Evaluation of novel hollow fibre membranes for NOM removal by advanced membrane autopsy
A. Keucken, Y. Wang, K. H. Tng, G. L. Leslie, Kenneth M. Persson, Stephan J. Köhler and Tom Spanjer

ABSTRACT
A full-scale inside out hollow fibre membrane module was operated in a pilot-scale water treatment plant in Sweden for a period of 12 months from August 2013 to July 2014. Liquid chromatography–organic carbon detection (LC-OCD) chromatogram indicated the membranes could effectively remove 86% of dissolved organic carbon and 92% of humic substances from the feedwater. Routine cleaning-in-place was conducted to remove any fouling material accumulated on the membranes. Autopsy of the aged membrane samples after 12 months’ operation suggested no significant changes were detected for the membrane samples obtained from the top, middle and bottom sections of the membrane module and were similar to the virgin membrane sample.

Key words | LC-OCD, membrane autopsy, natural organic matter (NOM) removal

INTRODUCTION
In the southern part of Sweden, a general tendency of browning of the lakes has been noticed. The current drinking water supplies to Stockholm rely on conventional filtration (sand filters followed by granular activated carbon) and UV disinfection. The increasing colour and chemical oxygen demand (COD) in Swedish surface waters requires a more strict and reliable technique that can provide high quality drinking water. Climate change may alter natural organic matter (NOM) character, as lake turnover time has a profound impact on NOM characteristics (Köhler et al. 2013). Microporous membranes have been used widely in recent years to meet the stringent regulations, and provide climate-independent sources of high quality water (Lebeau et al. 1998, Chae et al. 2008, Tng et al. 2015). Membranes are an exceptional barrier to particles, turbidity, and microorganisms, provided that fouling of the membrane surface is kept to a minimum and the hollow fibres maintain their integrity.

Previous research has been done on identification of fouling of UF membranes during NOM removal (Combe et al. 1999; Yuan & Zydney 1999; Jones & O’Melia 2000; Lee et al. 2004), using coagulant to reduce fouling (Lin et al. 2000 and Carroll et al. 2000) and improve NOM removal and cleaning strategies (Lee et al. 2001). In addition, many membrane characterisation efforts have focused on evaluation of degradation of polyethersulfone (PES) membranes after hypochlorite treatment (Belfer et al. 2000; Thominette et al. 2006; Arkhangelsky et al. 2007; Levitsky et al. 2011; Regula et al. 2014). Most of the
studies on NOM removal, and the effects of NOM on membrane fouling were based on laboratory-scale experiments using synthetic water, or with limited time of operation (hours or days). Therefore, it is important to assess the performance of membranes using real water and over a longer period. With regard to membrane degradation studies, the accelerated cleaning approach (i.e. cleaning using a high concentration of hypochlorite for a short period of time that gives an equivalent chlorine exposure (ppm hr) as the real cleaning schedule used in water treatment plants (WTPs)) has been widely used. The current literature therefore shows a lack of data on membrane degradation and performance declines from real-time fouling/cleaning cycles.

The aim of this paper was to evaluate the performance (NOM removal, fouling, and integrity) of a commercial full-scale hollow fibre membrane module, and the feasibility of using such hollow fibre membrane filtration for high quality drinking water supply. A total of 12 months of operational data were collected from a pilot plant operated at Görvälnverket WTP, owned by the water utility, Norrvatten, which provides drinking water for the northern part of the Swedish capital of Stockholm. A suite of membrane autopsy techniques, including tensile strength test, contact angle, atomic force microscopy (AFM), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS), were performed on the aged membrane samples and virgin membranes to evaluate the integrity of the membranes after 12 months’ operation.

**MATERIAL AND METHODS**

**Pilot plants at Görvälnverket WTP**

In the context of a national research project regarding NOM removal treatment processes, an extensive pilot facility (membrane combined with granulated activated carbon (GAC)) was established at Görvälnverket WTP in Sweden for various long-term trials (Figure 1). A membrane pilot plant with a treatment capacity of 29 m³/day (14.4 m³/day permeate production) was operated from August 2013 to July 2014. The surface water source feeding Görvälnverket WTP, is Lake Mälaren, the third largest lake in Sweden. The raw water was pretreated with sand filtration before feeding the pilot plant. The pilot plant was fitted with one 8 inch commercial size membrane module (Pentair X-Flow HFW1000) with an effective area of 40 m². Details of the membranes can be found in Table 1. The performance of the test module was monitored by continuously recording transmembrane pressure (TMP) over time. Regular membrane cleaning was performed by hydraulic backwash/forward flushing (every 60 minutes). Cleaning-in-place (CIP) was carried out every four to seven weeks on a preventive basis with respect to TMP profiles to avoid irreversible fouling. CIP solution consisted of 200 ppm sodium hypochlorite in the presence of sodium hydroxide to reach a pH of 12.4.

**Characterisation of NOM in feed water and treated water**

The nature of the organics presented in the raw water to the WTP, feedwater to the pilot plant, and effluent from
the WTP and the pilot plant were characterised using UV absorbance at 254 nm and liquid chromatography–organic carbon detection (LC-OCD). LC-OCD utilises size-exclusion coupled with three detectors (organic carbon, organic nitrogen and UV-absorbance). This technique allows for subdivision of organic matter into six major sub-fractions: biopolymers, humic substances (HS), building blocks, low molecular-weight acids, low molecular-weight neutrals, and hydrophobic organic carbon. From the results, the nitrogen content of the biopolymer and the HS can be estimated. The measurement of the protein content of the biopolymer fraction allows for the amount of bound nitrogen to be determined using the UV detector, while HS can be further characterised using the HS diagram which plots the aromaticity of HS against its nominal molecular weight. Detailed information of the LC-OCD technique can be found in the paper published by Huber et al. (2011).

