Effect of residual ozone on membrane fouling reduction in ozone resisting microfiltration (MF) membrane system

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Abstract The effect of residual ozone on reducing the membrane fouling was investigated using ozone resisting microfiltration membrane. It was found out that the fouling was reduced effectively by maintaining residual ozone in the membrane module. To clarify the reason why the residual ozone reduces the membrane fouling, research was focused on the molecular degradation reaction and particle destabilization reaction induced by residual ozone. The major reason of membrane fouling reduction was attributed to the reduction of reversible resistance induced by the cake layer. The reversible resistance was reduced due to degradation of organic substances in the cake layer. In addition to degradation reaction, the increase of fouling particle size due to residual ozone in the cake layer is another important process for fouling reduction. This effect has been referred to as ozone-induced destabilization reaction. The calcium present in the raw water influenced this reaction. The increase of fouling particles size improves the filterability through the cake layer and backwashing efficiency.

Keywords Calcium ion; complexation; degradation; humic substance; microfiltration; ozone; particle destabilization

Introduction

Combination of ozonation with membrane filtration is effective for the prevention of membrane fouling. However, most of the membranes are made of organic polymer material at present. Hollow fiber membranes made of organic polymer could not be used in conjunction with ozone because organic polymer materials generally have less resistance to ozone. Therefore, when ozonation is used as pretreatment prior to membrane filtration, additional de-aeration process is necessary to remove the residual ozone before the membrane module. Recently, Japanese membrane manufacturing companies have succeeded in developing the ozone resisting membrane module made by polyvinylidene fluoride (PVDF) with potting material having a high resistance to ozone. In the developed membrane module, water containing residual ozone can be directly filtered. It is known that this system can provide consistently high permeate flux for various waters, especially high turbidity raw water and secondary treated municipal wastewater (Mori et al., 1998).

In this study, the effect of residual ozone on fouling reduction was investigated using an ozone resisting MF membrane. Especially, the type of reactions with organic foulants in water was investigated. Among various reactions, we noticed two ozone-induced reactions. One is the degradation reaction of organic substances by residual ozone. The other is an ozone-induced destabilization reaction of particles on the membrane surface induced by residual ozone. The ozone-induced particle destabilization reaction has been reported by many researches (Chandrakanth and Amy, 1998; Grasso and Weber, 1988). Several researches have reported the advantages of pre-ozonation such as higher efficiency of turbidity removal, lower coagulant dosage, and increasing filter run time. (Saunier et al.,
These effects have been referred to ozone-induced particle destabilization of ozone in water treatment. Few systematic studies have been conducted to gain insight into the mechanisms of ozone-induced particle destabilization (Grasso and Weber, 1988; Dowbiggin and Singer, 1989; Edwards and Benjamin, 1991). The second reaction is the degradation of organic substances by residual ozone. The main object of this study is to investigate the effect of the two reactions on reducing membrane fouling.

**Experimental procedure**

Raw water was taken from an existing water treatment plant in Hokkaido, Japan. Short and long term experiments were carried out. The average raw water quality during the short term experiment was as follows: turbidity = 10.0 NTU, TOC concentration = 2.8 mg/L, Absorbance at 260 nm ($E_{260}$) = 0.097 1/cm, Ca$^{2+}$ concentration = 15.0 mg/L. Figure 1 shows a schematic diagram of the ozone resisting MF membrane system. It contains a MF membrane module (Asahi Chemical Co. Japan) with hollow fiber configuration. The specification of the membrane is summarized in Table 1. The ozone concentration of the permeate was maintained from 0.2–0.3 mg/L during both experiments. Process I is the direct MF filtration. Process II is the combination of pre-ozonation and MF membrane filtration. The system is designed to process filtration, back-washing, air-scrubbing and flushing sequentially and automatically. The object of the short-term experiment is to investigate the mechanisms of both reactions related to the membrane fouling reduction. In the short-term experiment, filtration is performed at constant filtration flux of 3.5 m/day until the fouling point without backwashing. Filtration was stopped when the trans-membrane pressure (TMP) reached about 60 kPa. At this point, backwashing was performed. The backwashing pressure and period were at 30 kPa and 7 min. respectively. All of the backwashed water was collected to measure the water quality. Because process I reached 60 kPa within 90 min., the permeate was taken 50 minutes after filtration started in both processes. The long-term experiment was carried out in order to confirm the effect of residual ozone on the operation efficiency. In the long-term operation, filtration, back washing, air scrubbing and flushing is conducted sequentially and automatically. The conditions during the long-term operation are summarized in Table 2. Parameters of interest included turbidity, total organic carbon (TOC), dissolved organic carbon (DOC), UV absorbance at 260 nm ($E_{260}$), inorganic ions (calcium, manganese, iron, aluminium), particle size distribution, apparent molecular size distribution. The particle size distribution of the backwash water was measured using a laser scattering particle size analyzer (SALD-3000, Shimadzu, Japan).

