Effect of ozonated water on membrane fouling


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Abstract Since 1999 the Mery-sur-Oise plant has operated using two processes in parallel: one, a membrane process using nanofiltration, and the other, a conventional biological process. For operational flexibility, it is desired to be able to transfer some of the sand-filtered ozonated water from the biological process to the membranes. Before carrying out this transfer, it was important to assess the role of ozonation on membrane fouling, by comparing the effects of ozonated water (SFOW) with non-ozonated water (SFW). Tests were performed, in spring and fall 2001, in a pilot unit comprising two nanofiltration lines in parallel. The first test emphasized the essential role of the pre-filter placed upstream of the membranes. This latter – supplied with ozonated water – released particles when saturated, linked to changes in the feed water quality. Despite very frequent pre-filter replacements, fouling proved to be greater for the membranes supplied by ozonated water. Even though the silt density index and total cell counts levels of SFOW were lower than SFW, ozonated water could increase membrane fouling. The action of ozone on the nature of organic matter appeared to be the main cause. Ozone modified the composition of natural organic matter, on one hand by reducing the hydrophobic fraction in favour of the hydrophilic fraction, which is harder for the membrane NF 200B to reject, and on the other hand by acting on the lyses of algal cells and the release of extracellular organic matter. The membrane autopsies confirmed that the deposit is essentially composed of organic matter. Images taken with a scanning electron microscope showed a more significant deposit for membranes fouled with SFOW. For the membrane fouled in spring, the images also revealed the presence of algae; for some, cells were lysed upon ozonation. HPSEC-UVA-DOC enabled the types of molecules to be identified according to size. Humic substances (1,000 to 5,000 daltons) and other low molecular weight components (400 to 600 daltons) represented a minor part of the fouling material with the major components being proteins (21,000 to 24,000 daltons). Also, humic substances were relatively more abundant in the membrane fouled with ozonated water in spring.

Keywords Algae; fouling; nanofiltration; organic matter; ozone

Introduction Since 1999, the Mery-sur-Oise plant has been using nanofiltration membranes to polish water from the Oise River, aiming at reducing the quantity of dissolved organic matter and limiting the escape of bacteria and micro-pollutants in the plant output (Ventresque et al., 2000). Without doubt, the success of this type of treatment relies on the pre-treatment steps of the membrane process, which minimize the fouling potential. Indeed, settling following ballasted flocculation, followed by ozonation, filter conditioning by the addition of an aluminum polymer, and microfiltration produces water with little fouling potential (number of particles > 1.5 μm less than 200/mL, silt density index (SDI) less than 3) and low concentration of organic matter (TOC concentration less than 2.7 mg/L), thus strongly limiting deposits of colloids and organic matter (Democrate et al., 2000).

Besides this membrane process, a conventional biological process accounts for 20% of total water production at the Mery-sur-Oise site. For operational flexibility, it is desired to be able to transfer some of the sand-filtered and ozonated water that comes from the biological process to nanofiltration membranes. Before performing this transfer, it is important to evaluate how membrane fouling is affected by an ozonation step just upstream.
of microfiltration, and according to seasonal conditions. Comparative tests of sand-filtered water with and without ozone treatment were therefore performed with a pilot unit.

Materials and methods

Pilot unit and membrane

The pilot unit is composed of two independent lines (Figure 1). Each line includes five modules: (i) low pressure pump, (ii) injection of acid and antiscalant, (iii) pre-filtration using 6 µm-absolute cut-off threshold pre-filter, (iv) high pressure pump, and (v) two pressure vessels assembled in series that can be equipped with type 2540 nanofiltration modules (25 inches in diameter and 40 inches long). The FILMTEC NF 200B membrane from Dow was studied.

Sensors and analyses

Hydraulic parameters were measured every 15 min and recorded with a data acquisition unit. Electromagnetic flow meters and pressure sensors were installed on the permeate circuits of modules 1 and 2, and the concentrate circuits of module 2. Differential pressure sensors measured pressure loss within the nanofiltration modules. A temperature probe measured the temperature downstream from the pre-filter. Physicochemical parameters were measured every week, except for pH, particle counts (>1.5 µm), and conductivity that were measured every day. The SDI (ratio of filtration rates at 15-min intervals) was measured using 0.45 µm sterile filters. UV$_{254}$ absorbance was measured using a UV/visible spectrophotometer. The Vivendi Water central laboratory performed analyses for total cell counts by epifluorescence, ionic balance and organic matter (DOC and BDOC). These analyses were done in compliance with current French standards.

Characterization of organic matter was further explored using other techniques at the University of Colorado. Passage over XAD-8 and XAD-4 resins was used to fractionate natural organic matter (NOM) into hydrophobic, transphilic, and hydrophilic substances (Her et al., 2000). A high performance size exclusion chromatography (HPSEC), equipped with a UV detector and a DOC detector assembled in series, characterized the aromatic and non-aromatic fractions of the NOM according to molecular weight (Her et al., 2002). Several techniques were used to characterize the fouling material found on nanofiltration membranes. Scanning electronic microscopy (SEM) provided images of deposit morphology and incongruities (Plottu-Pecheux et al., 2002). The deposit type was determined by Fourier transform infrared spectrometry (FTIR) and HPSEC chromatography +UV +DOC coupling.

