Removal of Natural Organic Matter (NOM) by Ozone Oxidation and Biological Filtration Using a Rope-Type Biofilter

Sang Jun Sim†, Youn Seok Kang*, and Woo Sik Kim*

Department of Chemical Engineering, Sungkyunkwan University, Kyunggi 440-746, Korea
*Department of Chemical Engineering, Kyung Hee University, Kyunggi 449-701, Korea

Received September 24, 2003; Accepted February 4, 2004

Abstract: As raw water quality gets worse, a great number of advanced techniques have been developed and adapted for water treatment to provide safe and high-quality drinking water. One of various water treatment processes is biological treatment, which is suitable for advanced water treatment, followed by conventional treatment processes. In this paper, we propose ozonation and biofiltration by a rope-type biofiltration contactor for the effective removal of natural organic matter (NOM) from the source of drinking water. The removal efficiencies of NOM were evaluated under various experimental conditions, such as ozone contact time, empty bed contact time (EBCT), media density of the sedimentation tank, and turbidity of the raw water. The combination of pre-ozonation and bio-filtration was found to be very effective for removing biodegradable organic matter as well as the turbidity of raw water. We expect that the biological rope media biofiltration contactor, with pre-ozonation, may be complimentary units for NOM removal when employed in a conventional water treatment process. This process can be easily introduced in small-and medium-scale water purification units.

Keywords: rope type media, bio-filtration, natural organic matter (NOM), ozonation, empty bed contact time (EBCT)

Introduction

In a process of treating drinking water chlorine is generally employed as a disinfectant for the inactivation of pathogenic microorganisms. The presence of natural organic matter (NOM) in water supplies, however, can lead to impaired drinking water quality as a result of its reaction with chlorine during this disinfection process, to form carcinogenic and teratologic compounds [i.e., disinfection by products (DBPs)]. From a public health perspective, reducing NOM levels (the precursor of DBPs) prior to terminal disinfection and distribution is important to provide safe and high-quality drinking water [1,2]. The NOM removal options include coagulation, granular activated carbon (GAC) adsorption, and membrane filtration. Among these processes, coagulation is the most widely used in the water industry, but when coagulation cannot remove adequate concentrations of NOM, so that it is difficult to control the disinfection by-products, other treatment technologies must be considered [3]. Of these technologies, the biofiltration process is known to be a promising process for the removal of NOM by the simultaneous adsorption and biodegradation through bacteria attached to activated carbon [4].

NOM is a complex mixture of organic compounds of unknown composition. NOM is fractionated into particulate organic carbon (POC) and dissolved organic carbon (DOC). DOC is organic matter that is filtered through a 0.45-μm membrane filter. Most NOM in raw water used as a drinking water supply is refractory in general. It is possible to increase the biodegradability of NOM by the use of oxidants, such as ozone (O₃), or advanced oxidation processes [5]. The application of ozone to NOM in raw water tends to partially oxidize high-molecular-weight NOM into smaller molecules.

In a previous study, we found that a biological treatment system equipped with rope-type media, which are easy to replace or regenerate, provides acceptable NOM removal efficiency when applied together with ultrafiltration.
Table 1. Quality of Service Water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.8 ~ 7.1</td>
<td>7.0</td>
</tr>
<tr>
<td>Alkalinity [mg as CaCO₃/L]</td>
<td>21 ~ 35</td>
<td>53</td>
</tr>
<tr>
<td>Hardness [mg as CaCO₃/L]</td>
<td>21 ~ 46</td>
<td>36</td>
</tr>
<tr>
<td>Turbidity [NTU]</td>
<td>0 ~ 0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>UV absorbance [cm⁻¹]</td>
<td>0.004 ~ 0.01</td>
<td>0.007</td>
</tr>
<tr>
<td>DOC [mg/L]</td>
<td>0 ~ 0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>T-N [mg/L]</td>
<td>0.03 ~ 0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>T-P [mg/L]</td>
<td>0 ~ 0.01</td>
<td>0</td>
</tr>
</tbody>
</table>

[6]. This paper describes an application of the rope-type media bio-filtration contactor to the removal of NOM in synthetic water. The bio-filtration contactor was employed in combination with ozonation to increase the biodegradability of NOM.

**Experimental**

**Water Source**
The principle element of NOM is humic acid. To investigate the yield of DOC removal from synthetic water using a biofiltration contactor, we added commercial humic acid (Aldrich, Inc.) to service water. Humic acid was dissolved in 1 L of deionized water, which had been pre-filtered through a 0.2-μm membrane filter to remove undissolved particles (1000 mg/L). Turbidity was induced by adding kaolin. Table 1 gives the average values for physical and chemical parameters of the service water.

