Improved mixing of hydrogen peroxide injection in advanced oxidation process treatment using computational fluid dynamics

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**Abstract**

The main issues with ozone-based advanced oxidation processes (AOPs) occur in the type of poor mixing, residual oxidizing agents, inadequate concentration control, and by-product formation. This study focused on improving the mixing effect of hydrogen peroxide by slightly modifying the existing injection facility by performing computational fluid dynamics (CFD) on the existing hydrogen peroxide injection system of the ozone-based AOP. CFD analysis showed that conventional diffuser systems were inefficient for mixing oxidizer and feed water. The mixing ratio was low since the momentum of the feed water could not be overcome by the hydrogen peroxide injection flow, and the length of the contact pipeline was not sufficient for the oxidizer to mix with the feed water. The problem could be overcome by increasing the number of diffusers to increase the injection flow of hydrogen peroxide. This study excluded dissociation and reaction between hydrogen peroxide and contaminants or scavengers, so further studies are needed.

**Keywords:** Advanced oxidation process; Computational fluid dynamics; Diffuser; Dispersion; Mixing; Hydrogen peroxide

1. Introduction

Advanced oxidation processes (AOPs) are considered to be attractive oxidation technologies to degrade natural organic matter, disinfection by-products (DBPs) precursors, and other non-degradable micropollutants and to disinfect pathogens [1–3]. Theoretically, AOPs can mineralize organic compounds to carbon dioxide and water, according to Eq. (1). AOPs have many options to select and combine oxidants such as ozone, hydrogen peroxide, photocatalyst, and electron beam to produce highly reactive ‘OH radicals [4–6].

\[ \text{R} - \text{H} + \text{OH}^* \rightarrow \text{H}_2\text{O} + \text{R}^* \]

AOPs used in a drinking water treatment plant can be classified into four groups: ozone-based processes (\text{O}_3/high pH, \text{O}_3/UV, \text{O}_3/H_2\text{O}_2, \text{O}_2/\text{Fe(II)}, \text{O}_2/\text{TiO}_2, \text{metal oxide catalyst}, \text{O}_2/ultrasound) [7]; photocatalytic process (H_2\text{O}_2/UV, \text{O}_3/UV/\text{H}_2\text{O}_2, \text{TiO}_2/UV, \text{H}_2\text{O}_2/\text{TiO}_2/UV, \text{O}_2/\text{TiO}_2/UV) [8]; the Fenton reaction-based processes (Fe^{2+}/\text{H}_2\text{O}_2, \text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{H}_2\text{O}_2) [9]; other processes which include ionizing radiation, electron beam technology [10]. Among them, ozone has been widely applied in water treatment since it is a strongly reactive and unstable allotrope of oxygen.

In Korea, the ozone-based AOP and ozone oxidation process are generally combined with the subsequent
adsorption or bio-adsorption processes in drinking water treatments as shown in Table 1 [11,12]. The application of advanced water treatment in Korea’s drinking water treatment plants is more than 43%, and granular activated carbon (GAC) or BAC are recommended to be positioned at the final process before post-disinfection. GAC processes have combined with ozone oxidation for improving bio-adsorption of macro organic compounds [13]. Eventually, a GAC turns into a BAC with both adsorption and biodegradation functions over operation times. Recently, GAC sandwich slow sand filtration (named FA – filtration adsorption in Korea), has been applied for removing taste and odor-causing compounds (2-MIB, Geosmin), DBP precursors, and emerging concern compounds [14,15]. Besides, only ozone oxidation before the BAC process was enhanced with other oxidants with UV or hydrogen peroxide to oxidize the emerging micropollutants.

Ozone was dosed with fine diffusers in the ozone contactors with 15–20 min of hydraulic retention time when ozone was first introduced into a water treatment plant. Recently, more than 70% of the ozone dose system has been injected using the side stream or full stream method into the feed pipeline linked to the ozone contact basin [16]. Also, most of the ozone retrofit project includes the injection system. The ozone dose was decided based on total organic carbon (TOC), T&O causing compounds, and water temperature. When ozone is used only for oxidants, ozone dose is controlled between 2 and 3 mg/L, and ozone dose is decreased by 25%–50% when combined with the other oxidant. AOP can be designed for the first time or modified to decrease by 25%~50% when combined with the other oxidant system. The ozone dose was decided based on total contaminant. AOP turns into a BAC with both adsorption and biodegradation functions over operation times. Recently, GAC sandwich slow sand filtration (named FA – filtration adsorption in Korea), has been applied for removing taste and odor-causing compounds (2-MIB, Geosmin), DBP precursors, and emerging concern compounds [14,15]. Besides, only ozone oxidation before the BAC process was enhanced with other oxidants with UV or hydrogen peroxide to oxidize the emerging micropollutants.

