.

This study is different from existing ozonation studies in that a pilot plant scale systems is used (O3/GAC, O3/H2O2/GAC, and GAC) and each unit is then compared to determine the removal efficiencies of NOM and TOCs.

**MATERIAL AND METHODS**

**Material**

A pilot plant was constructed to investigate three processes (O3/GAC, O3/H2O2/GAC, and GAC) using sand-filtered water as the source water to treat NOM and TOCs. The experiment was conducted over a 6-month period, including the summer, fall, and winter from August to December in 2014. Analyses were performed based on the sand-filtered water and treated water for each unit process. The granular activated carbon (GAC) used in these experiments was Noritz GAC 1240 (USA). The GAC specifications were as follows: fresh 12 mesh (1.70 mm) × 40 mesh (0.425 mm) GACs having a particle diameter (log mean) of 1.1 mm and a bed density of 0.48 g/cm3. The GAC was backwashed for 12 days before use, with the backwashing time designed as the turbidity over 0.3 nephelometric turbidity units (NTU) of the treated water captured. H2O2 of 35% purity was purchased from Daeyoung Chemical (South Korea). Characteristics of the raw water entering the pilot plant during the test period are shown in Table 1.

**Pilot plant**

The pilot plant was constructed as shown in Figure 1. Each process was designed to treat 30 m3/day. Three systems (O3 + GAC, O3/H2O2 + GAC, and GAC) were independently operated to treat the taste and odor and organic compounds. The specifications and operation conditions of the pilot plant are shown in Table 2. Process 1 was a combined ozonation and GAC system. In this process, ozone was supplied using a porous pipe in the concentration range of 0.5–2.5 mg O3/L. The ozone contact time was

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analytical value</th>
<th>Unit</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>10–11</td>
<td>°C</td>
</tr>
<tr>
<td>pH</td>
<td>7.01–7.82</td>
<td></td>
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<tr>
<td>Turbidity</td>
<td>0.2–0.4</td>
<td>NTU</td>
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<tr>
<td>Alkalinity</td>
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<td>mg/L</td>
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<td>TOC</td>
<td>1.9–2.3</td>
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<td>Dissolved organic carbon</td>
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<td>Geosmin</td>
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<td>2-MIB</td>
<td>0–16</td>
<td>ng/L</td>
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<td>THMs</td>
<td>0.1–0.8</td>
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<td>HAAs</td>
<td>0.095–0.1</td>
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<td>UV254</td>
<td>0.045–0.057</td>
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<td>1</td>
<td>TCU</td>
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<tr>
<td>NH3-N</td>
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<td>mg/L</td>
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<tr>
<td>NO2-N</td>
<td>0.3–0.4</td>
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<td>Total coliforms</td>
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<td>MPN/100 mL</td>
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<tr>
<td>Bromide</td>
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<td>mg/L</td>
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<tr>
<td>KMnO4</td>
<td>1.52–1.71</td>
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<td>Suspended solids</td>
<td>16–21</td>
<td>mg/L</td>
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15.5 min, and the ozone transfer efficiency was determined using Equation (1).

\[
\text{Ozone transfer efficiency} = \frac{(Q_{\text{feed}} - Q_{\text{out}})}{Q_{\text{feed}}} \quad (1)
\]

where \(Q_{\text{feed}}\) is feed gas ozone, \(Q_{\text{out}}\) is dissolved ozone in water. Ozone transfer efficiency from gas to water was 92% using 10wt% ozone using high purity oxygen. It was automatically monitored using OZM 7000 from Ozone Tec, South Korea. The empty bed contact time (EBCT) in the GAC system was 15 min. To compare the efficiency with Process 1, Process 2 was designed using AOPs by combining \(O_3\) and \(H_2O_2\) with the GAC system. Hydrogen peroxide was fed from a diluted aqueous solution in the range of 0.2–1 mg \(H_2O_2/L\). The \(H_2O_2\) to \(O_3\) ratios were varied from 0.3:1 to 3:1 to determine the best performance in the advanced ozonation process (Liang et al. 1999). Several studies have shown that an optimum \(H_2O_2\) dose can reduce bromate formation (Siddiqui et al. 1994; Liang et al. 1999; White 1999). Here, \(H_2O_2\) was injected at four different places in order to estimate the highest \(O_3\) solubility. The GAC EBCT was 15 min. Note that Process 3 only used the GAC, as this process was constructed to compare the efficiencies of Processes 1 and 2.
Spiking test