![Figure 1](https://iwaponline.com/wst/article-pdf/50/12/287/419521/287.pdf)
Results and discussions

Short-term experiment: mechanistic interpretation of residual ozone effect

We observed the effect of residual ozone on the trans-membrane pressure change. The results are shown in Figure 2 and indicate that the increase rate of trans-membrane pressure was considerably reduced under the presence of residual ozone.

Degradation reaction. At first, we investigated the degradation reaction in the cake layer induced by residual ozone was investigated. In order to confirm the degradation reaction of organic substances, the total amount of TOC in the backwash water in process I and II was measured. They were 202.3 mgC and 114.6 mgC respectively. Although the operation time of process II was about 3 hours longer than of process I, the total amount of TOC in process II is only 50% of that in process I. These results show that the total amount of TOC in the cake layer is reduced dramatically under the presence of residual ozone. Therefore, it was confirmed that the ozone-induced degradation reaction is the important reaction for fouling reduction. The concentration of humic substances (E$_{260}$) in the backwash water was measured in order to observe the degradation reaction of humic substances. The results of E$_{260}$ measurements during process I and II were 0.058 and 0.027 1/cm, respectively. From these results, it was concluded that the double bond of humic substances was broken by residual ozone leading to a shift to lower molecular weight substances. As a result, a large quantity of low molecular weight fraction of humic substances is spilled into the permeate. Table 3 shows the measurement results of TOC and humic substances in the permeate. From Table 3, it can be seen that the TOC concentration increased slightly but humic substances decreased greatly. It was supposed that organic substances including humic substances in the cake layer were degraded by residual ozone and then leached into the permeate. The molecular size distribution was measured in order to observe the degradation reaction of humic substances by residual ozone. From Table 4, the fraction of molecular weight which
is lower than 500 Da increased dramatically under the presence of residual ozone for both permeate and backwash water.

From these results, it was concluded that the degradation of humic substances to lower molecular weight fractions is an important process when residual ozone is introduced into the membrane module.

**Ozone induced particle destabilization.** Next, the increase of the particle size by ozone induced particle destabilization was investigated. It was reported that calcium ions in water also act as coagulant-aid under the presence of residual ozone (Chandrakanth and Amy, 1998) and combines with humic substances to increase membrane fouling (Minegishi, 2001). In addition, it was reported that calcium forms strong complexes with functional groups containing oxygen (Nieboer and Richardson, 1980).

Therefore, the total amount of inorganic ions in the backwashed water was measured. The results are summarized in Table 5. As shown in Table 5, the total amount of calcium and iron ions increased under the presence of residual ozone. It is also known that ozonation of NOM produces more low-molecular-weight, polar, oxygen-rich compounds resulting in an increase of the content of hydroxyl, carboxyl, and carboxylic groups. In the present work, MW changes indicated that ozonation led to an increase of low-molecular-weight compounds. Therefore, it is supposed that the total amount of calcium ion increased through the complexation reaction between calcium and low molecular weight substances by residual ozone. The increased calcium ions in the cake layer acted as coagulant-aid and induced the particle size increase.

The iron ion was changed from Fe$^{2+}$ to Fe$^{3+}$, hydrolyzed, coagulated and sedimented in the presence of ozone. It was reported that metal ions can bind with various organic complexation sites, i.e. carboxylates, phenolates, or stronger nitrogen/sulfur-containing sites such as amino acids (Odem, Amy and Conklin, 1993). Therefore, it is thought that the total amount of iron ions increased through the oxidation reaction and complexation reactions between iron and low molecular weight substances were induced by residual ozone.

The manganese ion was oxidized to un-dissolved MnO$_2$ under the presence of ozone. However, Mn$^{2+}$ and Mn$^{4+}$ were changed to dissolve MnO$_4$ in the case of excessive ozone. In the present study, the excessive ozone resided in the membrane module. Therefore, it was thought that the total amount of manganese was nearly the same in the cases with and without residual ozone. From the results of the total increase of calcium and iron ions in the presence of residual ozone, the particle size in the cake layer increased by the coagulant-aid reaction of calcium and the complexation reaction between calcium, iron ions and low molecular weight substances.