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Oxidizing agents used for ozone-based AOP of a water treatment plant should be selected in consideration of target compound removal, mixing efficiency, work safety, the convenience of O&M, and economics. The main issues in the AOP operation using an oxidizing agent are poor mixing, residual oxidizer, inadequate concentration control, and by-product formation, which might be resulted from the limitations in scaling up to actual facilities and lower operation rate less than design capacity [17]. The success of the AOP operation depends on the activation of the agent in water. Oxidation of contaminants by ozone has two pathways; direct oxidation and indirect oxidation for target microcontaminants shown in Fig. 1. ‘OH initiates ozone decomposition, and the initiation of ozone decomposition can be accelerated by adding hydrogen peroxide. This reaction is fast and important particularly when the ‘OH scavenger concentration is low in the water. It leads to the consumption of ozone and ‘OH, lowering the oxidation capacity of the system. A low concentration of hydrogen peroxide tends to be inactive, however, it can be a scavenger in high concentration to ozone. It is important to control the proper concentration of agents in treatment water. For that reason, rapid mixing and accurate injection are required to secure instantaneous contact between oxidizing agents and organics in water.

There have been many studies that evaluate the removal performance of contaminant using a laboratory experiment. They are indirect and qualitative approaches but they do not reflect actual conditions and give quantitative data such as mixing time or uniformity of agent. Moreover, the operating plant has a huge scale and the real testing experiment itself is risky and extensive. For that reason, the numerical experiment can be an alternative to predict mixing, mass transfer and contaminant removal in the oxidation process is fundamental for process development and scale-up [18]. Computational fluid dynamics is one of the parts of fluid mechanics and calculating numerical methods are solving

<table>
<thead>
<tr>
<th>Water resource</th>
<th>Combination processes</th>
<th>Capacity (m³/d)</th>
<th>Ozone dosage method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Han River</td>
<td>S/F → O₃ → BAC</td>
<td>1,950,000</td>
<td>2 mg/L, injector</td>
</tr>
<tr>
<td></td>
<td>S/F → H₂O₂/O₃ → BAC</td>
<td>2,100,000</td>
<td>1.5 mg/L, injector</td>
</tr>
<tr>
<td></td>
<td>MF → H₂O₂/O₃ → BAC</td>
<td>50,000</td>
<td>1.5 mg/L, injector</td>
</tr>
<tr>
<td>Paldang Dam</td>
<td>S/F → O₃ → FA</td>
<td>1,496,000</td>
<td>2-3 mg/L, injector</td>
</tr>
<tr>
<td></td>
<td>S/F → O₃ → FA</td>
<td>530,000</td>
<td>2-3 mg/L, injector</td>
</tr>
<tr>
<td></td>
<td>S/F-UV/O₃ → FA</td>
<td>110,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S/F → GAC</td>
<td>145,000</td>
<td></td>
</tr>
<tr>
<td>Nakdong River</td>
<td>O₃ → S/F → O₃ → BAC</td>
<td>4,208,000</td>
<td>2-3 mg/L, diffuser</td>
</tr>
<tr>
<td></td>
<td>S/F → O₃ → BAC</td>
<td>422,000</td>
<td>2-2.5 mg/L, diffuser</td>
</tr>
<tr>
<td></td>
<td>S/F → H₂O₂/O₃ → FA</td>
<td>120,000</td>
<td>3 mg/L, diffuser</td>
</tr>
<tr>
<td></td>
<td>S/F → GAC</td>
<td>70,000</td>
<td>2 mg/L, diffuser</td>
</tr>
<tr>
<td></td>
<td>S/F → H₂O₂/O₃ → BAC</td>
<td>36,000</td>
<td>3 mg/L, diffuser</td>
</tr>
<tr>
<td></td>
<td>MF → GAC</td>
<td>16,000</td>
<td></td>
</tr>
<tr>
<td>Geum River</td>
<td>S/F → GAC</td>
<td>100,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S/F → GAC</td>
<td>28,000</td>
<td></td>
</tr>
<tr>
<td>Nam River and related dam</td>
<td>S/F → O₃ → BAC</td>
<td>433,000</td>
<td>2 mg/L, diffuser</td>
</tr>
<tr>
<td></td>
<td>S/F → GAC</td>
<td>661,000</td>
<td></td>
</tr>
</tbody>
</table>

S/F: sand filtration; MF: microfiltration; FA: filtration adsorption; GAC: granular activated carbon; sandwich slow sand filtration.
the various flows of fluid [19]. Two-dimensional models, which is to solve the flow rate of fluid and analyze the mathematical operations. This analysis process can show the effects of temperature and static pressure, velocity on the mixing or dispersion of oxidant before designing and constructing the injection device at the field.