Geosmin and 2-MIB spiking tests were conducted as no high concentrations of geosmin and 2-MIB were observed during the experimental period (Table 1). The test samples were prepared by diluting sand-filtered water obtained from the Gwangju Water Treatment Plant, South Korea with geosmin and 2-MIB (100 μg/mL methanol) obtained from Supelco (USA); the geosmin concentrations were 100, 500, and 1,000 ng/L, and the 2-MIB concentrations were 100, 200, and 300 ng/L. These concentrations were set according to the high concentrations of geosmin observed during the summer 2014 in South Korea (Lee & Kim 2014).

Analysis

Drinking water quality analyses were conducted under three different conditions: sand-filtered water, O3 or O3 + H2O2 treated water, and GAC treated water. Daily measured analysis items included pH, temperature, alkalinity, and turbidity. Weekly measured items were geosmin, 2-MIB, THMs, HAAs, KMnO4 (potassium permanganate), total organic carbon (TOC), dissolved organic carbon (DOC), suspended solids (SS), color, NH3-N, NO3-N, and BrO3−. For the geosmin and 2-MIB analyses, a fast stir bar sportive extraction combined with gas chromatography (GC; 6890N, Agilent, USA)/mass spectrometry (MS; 5973N, Agilent, USA) system was used. A purge-trap combined with GC/MS (USEPA standard method 6010D) was used to measure THMs, and HAAs were measured using GC/MS (GC; 6890N, Agilent, MS; 5973N, Agilent, USA). KMnO4 was measured using USEPA Standard Method 7D. TOC, DOC, and UV254 were measured using USEPA Standard Method 415.5 using a Shimadzu V-series TOC analyzer (Japan). Color was measured using a color-visual comparison method (USEPA Standard Method 2120). SS was measured using a total solid dried weight method (USEPA Standard Method 2540B). Nitrate nitrogen and ammonium nitrogen were analyzed using UV visible spectrometry (USEPA Standard Method 4500). Bromate was analyzed using ion chromatography (USEPA Standard Method 326).

RESULTS AND DISCUSSION

Effects of NOM removal

The presence of organic matter in raw water negatively affects the ability of the ozone and GAC system to remove geosmin and 2-MIB. In addition, high NOM and DOC can generate disinfection by-products (DBPs) such as THMs and HAAs, which are known cancer-causing materials. The United States Environmental Protection Agency (2003) set the maximum contaminant levels for total THMs at 0.08 mg/L and HAAs at 0.06 mg/L, based on annual averages.

In this study, 12 different analysis items (THMs, HAAs, KMnO4, TOC, DOC, UV254, SS, color, NH3-N, NO3-N, BrO3−, and total coliform) were analyzed in terms of organic compound removal and to determine the effect of ozonation and advanced ozonation processes. During the 6 months of operation, four main parameters (DOC, HAAs, BrO3−, UV254) were determined as being significant factors; other analytical items from the sand-filtered water were found in extremely small quantities, incurring negligible changes. All analytical items are shown as average values in Table 3. During the pilot plant operation, the O3 dosages were varied from 0.5 to 2.5 mg/L, while the data for organic

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Operating parameters of the pilot plant</th>
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<tbody>
<tr>
<td>Process</td>
<td>Unit process</td>
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<td>Process 1</td>
<td>O3</td>
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<td>Process 2</td>
<td>O3 + H2O2</td>
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<td>Process 3</td>
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matter removal were selected at dosages of 1 mg O₃/L and 1 mg O₃/L: 0.42 mg H₂O₂/L.

Effects of DOC

DOC, especially biodegradable organic carbon (BDOC), is a significant parameter used to determine the formation potential of chlorination DBPs such as THMs and HAAs (Siddiqui et al. 1997). This study evaluated DOC values during the 6 months of pilot plant operation using O₃, O₃ + H₂O₂, and GAC. The results are shown in Figure 2.