**Table 3** Concentration of TOC and E260 in permeate

<table>
<thead>
<tr>
<th></th>
<th>Process I</th>
<th>Process II</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (mg/L)</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>DOC/TOC ratio</td>
<td>0.98</td>
<td>0.99</td>
</tr>
<tr>
<td>E260 (1/cm)</td>
<td>0.062</td>
<td>0.034</td>
</tr>
<tr>
<td>E260/DOC (m$^{-1}$/mg/L)</td>
<td>25.8</td>
<td>13.1</td>
</tr>
</tbody>
</table>

**Table 4** Change of apparent molecular size distribution less than 500 Da

<table>
<thead>
<tr>
<th>System</th>
<th>Sample</th>
<th>Absolute % change</th>
<th>Relative % change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process I</td>
<td>Permeate</td>
<td>+134.8%</td>
<td>−53.3%</td>
</tr>
<tr>
<td></td>
<td>Backwash</td>
<td>+66.8%</td>
<td>+39.4%</td>
</tr>
<tr>
<td>Process II</td>
<td>Permeate</td>
<td>−52.1%</td>
<td>+59.1%</td>
</tr>
<tr>
<td></td>
<td>Backwash</td>
<td>+106.6%</td>
<td>+188.0%</td>
</tr>
</tbody>
</table>
It was reported that the turbidity decreases while the particle size increases due to the decrease of light scattering at constant wavelength (Grasso and Weber Jr, 1998). Therefore, the turbidity of the backwash water in the two processes was measured. The result of the turbidity measurements of processes I and II were 110 and 78 NTU, respectively. From these results, it was concluded that size of fouling particles, consisting of the cake layer on the membrane surface, increased due to the ozone-induced particle destabilization reaction. Figure 3 shows the size distribution of fouling particles in the backwash water. As shown in Figure 3, the size of the fouling particles increased under the presence of residual ozone. This effect has occasionally been referred to as ozone-induced particle destabilization effects of ozone in water treatment.

**Loading rate of humic substances and inorganic ions to the membrane surface.** In order to observe the loading rate of humic substances and inorganic ions in the cake layer, the inorganic ion/E260 ratio in backwash water was calculated. The results are shown in Table 6. From the result, it was found that the loading rate of humic substances, known as major membrane fouling material, dramatically decreased. The fraction of inorganic ions, which can be more easily removed by backwashing than humic substances, increased. Therefore, the loading rate of humic substances onto the membrane surface was reduced and the efficiency of backwashing was improved.

**Long-term experiment**

Long-term experiments were performed in order to confirm the effect of residual ozone on operation efficiency. Figure 4 shows the TMP development for the two operation conditions. Like in the short-term experiments, the increase rate of trans-membrane pressure is effectively reduced due to residual ozone. It is a result of the decrease of the humic substances loading rate by the degradation reaction and the increase of fouling particle size due to particle destabilization by ozone. Hence the reversible resistance was reduced and the backwash efficiency was improved.

**Conclusions**

From the experimental investigations, the mechanisms of reduced membrane fouling by residual ozone in the membrane module can be described as follows.

1. The residual ozone degrades the organic material that causes the fouling such as humic substances dramatically and reduces the loading rate of the fouling material.

**Table 5** Total amount of inorganic ion in backwashed water

<table>
<thead>
<tr>
<th></th>
<th>Calcium</th>
<th>Manganese</th>
<th>Iron</th>
<th>Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process I</td>
<td>13.2 mg</td>
<td>6.2 mg</td>
<td>165.4 mg</td>
<td>10.3 mg</td>
</tr>
<tr>
<td>Process II</td>
<td>26.6 mg</td>
<td>5.9 mg</td>
<td>240.4 mg</td>
<td>10.5 mg</td>
</tr>
</tbody>
</table>

**Figure 3** Size distribution of fouling particles in backwashed water
2. The concentration of inorganic ions, which are easily removed by backwashing relatively to humic substances, increases in the cake layer by residual ozone, whereas humic substances decrease. This can improve the backwash efficiency.

3. The increase of the fouling particle size in the cake layer reduces the reversible membrane resistance and improves the backwash efficiency. Therefore, the overall operation efficiency under the presence of residual ozone could be considerably improved.

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References