When the operation rate of a water treatment plant decreased less than the initial design capacity, the hydraulic condition of the oxidant injection system can be changed. Therefore, in this study, a computational fluid analysis for the hydrogen peroxide injection system was performed to analyze and improve the existing mixing effect of hydrogen peroxide in the ozone-based AOP process. Finally, the computational fluid dynamics (CFD) simulation of hydrogen peroxide injection could suggest improved mixing approaches for the injection system with minor modification.

2. Material and methods

2.1. Testbed for the AOP

The water treatment plants using the Han River are supplying tap water of advanced water treatment to citizens as shown in Table 1 by 100% of advanced water treatment as shown in Table 1. The testbed where the CFD was performed is a drinking water treatment plant with ozone-based AOP facilities. The process of water purification plant, where the AOP was designed by hydrogen peroxide and ozone. Hydrogen peroxide was injected into the pipeline and then mixed into the side stream system of ozone, causing an immediate mixing reaction in seconds.

Table 2 shows the goal of final water after advanced water treatment at the testbed. DBP and the concentration of them should be controlled by; less than 8 ng/L of Geosmin and 2-MIB, less than 1.0 mg/L of TOC, and less than 30 µg/L of trihalomethane (THM). Besides, the goal of Giardia lamblia, was less than 0.5 log removal at a reservoir because ozone has a role in disinfection.

The AOP process was operated by combining ozone and hydrogen peroxide as the primary and secondary oxidizing agents, respectively, shown in Fig. 3. Hydrogen peroxide was diluted with feed water of sand filtrate within a static mixer, then injected into the diffuser. The dilute H₂O₂ solution flew out of the main pipe after contact of 3.5 s after injection in case of a conventional diffuser and it diffused slowly with a parallel streamline.

2.2. CFD analysis procedure

The numerical analysis of the hydrogen peroxide injection and mixing was performed using commercial software ANSYS Fluent Ver. 16.0. The flow transfer of fluid in 3D

![Fig. 1. Oxidation pathways of microcontaminants by ozone.](image1)

![Fig. 2. Process of water treatment plant as a testbed.](image2)

![Table 2. Goal of final water after advanced water treatment at the testbed](table2)
space used the realized $k$–$\varepsilon$ turbulence model. It considered the momentum transfer and mass diffusion by turbulence where the mass conservation equation and the momentum conservation equation were used. Meanwhile, a mass of fluid is conserved and the mass conservation equations for simulation are described as followed.

For mass conservation:

$$\frac{\partial \rho}{\partial t} + \nabla (\rho \mathbf{v}) = S_m$$

(2)

where $S_m$ is the source from the dispersed second phase and to be added to the continuous phase.

For conservation momentum:

$$\frac{\partial}{\partial t} (\rho \mathbf{v}) + \nabla (\rho \mathbf{v} \mathbf{v}) = -\nabla \mathbf{P} + \mathbf{V} (\overline{\mathbf{T}}) + \rho \mathbf{g} + \mathbf{P}$$

(3)

where $\overline{T}$ is stress tensor, $P$ is static pressure, $\rho g$ is gravitational body force and $\mathbf{P}$ is external body forces.

In ANSYS Fluent, realized $k$–$\varepsilon$ model performs the best of all versions of $k$–$\varepsilon$ model from several validations of flow. Therefore, the realized $k$–$\varepsilon$ model has been implemented during this numerical modeling.

For realized $k$–$\varepsilon$ model:

$$\frac{\partial \rho k}{\partial t} + \nabla (\rho k \mathbf{v}) = \frac{\partial}{\partial x_i} \left[ \mu + \frac{\mu_t}{\sigma_k} \frac{\partial k}{\partial x_i} \right] + G_{k} + G_{s} - \rho \varepsilon - Y_{\varepsilon} + S_{k}$$

(4)

$$\frac{\partial \rho \varepsilon}{\partial t} + \nabla (\rho \varepsilon \mathbf{v}) = \frac{\partial}{\partial x_i} \left[ \mu + \frac{\mu_t}{\sigma_{\varepsilon}} \frac{\partial \varepsilon}{\partial x_i} \right] + C_{1\varepsilon} \frac{\varepsilon}{k} (G_{k} + G_{s} - G_{\varepsilon}) - C_{2\varepsilon} \rho \frac{\varepsilon^2}{k} + S_{\varepsilon}$$

(5)

where $G_{k}$ is the production of turbulence energy due to mean velocity gradients.