Figure 2 presents the DOC comparison study for O₃, O₃ + H₂O₂, and GAC. In Process 1, the effect on DOC reduction in O₃ treated water was 16%, and reached 52% after GAC treatment. In Process 2, the DOC removal from the O₃ + H₂O₂ treated water was 19%, and the total DOC removed from O₃ + H₂O₂ + GAC was 55%. In Process 3, a DOC removal of 46% was observed. These results indicate two significant factors: O₃ + H₂O₂ provides only a 3% improvement over O₃ in terms of DOC removal; Process 2 provides the greatest removal efficiency among the three processes. These results are in agreement with Kim et al. (1997), who indicated that the O₃ + BAC process can increase the elimination efficiency of DOC, which is about 20% by biodegradation.

Effects of HAAs

DBPs are formed with NOM that is not removed during water treatment as it comes in contact with a disinfectant. In the water treatment process, common DBPs are THMs and HAAs, both of which pose regulatory and health concerns (Bruce et al. 2002). The release of algal organic matter (AOM), extracellular or intracellular, produces chloramines and haloacetaldehydes in drinking water systems, as AOM is not removed by common treatment techniques (Fang et al. 2010). In this study, HAAs were investigated during pilot plant operation. In Figure 3, HAAs concentrations from the sand-filtered water using as raw water are not much varied and contain an average of 0.097 mg/L of HAAs. Raw water was not contacted with any disinfection process before ozonation.

After the O₃ process, the HAAs removal was 38 and 99.3% after O₃ + GAC treatment. In Process 2, the HAAs removal was 48% during the O₃ + H₂O₂ process and 99.7% after the O₃ + H₂O₂ + GAC process. In Process 3,
the HAAs removal averaged 98.3%. Based on these results, the O$_3$ + H$_2$O$_2$ + GAC process was found to remove the greatest amount of HAAs at a dosage of 1 mg O$_3$/L: 0.42 mg H$_2$O$_2$/L. Therefore, two significant findings are, as follows: the O$_3$ + H$_2$O$_2$ process removed 10% more HAAs than the O$_3$ process, and that HAAs concentrations around 0.1 mg/L can almost be completely removed by the GAC process. These results have been confirmed by several studies. AOPs can potentially be used to minimize the formation of DBPs (Zhou & Smith 2002; Chin & Bérubé 2005), and the formation potentials of THMs, HAAs, and chloral hydrate were reduced by as much as 70–80% using a UV-AOP treatment (Chin & Bérubé 2005).

**Effects of bromate (BrO$_3^-$)**

Bromide (Br$^-$) ions in water are known to produce BrO$_3^-$ by reacting with OH$^-$ and molecular O$_3$ during the ozonation process. The conversion of bromide to bromate is usually between 10 and 50% during ozonation (Song et al. 1996). Huang et al. (2004) further indicated that the ozonation of water containing bromide will produce brominated organic compounds such as CHBr$_3$, DBAA, 2, 4-DPB, DBAC, and DBAN, the formation threshold levels of which were 0.15 mg/L, 0.25 mg/L, 0.25 mg/L, 0.1 mg/L, and 0.45 mg/L, respectively. At a bromide level of 50 µg/L, only 35–50% of MTBE could be eliminated by the AOP (O$_3$/H$_2$O$_2$) process without exceeding the current drinking water standard of bromate (10 µg/L) (Guntén & Oliveras 1997). As such, it is posited that the quick decay of O$_3$ in the H$_2$O$_2$/O$_3$ hybrid process and catalytic ozonation may inhibit the formation of BrO$_3^-$, as molecular O$_3$ is known to play an important role in the oxidation process from Br$^-$ to BrO$_3^-$ (Zhang et al. 2008). In this experiment, bromate formation from bromide and the removal of bromate in O$_3$ + GAC, O$_3$ + H$_2$O$_2$ + GAC, and GAC systems was evaluated (Figure 4).

The average concentration of bromide from the influent was observed to be 0.05 mg/L, which is less than the Korea drinking water standard of 0.1 mg/L. However, though bromide exists in the source water, bromate formation is positive in sanitation processes (Song et al. 1996). In Process 1, an average of 0.02 mg BrO$_3^-$ /L was formed after ozonation, which was completely removed after the GAC process. In Process 2, an average of 0.011 mg BrO$_3^-$ /L was formed through the O$_3$ + H$_2$O$_2$ process. After the GAC process, less BrO$_3^-$ was removed. In Process 3, the GAC removed all BrO$_3^-$ from raw water inclusion. Therefore, according to these results, 18% less bromate was formed in the O$_3$ + H$_2$O$_2$ process than in the O$_3$ process.
**Effects of specific UV absorbance**

The specific UV absorbance (SUVA) is a good indicator for classifying NOM characteristics using UV254/DOC × 100 (Weishaar et al. 2003). When the SUVA values range from 4 to 5, the DOC is comparatively hydrophobic; when SUVA is less than 3, the DOC is composed of hydrophilic low-molecular-weight organic matter (Ghernaout 2014). This experiment was conducted in order to determine the effect on SUVA values for classifying NOM characteristics (Figure 5).