Control of membrane fouling

The degree of membrane fouling was examined by monitoring two parameters:
permeability, which represents fouling of the membrane surface as well as within the pores, and longitudinal pressure loss, which represents fouling in the feed hydraulic flow. In order to eliminate temperature effects, permeability was corrected to 25°C.

**Water quality**

One pilot line was supplied with ozonated water (SFOW) and the other one with non-ozonated water (SFW). SFW was pumped from the biological process unit, after the coagulation-flocculation-settling and sand filtration steps. SFW was pumped after the ozonation and ozone residual elimination steps. Table 1 shows average and extreme variations of feed water according to the period studied. Water quality varied little between spring and fall 2001. SFOW and SFW exhibited similar inorganic compositions. However, the two types of water were different on the basis of parameters like total cell counts, particles > 1.5 μm, SDI, UV$_{254}$ and SUVA aromaticity index (ratio of UVA at 254 nm/DOC). Indeed, ozone very significantly reduced the number of bacteria. It also strongly decreased the SDI and, to a lesser extent, particles counts. Moreover, the aromaticity index (SUVA) indicated that ozone modifies the nature of organic matter. Ozonated, filtered water thus seemed to contain less particulate and biological matter, and exhibited an aromaticity index that is half the value of non-ozonated water.

**Methodology**

Two tests were performed, one during the spring (when the risk of algae bloom occurrence is the greatest) and the other during the fall (in the past, this water quality appeared to be more damaging for membranes). At the start of each test, clean nanofiltration modules were used. A test consisted of several steps:

- CaCl$_2$ characterization test, required to measure permeability and calcium passage of the clean membrane;
- test run lasting roughly eight weeks;
- analysis of dissolved organic matter in the two feed waters at the end of the test run;
- after the test run, membrane autopsies to determine the amount and type of clogging in relation to feed water quality.

Operating conditions for the test run were the same for all tests and were representative of first stage module operation (Table 2). Pre-filters placed upstream of membranes were systematically and simultaneously changed on the two lines according to the pressure loss criterion or time criterion.

**Table 1** Feed water quality after pre-filtration in the spring and fall of 2001 (average (minimum–maximum))

<table>
<thead>
<tr>
<th>Parameters</th>
<th>March–May 2001</th>
<th>November–December 2001</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>SFOW</td>
<td>SFW</td>
</tr>
<tr>
<td>Conductivity at 25°C (μS/cm)</td>
<td>576 (488–663)</td>
<td>578 (487–662)</td>
</tr>
<tr>
<td>Total cell count (#/ml)</td>
<td>6x10$^4$</td>
<td>2.8x10$^6$</td>
</tr>
<tr>
<td></td>
<td>(2x10$^5$–10x10$^6$)</td>
<td>(1x10$^5$–10x10$^6$)</td>
</tr>
<tr>
<td>SDI</td>
<td>2.5 (1.4–3.1)</td>
<td>4.1 (3.3–4.4)</td>
</tr>
<tr>
<td>Particles &gt; 1.5 μm (#/ml)</td>
<td>61 (11–281)</td>
<td>121 (24–357)</td>
</tr>
<tr>
<td>UVA$_{254}$ (cm$^{-1}$)</td>
<td>0.025</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>(0.017–0.033)</td>
<td>(0.04–0.07)</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>2.5 (1.8–2.9)</td>
<td>2.8 (1.8–3.8)</td>
</tr>
<tr>
<td>BDOC (mg/L)</td>
<td>0.7 (0.4–1.1)</td>
<td>0.6 (0.1–1.4)</td>
</tr>
<tr>
<td>SUVA (L/m.mg)</td>
<td>1.07 (0.95–1.14)</td>
<td>2.12 (1.71–2.47)</td>
</tr>
</tbody>
</table>
Results and discussion

Pre-filters

Pre-filters acted differently depending on the feed water (SFW or SFOW). In the case of SFW, particles larger than 6 µm seemed to accumulate on the pre-filter surface and formed a compact cake, which blocked any passage of particles. Nevertheless, in the case of SFOW, particles accumulated in the pre-filter until it was saturated and were released downstream afterwards.

At the beginning of the spring test, the criterion of changing pre-filters at a pressure loss of 1 bar appeared not to be effective. For the following tests, pre-filters were changed every two to three days. This new criterion was efficient enough, except on May 22, when particle leakage occurred downstream from the pre-filter. This was due to a strong degradation of feed water quality linked to a feed flow rate increase and/or algae development during very sunny periods around May 19.

Membrane fouling

Figure 2 shows changes in permeability and longitudinal pressure loss for the two tests. The loss of permeability was estimated by the ratio of permeability at time t versus initial membrane permeability. It is important to note that during the spring test, several stoppages of the pilot unit occurred. Water re-filling partially dislodged the fouling material, resulting in a decreased pressure loss associated with a slight increase in permeability.