For chemical conservation:

$$\frac{\partial}{\partial t} (\rho \alpha_i Y_I) + \nabla (\rho \alpha_i Y_I \mathbf{v}) = -\nabla \mathbf{F}_i + \alpha_i S_{\alpha_i}$$

$$+ \sum_{j=1}^{N} (\alpha_j Y_j' - \alpha_i Y_i')$$

where $p$ is static pressure, $Y_i$ is the local mass fraction for the species, $\alpha_i Y_i'$ is mass transfer source between species, $\alpha_i$ is volume fraction for phase $i$, and $S_{\alpha_i}$ is the rate of creation by addition from the dispersed.

The distribution and mixing between target substances were determined based on the qualification of species mixing, individually. Therefore, the degree of mixing of the target component was determined as ‘uniformity’, which is calculated by the volume fraction efficiency of the target at the cross-section, and the closer to 1 means a uniform distribution.

For uniformity:

$$\text{uniformity} = 1 - \frac{\sum_{i=1}^{N} \sqrt{(x_i - \overline{x})^2 A_i}}{2\pi A}$$

(7)

where $A_i$ is surface area at the $i$-th cell, $x_i$ is variable (fraction or concentration) at the $i$-th cell, and $\overline{x}$ is the area-weighted variable of surface,

The assumption of analysis is provided as follows.

- Dilute $\text{H}_2\text{O}_2$ is the perfect mixture.
- Diluted hydrogen peroxide contains $\text{H}_2\text{O}_2$ and feed water of sand filtrate.
- Physical properties of density, molecular weight are based on 25°C, 1 bar condition of pure water.
- Feedwater flow has been distributed at the main solution feed pipe.
- Chemical reactions or heat transfer are not considered.

3. Results and discussions

3.1. Operation conditions of AOP

The dose of oxidizing agents was calculated based on the water quality, especially the target of Geosmin and
2-MIB. The dosing table of ozone and peroxide was recommended based on the seasonal main event; algal booming, water temperature. The hydrogen peroxide concentration was determined at a ratio of 1:0.5 based on the ozone dose concentration, and in the low-temperature season below 5°C, the injection concentration was made to be 1:5 due to the low reactivity of oxidant. Table 4 is a table of basic oxidizer injection for AOP process operation, but the oxidant injection rate could be flexibly adjusted according to the site conditions such as raw water quality and residual oxidant concentration.

The H₂O₂ stock solution used 35% concentration. The injection flow of hydrogen peroxide was 0.12–0.5 L/min based on the dosing conditions and 450,000 m³/d of design capacity. Since hydrogen peroxide was injected into the two main pipelines linked to the ozone contact basins, two tube pumps were selected and covered 62–311 mL/min flow rate, respectively. Table 5 shows the specifications of the diffuser for injecting the diluted hydrogen peroxide into the main pipe. However, operation flow was 225,000 m³/d (9,375 m³/h) at the testbed, therefore the velocity of feed water was reduced by 1.22 m/s, that of the diluted H₂O₂ was reduced by 2.23 m/s (63 m³/h of flow rate), and the velocity was 15 m/s at the orifice as shown in Table 5. Feedwater which should be treated flows and it would dominate the flow in the solution main pipe. The ratio of flow rate between feed water and dilute H₂O₂ was about 149. It is necessary to inject oxidant with enough pressure into the feed water instantly.

3.2. Analysis of existing hydrogen peroxide injection device

Hydrogen peroxide with a concentration of 35% was diluted with the sand filtrate. The dilute H₂O₂ was injected into the main pipeline at a lower flow rate less than 149 times of feed water as shown in Fig. 5. The feed water dominated the whole movement of fluid as described by the volume fraction of hydrogen peroxide in Fig. 6. It was considered that there were no other disturbance elements for the flow other than the diffuser in the main pipe. The retention time of oxidant flow was about 3.5 s in the main pipeline. The oxidant dispersed after radial injection with the same direction gradually and the streamlines of the diluted H₂O₂ solution showed parallel flow in the main pipeline (Fig. 7).

The volume fraction of dilute H₂O₂ at cross-sections along flow direction is plotted in Fig. 8. The mixture gradually formed a uniform distribution from 0.02 to 0.56 as diffusion toward flow direction occurred. Besides, the path distance of hydrogen peroxide flow was not enough in the main pipeline due to low injection pressure as shown in Fig. 9. Fig. 10 shows there was a poor mixing area between injection points.