Figure 5 presents the SUVA values based on UV254 and DOC results during the pilot plant operation. The average SUVA from the influent was 2.53 mg/L m; a SUVA value less than 2 mg/L m does not affect water quality during ozonation. In Process 1, the average SUVA value calculated was 1.53 mg/L m after the O3 process, with the GAC process reducing the average SUVA value by 97%. In Process 2, the SUVA value obtained by the O3 + H2O2 treatment was 1.2 mg/L m, with GAC removing 98% of the SUVA value. In Process 3, the average SUVA value was reduced by 91%. Overall, the O3 + H2O2 process provides a more effective removal of organic matter in drinking water than the O3 process. Similar results revealed that the removal efficiency of UV254 was 45.7% when using the rapid sand filtration process, 57.6% by the combined GAC process, 81.5% by the combined O3/BAC process, and 94% by the combined ultrafiltration-nanofiltration (UF-NF) membrane process (Yang et al. 2010).

**Effects of geosmin and 2-MIB removal**

This experiment was conducted to determine the geosmin and 2-MIB removal efficiencies for different concentrations and dosage changes during the three processes (O3 + GAC, O3 + H2O2 + GAC, and GAC) at an ambient temperature of 10–11°C during October through November (i.e., the winter season) in South Korea. Owing to the taste and odor control before sand filtration by powdered activated carbon in the Gwangju Water Treatment Plant, geosmin was artificially spiked at concentrations of 50, 100, 300, 500, 700, and 1,000 ng/L. Similarly, 2-MIB concentrations were spiked at 300, 250, 200, 150, 100, and 50 ng/L.

**Geosmin and 2-MIB removal using O3 + GAC**

The removal of geosmin and 2-MIB using O3 + GAC has been actively investigated since the 1980s, with several studies confirming its efficiency. Notably, Lundgren et al. (1988) removed more than 95% of geosmin and MIB using 7 mg/L O3 in 50 ng/L of MIB and geosmin water. Bruce et al. (2002) reported removal rates of 97% at 12 min and 20 min—with 81% removal in the first minute—at an initial geosmin concentration of 100 ng/L and ozone dose of 2.5 mg/L. More recently, Elhadi et al. (2004) investigated the removal of geosmin and 2-MIB using O3 + GAC and obtained total geosmin removal rates ranging from 76 to 100%, and total 2-MIB removal from 47 to 100%. This current study evaluated the ability for a pilot-scale experiment using O3 + GAC to remove geosmin and 2-MIB. The experimental results are shown in Figure 6.

Geosmin removal using O3 was 40–100% at O3 dosages of 0.5–2.5 mg/L (Figure 6(a)). At 1,000 ng/L of geosmin, the suitable O3 dosage was 1.5 mg/L, resulting in a 60% geosmin removal efficiency. The least geosmin was adsorbed by GAC (39.4%) and provided a final concentration of 6 ng/L, satisfying our aim of <10 ng/L (Figure 6(b)). At a 700 ng/L geosmin concentration, a 1.5 mg O3/L dose was determined to be the finest, attaining a 62.3% removal
After treated by GAC, the geosmin concentration decreased to 5 ng/L, for a 99.3% removal efficiency (Figure 6(a)). For initial geosmin concentrations from 300 to 500 ng/L, the suitable O₃ dosage was 1 mg/L, resulting in removal efficiencies of 60.8% at 300 ng/L and 55.7% at 500 ng/L (Figure 6(a)). In the process using O₃ + GAC, geosmin removals were 98.6% at 300 ng/L and 97.3% at 500 ng/L. At initial concentrations of 100 ng/L and 50 ng/L, the suitable O₃ dosage was found to be 0.5 mg/L with geosmin concentrations of 55 ng/L at 100 ng/L and 23 ng/L remaining at 50 ng/L (Figure 6(a)). After the GAC process, 55 and 23 ng/L of geosmin were removed to below 10 ng/L (Figure 6(b)). Therefore, the finest O₃ dosages were determined to be 1.5 mg/L for 700 mg/L to 1,000 mg/L of geosmin, and 1.0 mg/L at 300 to 500 ng/L of geosmin. At concentrations below 100 ng/L of geosmin, the influent could be removed using the GAC itself.