**Rope-Type Biofiltration Media and Contactor**
A rope-type biofiltration contactor was designed with the goals of easy maintenance and excellent effluent quality. Because microorganisms are grown on the media, the simple fashion of this system results in easy installation or replacement to an existing water purification process.

The batch biodegradation experiments were performed by adding raw or ozonated NOM. To remove the NOM, a method using a fixed biological contactor was developed. The rope media consists of Y-shaped nylon BCF multifilaments and nylon monofilaments. The Y-shaped nylon BCF multifilaments significantly enlarge the surface area. The cross section is 40 ~ 45 mm in diameter. The rope media size is used in the range 14 ~ 15 cm. The biological rope media sedimentation tank has a 0.5 L volume on the laboratory-scale test; it is constructed of poly(methyl meth acrylate) (PMMA). To provide sufficient contact, an obstacle plate is installed in the middle of tank (Figure 1).

**Ozone Oxidation and Biofilter Operation**
It is well known that ozonation increases the biodegradability of humic substances and, hence, their removal in a given biofilter. In this experiment, ozonation was performed before biofiltration. The ozone generator operated at a voltage of 90 mV and an oxygen quantity of 5 LPM. Laboratory-scale experiments were conducted using a biological rope media sedimentation tank containing a 15-liter solution of humic acid prepared in service water. The removal of NOM was evaluated under various experimental conditions within the biological rope media sedimentation tank, such as the ozone contact time of the synthetic water, EBCT (empty bed contact time), the media density of the sedimentation tank, and the turbidity of the synthetic water. NOM removal data were obtained under the same EBCT and density of media conditions to examine the removal yield with respect to various ozone contact times of the synthetic water. After that, the removal yields of various EBCT conditions were examined. Experiments were also conducted upon varying the density of the media from 13 to 52 g/L. Addition of kaolin was conducted before ozonation of the synthetic water. The rope media was precultured for 20 days using natural water. The temperature was maintained at 25°C during all of these processes.

**Analytical Methods**
The DOC concentration was determined using a TOC analyzer (Pharma TOC, Analytikjena, Germany). The filtered (through a 0.45-μm membrane filter) DOC samples were prepared by acidifying with hydrochloric acid to below pH 2 and stripping with oxygen gas to remove inorganic carbon (CO₃²⁻, HCO₃⁻, dissolved CO₂) prior to injection. The UV absorbance at 254 nm of the filtered (through a 0.45-μm membrane filter) samples was measured using a Ultraviolet-Visible Spectrophotometer (UV-2000, Shimadzu, Japan) equipped with a 10 mm × 45 mm quartz cell. A turbidimeter (Model-16800, Hach, U.S.A) was used to measure the turbidities of the water samples in nephelometric turbidity units (NTU). Gel permeation chromatography (GPC; Model SB-802 HQ, RI-71 Shodex Co. Japan) was performed to determine the molecular weight distribution of NOM in the water.
Results and Discussion

Characteristics of the Synthetic Water
The average DOC concentration level in the water from Paldang reservoir ranges from 0.5 to 2 mg/L (data not shown). Therefore, to investigate the DOC removal efficiency in the biofiltration contactor, we prepared a synthetic water source, including commercial humic acid, from service water. We compared the molecular weight distributions of the synthetic water and the natural water from Paldang reservoir by measuring GPC (gel permeation chromatography) data (Figure 2). The molecular weight distribution was spread from about 1500 to $10^6$ Daltons. The synthetic and natural waters follow similar trends below 30000 Daltons, but above this value the two water samples follow different trends. The molecular weight distribution of the natural water was broader than that of the synthetic water. In this study, therefore, the removal efficiency of DOC below 60000 Daltons could be investigated.

Removal of DOC after Various Ozone Contact Times and Empty Bed Contact Times
Figure 3 shows the removal efficiency of DOC after various ozone contact times in synthetic water. The EBCT of the biological rope media contactor was 2 h. The density of the media was 52 g/L. We found that the removal yields of DOC were proportionally dependent on the ozone contact time of the synthetic water (Figure 3). The removal yields of DOC increased from 7 to 52%. We found that ozone oxidation was an effective process for the biodegradation of NOM. In addition, we observed that the initial concentration of DOC in synthetic water changed with ozone contact time: after ozonation, the initial concentration of DOC in the synthetic water decreased from 8 to 4.7 mg/L, which indicates that direct ozone oxidation and degradation occurred. It is well known that ozone decomposes NOM into dissolved components or completely oxidized substances [7,8]. These results clearly indicate that ozonation not only increases the biodegradability of organic compounds consistently but it also decreases the initial concentration of NOM in the case of a 30 min ozone contact time (90 mV; 5 LPM oxygen quantity).