In the existing injection device, the distribution range of dilute H₂O₂ fraction was from 0% to 3% at the discharge surface and its uniformity at the outlet of the orifice was

<table>
<thead>
<tr>
<th>Modes</th>
<th>Oxidizing agents</th>
<th>Dry</th>
<th>Normal</th>
<th>Cold</th>
<th>Emergency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only ozone</td>
<td>O₃ (mg/L)</td>
<td>1.0–1.5</td>
<td>0.5–1.0</td>
<td>0.1–0.5</td>
<td>1.5–2.0</td>
</tr>
<tr>
<td>AOP</td>
<td>O₃ (mg/L)</td>
<td>0.5–0.75</td>
<td>0.25–0.5</td>
<td>0.1–0.3</td>
<td>0.7–1.0</td>
</tr>
<tr>
<td>AOP</td>
<td>H₂O₂ (mg/L)</td>
<td>0.25–0.30</td>
<td>0.15–0.25</td>
<td>0.3–0.5</td>
<td>0.35–0.5</td>
</tr>
</tbody>
</table>

calculated by 56%. The volume fraction and the uniformity value of dilute H₂O₂ at cross-sections along flow direction are plotted in Fig. 10.

3.3. Analysis of modified hydrogen peroxide injection device

The injection conditions of the oxidant were examined to enhance the injection pressure or to disperse the oxidizer in the radial direction for atomization and diffusion of the solution. The case studies for modification on diffusers were reviewed to divide the stream of oxidant flow into several separate parts.

The orifice hole number of the diffuser was doubled from 90° interval to 45° interval. The number of holes was doubled, but the individual hole diameter was reduced from Ø 21 mm to Ø 15 mm so that the total hole area is the same as the previous diffuser. That is, the velocity at the orifice hole was kept as the previous design by adjusting the hole size. Rather, the result showed that the stream did not have enough radial momentum, causing it tended to converge at the center of the injection pipe. As a result, the dilute H₂O₂ solution was swept away by feed water and it made the uniformity decreased. The final uniformity of dilute H₂O₂ fraction was calculated at 35% at the discharge surface of the diffuser as shown in Fig. 11.

To split the stream of hydrogen peroxide, the number of existing diffusers was increased. Each diffuser had four holes, but one had + arrangement and the other had × arrangement. Here, the length of the entire pipe was extended to set the distance from the downstream side to the outlet, equally. The fluid conditions were the same as the previous experiment, but the dilute oxidant was divided into two diffusers with the same flow rate. The flow rate of the oxidant injected
into one diffuser was reduced in half, and it resulted in a decrease of uniformity when the number of the diffuser was doubled. It was considered that it was because the stream did not have enough radial momentum, causing the tendency of converging at the center of the diffuser as shown in Fig. 12. The split of the injection stream resulted in lessening the momentum of fluid. Finally, it was swept away by feed water and converged in the central region of the diffuser. The fraction of diluted H₂O₂ obtained a worse uniformity of 34% at the diffuser outlet surface as shown in Fig. 13.

To increase the injection velocity of the oxidizing agent for turbulent flow in the pipe, the dilute ratio of H₂O₂ was doubled and the same designs related to the diffuser were applied. When the flow rate of the dilute H₂O₂ was doubled and the pressure at the nozzle was strengthened, the uniformity of the outlet was improved up to 79%. Besides, a diffuser with 8 holes and a doubled flow rate of H₂O₂ improved the mixing rate up to 83% as shown in Fig. 14. It showed sufficient hydraulic pressure should be secured first for efficient mass transfer with dispersion, and radially distributed orifice can lessen dead zone in mixing.

In this study, the dispersion of oxidants was reviewed, focusing on the oxidizer injection conditions to improve the mixing rate within a short contact time of 5 s in the pipe. To increase oxidation efficiency in the AOP unit, it is
necessary to maintain sufficient water pressure and to be injected at dispersed points in the pipe.

4. Conclusions

When the AOP process is operated in a water purification plant, the mixing effect of the oxidant injection device may be degraded due to the lower operation rate than the initial design capacity. Therefore, this study focused on upgrading the mixing performance of hydrogen peroxide in the existing ozone-based AOP system using the CFD. The analysis results showed that the existing design of the mixing system was inadequate for efficient mixing between oxidant and treated water; The injection flow of hydrogen peroxide could not overcome the momentum of the feed water, and the main pipe length was short to provide the contact time for the oxidant and feed water. The mixing effect of the oxidant could be improved through modification of the injection conditions, and an increase of flow rate and dispersion injection points could maintain sufficient injection pressure in the main pipeline. However, dissociation and reactivity of hydrogen peroxide with pollutants or scavengers should be further analyzed using the CFD analysis.

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