Figure 7 shows the results of 2-MIB removal by the O₃ and O₃ + GAC processes. O₃ dosages of 0.5–2.5 mg/L removed 25–100% of the 2-MIB present (Figure 7(a)). Notably, a removal rate of 36.3% 2-MIB was observed at a 1.5 mg O₃/L dose for the 2-MIB concentration of 300 ng/L (Figure 7(a)). After the GAC treatment, 97% of 2-MIB was removed at a concentration of 9 ng/L (Figure 7(b)). At the initial 250 ng/L 2-MIB concentration, a 1.5 mg O₃/L dose was determined to be the finest, resulting in an initial O₃ removal rate of 43.6, and 97.6% after the GAC process (Figure 7). For 2-MIB concentrations of 200 and 150 ng/L, the suitable O₃ dosage was 1 mg/L, with corresponding O₃ removal rates of 57 and 48.7% and O₃ + GAC removal rates of 94.6 and 95%. At initial 2-MIB concentrations of 100 ng/L and 50 ng/L, the suitable O₃ dose was determined to be 0.5 mg/L, with O₃ removal rates of 55% and 60% and
O₃ + GAC removal rates of 100% and 100%, respectively. These results were then compared to the Ham et al. (2012) study, who reported that in ozone/GAC processes, a single ozone process had geosmin and 2-MIB removal rates of 60–80% for geosmin and 2-MIB concentrations of 500–50 ng/L. For both geosmin and 2-MIB, the combined O₃/GAC process displayed removal rates above 95%. These results shown here are similar to previous findings, though this study provided a greater concentrations range of both geosmin and 2-MIB and investigated various processes.

**Geosmin and 2-MIB removal using O₃ + H₂O₂ + GAC**

Currently developed or researched AOP technologies include O₃, H₂O₂, UV, and TiO₂. Among these technologies, this study investigated the well-developed O₃ + H₂O₂ + GAC process in a pilot-scale AOP construction for a drinking water treatment plant in Gwangju, South Korea. The results of this study are shown in Figure 8.

The results were obtained using O₃ + H₂O₂ + GAC and separately drawn O₃ + H₂O₂. Before this experiment, the ratio of O₃ + H₂O₂ was investigated in order to determine the optimized H₂O₂ dose. The experiment was conducted by varying the H₂O₂ ratio from 0.2 to 0.5 at a 1 mg O₃/L dose. The finest dosage was determined to be 0.42 mg H₂O₂/L for 1 mg O₃/L. Therefore, the ratio was 0.7 O₃:0.3 H₂O₂. By applying this ratio, the geosmin removal rates were 56–100% at an O₃ + H₂O₂ dose of 0.65–3.25 mg/L (Figure 8(a)).

The finest O₃ + H₂O₂ dosage at 1,000 and 700 ng/L of geosmin was determined to be 1 mg O₃/L + 0.42 mg H₂O₂/L, which resulted in respective removal efficiencies of 65 and 67%. The final geosmin concentrations were 6 ng/L at an initial geosmin concentration of 1,000 ng/L, and 5 ng/L at an initial geosmin concentration of 700 ng/L. For geosmin concentrations range of 500–300 ng/L, the finest O₃ + H₂O₂ dosage was 1 mg O₃/L + 0.42 mg H₂O₂/L, which resulted in removal rates of 67–70%. The final geosmin concentrations after GAC were 3 ng/L at 500 ng/L and 2 ng/L at 300 ng/L. At 100 ng/L and 50 ng/L geosmin concentrations, 0.7 mg/L O₃ + 0.3 mg/L H₂O₂ was provided final concentrations of 37–39 ng/L. After the GAC process, the remaining geosmin concentrations were in the range from 2 to 1 ng/L. These results confirm that the geosmin removal efficiencies improved by an average of 10–25% over that obtained using ozone alone.