Figure 4 shows the removal yields of DOC in the synthetic water with respect to two different variables: ozone contact time for the synthetic water and EBCT for the biofilter contactor. We found that the removal yields of
Density of media (g/l)

Figure 5. Removal yield of DOC vs. density of media for different values of EBCT (ozone contact time: 15 min; ozone: 90 mV, 5 LPM oxygen quantity; temperature: 25°C).

DOC removal yield (%)

1.5 h EBCT
2 h EBCT
4 h EBCT

Density of media (g/l)

Figure 6. Removal yield of DOC vs. density of media at various values of EBCT (ozone contact time: 30 min; ozone: 90 mV, 5 LPM oxygen quantity; temperature: 25°C).

Removal of DOC with Respect to Density of Media and Empty Bed Contact Time

The effect of the media density on the DOC removal yield in the biofiltration contactor was investigated. Figure 5 shows the removal yields of DOC in the synthetic water with respect to two different variables: the density of media and the EBCT for the biofiltration contactor for an ozone contact time of 15 min. Figure 6 shows the results for an ozone contact time of 30 min.

The removal yield of DOC increased as the media density and EBCT increased. The increase of the DOC removal yield was more remarkable when the ozone contact time was 30 min than when it was 15 min. These results indicate that ozonation increases the biodegradability of organic compounds in water. The removal yield of DOC increased steadily up to media density of 52 g/L. It seems that a high density of media was very important for DOC removal, but, when the EBCT was under 2 h, there were no significant differences in the DOC removal yield. Consequently, the EBCT is a more dominant factor than is the density of media in the removal of DOC. When the 52 g/L medium was added to the contactor and the EBCT reached 4 h, the final DOC removal yield was > 30%. We conclude that the optimal operation conditions for the removal of DOC are a media density of 52 g/L of and a 4-h EBCT, respectively.

Removal of DOC and Turbidity from Turbid Synthetic Water

To investigate the removal efficiency of turbidity and DOC from the turbid synthetic water, we carried out laboratory-scale experiments synthetic water having different turbidities. After kaolin was added, the synthetic water was contacted with ozone for 30 min. The DOC and turbidity removal results are shown in Figures 7 and 8, respectively.

The EBCT of the sedimentation tank was 4 h. The
removal yield of DOC decreased as the turbidity of the synthetic water increased. We found that the removal yields of DOC were also proportionally dependent on the media density in the sedimentation tank. The turbidity removal patterns at media densities of 26 and 39 g/L were different. The turbidity was removed under 1 NTU in the sample having a medium density of 39 g/L. This observation might be due to the adsorption of suspended solids on the rope media in the sedimentation tank [9]. We found that the optimal media density for the economic removal of DOC and turbidity was 52 g/L.

**CONCLUSION**

Typical purification processes for drinking water include coagulation, flocculation, sedimentation, sand filtration, and disinfection. There are several approaches for removing NOM from water to limit DBP formation, such as coagulation, granular activated carbon (GAC) adsorption, membrane filtration, or biofiltration. Because the majority of NOM in natural water is recalcitrant, preceding biofiltration by ozonation typically enhances the NOM biodegradability and increases the overall removal of NOM when compared to biofiltration alone [10,11].

In this study, we used laboratory-scale batch experiments to evaluate the effects of ozone contact time, empty bed contact time, density of media, and turbidity of raw water on the removal of NOM in a biological rope media sedimentation tank. The combination of preozonation and rope media treatment is very effective in removing biodegradable organic matter. An additional benefit includes a significant reduction in the turbidity of raw water. It is clear that ozonation consistently increases the biodegradability of organic compounds in water. We also found that the optimum media density and EBCT were very important parameters for the successful removal of both NOM and turbidity. From the results of these experiments, the optimal operation conditions of the rope media sedimentation tank were a medium density of 52 g/L, an EBCT of 4 h, and an ozone contact time of 1 h. The biological rope media contactor, in conjunction with pre-ozonation, can be a complimentary unit for NOM removal when it is employed in a conventional water treatment process. The rope-type biofilter system that we used in this study for the treatment of drinking water has several advantages. First, it was designed for easy maintenance and to provide excellent effluent quality. Second, the simple design of this system results in its easy installation or replacement within an existing water purification process. It can be installed after the coagulation or sedimentation systems of a conventional process to remove the NOM or turbidity.

**References**