The membranes behaved differently depending on the type of water. For SFW, membrane fouling was gradual and remained less than 10% after 64 days and 44 days of filtration in the spring and fall, respectively. For SFOW, membrane fouling appeared two times higher, and seemed to depend on variations in water quality. In spring 2001, SFOW led to fouling, the evolution of which was different according to the pre-filter change criterion. During the third week of the test run, permeability decreased more significantly on the head module (13%) than the second module (8%). This was associated with an increased longitudinal pressure loss on the head module (increase of 0.55 bar in 10 days), which indicated mainly particulate fouling. This fouling was due to colloids that passed through the pre-filter. During the weeks after, pre-filters were changed every two to three days. Then, gradual membrane clogging occurred and seemed to evolve in the same manner for both feed waters. It should be noted that algae development starting around May 19 had no visible effect on either permeability or longitudinal pressure loss.

In fall 2001, the permeability of membranes fed with ozonated water fell roughly 10% during the first 11 days of the test run. After that, changes in permeability were regular and almost identical to those observed with non-ozonated water. Even though SFOW contained less particulate and biological matters, it seemed at times to exhibit more fouling potential for membranes.

Table 2 Operating conditions

<table>
<thead>
<tr>
<th>Characterisation test</th>
<th>Spring test</th>
<th>Fall test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed water</td>
<td>CaCl₂</td>
<td>SFOW or SFW</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C</td>
<td>9–20°C</td>
</tr>
<tr>
<td>Feed flow rate</td>
<td>434 L/h</td>
<td>385 L/h</td>
</tr>
<tr>
<td>Recovery</td>
<td>15%</td>
<td>12% module 1 and 13% module 2</td>
</tr>
<tr>
<td>Antiscalant</td>
<td>–</td>
<td>2.1 g/m³</td>
</tr>
<tr>
<td>(mix of polycarboxylate and phosphonic acid)</td>
<td>–</td>
<td>pH set to 6.9</td>
</tr>
<tr>
<td>Sulfuric acid at 4%</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

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Analyses performed for SFOW and SFW indicated that water quality, particularly the type of organic matter, is highly modified by ozonation. Ozone decreased the aromaticity index (SUVA, Table 2) by breaking the aromatic bonds of organic molecules, and decreased the hydrophobic fraction in favor of transphilic and hydrophilic fractions (78% for SFOW versus 57–62% for SFW). However, the hydrophilic fraction of ozonated water was larger in May (50%) than in December (43%). This fraction could have an effect on membrane clogging since it is not expected to be easily rejected by the NF200B membrane, relatively hydrophilic and negatively charged. HPSEC + SUVA chromatography on feed water after 0.45-μm filtration emphasized the presence of humic substances (1,000 to 5,000 daltons) and aliphatic compounds (160 to 210 daltons).

The membrane autopsies showed that the deposit chiefly comprised organic matter. The CO-NH and C-O peaks measured by infrared spectrophotometry revealed the presence of proteins and polysaccharides in the deposit. Images taken with a scanning electron microscope showed a larger deposit for membranes fouled with SFOW. This deposit contained bacteria. Ozonation may have increased the bacterial food source and thus increased bacterial cell growth.

For the membrane fouled in spring, when algal bloom occurred in May, the images also revealed the presence of algae. These algae passed through the 6-μm pre-filter and were deposited on the membrane (Figure 3).

Some deposits were extracted from membranes by soaking in a high ionic strength solution (0.1 M Na₂SO₄) followed by filtration at 0.45 μm, and analyzed by HPSEC + SUVA chromatography. This analytical method showed that humic substances (1,000 to 5,000 daltons) and other low molecular weight components (400 to 600 daltons) represented a
minor part of the fouling material, the major components being proteins (21,000 to 24,000 daltons). Humic substances were more abundant in the membrane fouled with ozonated water in spring (Figure 4). Indeed, upon ozonation, algae contained in the water can release large quantities of extracellular organic matter (EOM), which may increase membrane fouling.

**Conclusions**

For two years now, the Mery-sur-Oise plant has operated using two processes in parallel: one, a conventional biological process, and the other, a membrane process using nanofiltration. Before transferring some of the SFW from the biological process to the membranes, the role of ozonation on membrane fouling was examined by comparing the effects of ozonated water with non-ozonated water. Results from the comparative tests performed in spring and fall showed that SFW exhibited a greater membrane fouling potential under certain conditions, particularly during periods of algal bloom. Ozone lysed algae and liberated extracellular organic matter that may act as glue between membrane surface and foulants including humic substances. Ozone also modified the composition of organic matter by increasing the hydrophilic fraction that is more difficult for the membrane to reject. Usual indicators describing the fouling potential of feed waters, such as the SDI for levels less than 4, cannot be used to predict membrane fouling. Therefore, 100% transfer of
SFOW to membranes is not recommended. However, transferring a maximum of 15%, which dilutes the effects of ozonated water, is conceivable.

References