In Figure 9, 2-MIB the removal rates obtained using O₃ + H₂O₂ was 34–100% at dosages of 0.5–2.5 mg O₃/L and 0.15–0.75 mg H₂O₂/L. At 300 ng/L and 250 ng/L of 2-MIB, the finest O₃ + H₂O₂ dosage was 1 mg O₃/L + 0.42 mg H₂O₂/L, which resulted in 2-MIB removal rates of 34% and 49%, respectively. From 50 to 200 ng/L of 2-MIB, a 0.5 mg O₃/L + 0.15 mg H₂O₂/L dose was determined as the finest, with the removal rate ranging from 50 to 64%. The final concentrations after the GAC process was below 10 ng/L of 2-MIB. These obtained results matched well with previous TOC research. For example, Westerhoff et al. (2006) conducted batch ozonation experiments to study the effect of ozone oxidation parameters such as pH, ozone, and H₂O₂ dosage, and water quality
parameters such as temperature and initial concentrations on the removal of MIB/geosmin. Their results showed that removal efficiencies for both MIB/geosmin increased with an increase in temperature, ozone dosage, pH, and H₂O₂ concentration. Koch et al. (1992) used O₃ dosages of 1, 2, and 4 mg/L with 0.2 mg H₂O₂:mg O₃ and improved the MIB removal efficiency by 20%.

**Geosmin and 2-MIB removal using GAC**

Although the GAC process is a common TOC treatment in drinking water treatment plants, the high input concentrations of TOCs cannot be controlled by the GAC treatment alone. In this experiment, the GAC process was investigated using a pilot plant scale and then compared with O₃ + GAC and O₃ + H₂O₂ + GAC. The results are shown in Figure 10.

After Process 3 (GAC), the remaining geosmin concentrations were 176 ng/L at 1,000 ng/L, 118 ng/L at 700 ng/L, 80 ng/L at 500 ng/L, 41 ng/L at 300 ng/L, 6 ng/L at 100 ng/L, and 1 ng/L at 50 ng/L (Figure 10(a)). These results indicate two significant factors: that the input geosmin range from 300 to 1,000 ng/L cannot be treated to below 10 ng/L using GAC itself, where input geosmin concentrations below 100 ng/L can be treated using only the GAC process. Therefore, there is no need to apply O₃ or O₃ + H₂O for input geosmin concentrations <100 ng/L. Further, at geosmin concentrations >100 ng/L, or where there is a high NOM concentration, GAC cannot reduce geosmin down to <10 ng/L.

For 2-MIB removal using the GAC process, the 2-MIB concentrations remaining were 57 ng/L at 300 ng/L, 44 ng/L at 250 ng/L, 32 ng/L at 200 ng/L, 21 ng/L at 150 ng/L, 13 ng/L at 100 ng/L, and 1 ng/L at 50 ng/L.

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**Figure 9** | 2-MIB removal percentages by (a) O₃ + H₂O₂ and (b) O₂ + H₂O₂ + GAC in Process 2.

**Figure 10** | (a) Geosmin and (b) 2-MIB removal percentages obtained by varying the initial concentrations ranges in Process 3 (GAC).
From these results, 2-MIB displayed a 20–30% lower removal efficiency than geosmin, and the input concentration of 50 ng/L 2-MIB was the only condition to have a satisfactory removal (<10 ng/L).

Overall, three processes were investigated by varying the geosmin (50–1,000 ng/L) and 2-MIB concentrations (50–300 ng/L). Comparing Process 1 to Process 2, it was observed that Process 1 delivered the best O₃ dosage of 1.5 mg/L for geosmin (1,000 ng/L) and 2-MIB (300 ng/L) removal, whereas Process 2 used a 1 mg O₃/L + 0.42 mg H₂O₂/L dosage for geosmin (1,000 ng/L) and 2-MIB (300 ng/L) removal. The results indicate that using hydrogen peroxide with ozone can deliver a 10–25% higher removal efficiency than using ozone alone. In the GAC process, in cases where there is less than 100 ng/L geosmin and 50 ng/L 2-MIB, these could be completely removed; here, the 300 ng/L geosmin and 100 ng/L 2-MIB were only partly removed. In other words, the GAC process cannot removed >300 ng/L of geosmin and 100 ng/L of 2-MIB to below our stated standard of 10 ng/L. In this study, the highest geosmin and 2-MIB removal efficiencies were observed when using O₃ + H₂O₂ + GAC for 50–1,000 ng/L of geosmin and 50–300 ng/L of 2-MIB.

Cost estimation of treatment processes

The operating cost of a 60,000 m³/day scale water treatment plant was estimated using the operating parameters from the pilot plant, based on the wattmeters of each process. The results are shown in Table 4. For the O₃ process, O₃ generation and pump electricity and oxygen purchasing costs were considered in order to calculate the total cost for a 1 ppm O₃ dosage. For the O₃ and H₂O₂ process, O₃ costs and H₂O₂ costs were added based on the ratio of 0.7 O₃ dose to 0.3 H₂O₂ dose. The GAC costs were determined based on the regeneration time per year. In the O₃ + GAC process, the total operating cost was estimated to be US$540,437 per year. In the O₃ + H₂O₂ + GAC process, the total operating cost was estimated to be US$528,497 per year. In the GAC process, the total operating cost was estimated to be US$381,411 per year; the GAC process is seen to be the most economical, though it could not remove over 300 ng/L geosmin and over 100 ng/L 2-MIB. Therefore, after considering the overall operational costs and odor removal rates, O₃ + H₂O₂ + GAC was recommended for construction for an advanced water treatment plant.

CONCLUSION

This study evaluated the performance of advanced O₃ processes using three processes for NOM and TOC compounds. The conclusion of the pilot-plant study into the processing characteristics of O₃ + GAC, O₃ + H₂O₂ + GAC, and GAC used in Gwangju, Korea is as follows:

- The O₃ + GAC process can remove 52% of the DOC at an initial concentration of 2 mg/L, 99.3% of HAAs at

### Table 4  Removal efficiencies of 12 water parameters by various treatment units

<table>
<thead>
<tr>
<th>Unit process</th>
<th>Cost estimation parameter</th>
<th>Operating cost (US$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃</td>
<td>Electricity cost</td>
<td>37,576</td>
</tr>
<tr>
<td></td>
<td>Oxygen cost</td>
<td>365,050</td>
</tr>
<tr>
<td></td>
<td>Total cost</td>
<td>402,626</td>
</tr>
<tr>
<td>O₃ + H₂O₂</td>
<td>Electricity cost</td>
<td>26,303</td>
</tr>
<tr>
<td></td>
<td>Oxygen cost</td>
<td>281,838</td>
</tr>
<tr>
<td></td>
<td>H₂O₂ cost + Electricity cost</td>
<td>82,545</td>
</tr>
<tr>
<td></td>
<td>Total cost</td>
<td>390,686</td>
</tr>
<tr>
<td>GAC</td>
<td>Regeneration cost</td>
<td>100,800</td>
</tr>
<tr>
<td></td>
<td>1 year regeneration</td>
<td>33,600</td>
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<td></td>
<td>3 year regeneration</td>
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<td></td>
<td>5 year regeneration</td>
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<tr>
<td></td>
<td>Transport cost</td>
<td>88,200</td>
</tr>
<tr>
<td></td>
<td>GAC replacement cost</td>
<td>176,400</td>
</tr>
<tr>
<td></td>
<td>Backwash operation cost</td>
<td>16,011</td>
</tr>
<tr>
<td></td>
<td>Total cost</td>
<td>381,411</td>
</tr>
</tbody>
</table>
an initial concentration of 0.097 mg/L, 100% of bromate at an initial bromide of concentrations of 0.05 mg/L, 94–100% of geosmin at a 50–1,000 ng/L, and 87–100% 2-MIB at 50–300 ng/L.

- The O₃ + H₂O₂ + GAC process provides almost the same removal rate of NOM and 10–30% higher geosmin and 2-MIB removal rates compared to the O₃ + GAC process.
- Although the GAC process is more economical than the O₃ + GAC and O₃ + H₂O₂ + GAC processes, it is unable satisfy the aim of reducing the final geosmin and 2-MIB concentrations to below 10 ng/L when there are high initial concentrations (700–1,000 ng/L of geosmin, 250–300 ng/L of 2-MIB).
- Based on the removal efficiencies and economic analysis, O₃ + H₂O₂ + GAC was determined to be the most efficient system for use in construction of an actual water treatment plant in Gwangju, Korea.

Since TOCs and NOM are common problems for drinking water treatment systems, this research would be helpful to establish guidelines to effectively control these contaminants and to operate ozone-related processes in municipal water treatment plants.

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