**Evaluation of membrane fouling and integrity**

Membrane samples were collected from top, middle and bottom sections of the module after a CIP on 9 July 2014. All samples were rinsed with deionised water and dried in a desiccator for at least 24 hrs prior to analysis.

**Mechanical properties**

Tensile strength of the membranes was measured using a TA-XT2 Tensile Analyser (Stable Micro Systems, USA).

The dried hollow fibre samples were cut into test samples of 80.0 ± 1.0 mm in length and subjected to a vertical elongation at a speed of 60 mm/min until the sample yielded and fractured. Five repeats per sample were performed and Young’s Modulus and breaking force were calculated via the stress–strain curve obtained after each test.

**Hydrophilicity**

The hydrophilicity and wettability of the lumen side (i.e. the feed side) of the membranes were determined by static sessile drop contact angle analysis method using a goniometer (KSV CAM200 Contact Angle System). The reported contact angle was the average value of the left and right side contact angles obtained for at least five different locations along the test sample.

**Surface roughness**

The roughness of both surfaces of the lumen and shell side of the membrane samples were analysed using AFM (Bruker Dimension Icon). An in-air, tapping mode, TM-AFM at 1 Hz scan rate and 512 × 512 pixel resolution, was used to collect images from a 2 μm × 2 μm scanning area with a 15.5 μm Z-range. Images presented are with a 100 nm Z-range (0 to 100 nm) and 200 nm Z-range (−100 nm to 200 nm) for lumen side and shell side, respectively. The root mean squared (RMS) roughness, \( R_q \), and the average roughness, \( R_a \), were calculated from three different sections of each sample and the average values were reported.

**Chemical degradation**

The Perkin Elmer Spotlight 400 FTIR Microscope (Perkin Elmer, USA) equipped with an ATR crystal was used to analyse and detect any degradation of the polymer material’s chemical composition due to chemical exposure during CIP. All spectra were collected with 32 scans at 1 cm\(^{-1}\) resolution from 650 to 4,000 cm\(^{-1}\).

The thermal stability of the membrane material was analysed by thermogravimetric analyser (Perkin Elmer, USA). An empty platinum pan was used as the reference for measuring the change in mass of the sample. Samples at

<table>
<thead>
<tr>
<th>Intrinsic properties of the hollow fibre membrane and module</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Membrane material</strong></td>
</tr>
<tr>
<td>Permeability (L/m(^2) hr bar)</td>
</tr>
<tr>
<td>MWCO based on PEG (Da)</td>
</tr>
<tr>
<td>o.d./i.d. (mm)</td>
</tr>
<tr>
<td>Collapse pressure (bar)</td>
</tr>
<tr>
<td>Burst pressure (bar)</td>
</tr>
<tr>
<td>Membrane area (m(^2))</td>
</tr>
<tr>
<td>Number of fibres</td>
</tr>
<tr>
<td>Module diameter (m)</td>
</tr>
<tr>
<td>Module length (m)</td>
</tr>
</tbody>
</table>
room temperature were heated up to a temperature of 600°C at a constant rate of 50°C/min in a dry nitrogen atmosphere. Variation in the thermal decomposition profiles of would help detect changes to the sample’s chemical composition.

Membrane surface morphology and foulants characterisation

A SEM (Hitachi S3400) was used to produce 2D images of the cross-section and surface (both lumen and shell side) morphology of the membranes. The elemental composition of the surfaces of the samples were analysed using EDS. All samples were sputter coated with a thin layer of carbon before SEM-EDS analysis.

RESULTS AND DISCUSSION

Membrane performance during filtration and cleaning

Membrane filtration performance of the pilot plant was monitored by continuously recording TMP and permeability over time. Figure 2 shows variation of TMP and temperature for 90 days of operation (1 January 2014–30 April 2014). During long-term trials a manual chemically enhanced

![Figure 2](https://iwaponline.com/ws/article-pdf/16/3/628/412708/ws016030628.pdf)
backwash (CEB) interval of 40 to 50 days was applied by operating the membrane pilot continuously at flux levels of 15 L/(m² h) (LMH) with crossflow velocity of 0.5 m/s, intermittent forward flushing every 60 minutes and permeate recovery rates around 50%. As shown in Figure 2(a) the TMP increased by 0.26 bar (1.47 to 1.73 bar) during an operation cycle of 38 days, while permeability (Figure 2(b)) decreased by 1.48 LMH/bar (9.28 to 7.80 LMH/bar) at low water temperatures (1 to 3 °C). During this operational period, the feedwater (i.e. sand filtration (SF) filtrate) turbidity remained at 0.059 (±0.005) Formazin Turbidity Unit (Figure 2(b)). Such low turbidity is comparable with the turbidity of microfiltration’s permeate and with the CIPs restoring the membrane’s permeability after prolonged filtration, further shows the low risk of membrane filtration of sand filter effluent for extended operating cycles. These results indicated that membrane filtration of sand filtered water allowed long filtration cycles with no risk of irreversible membrane fouling.

Characterisation of NOM

LC-OCD chromatogram suggested that NOM present in the feed water was effectively removed by the membranes (Figure 3). Raw water NOM (total organic carbon (TOC) = 8.8 ppm) consists of around 70% HS, two-thirds of which were removed in the flocculation/coagulation process (TOC after rapid SF was 4.5 ppm). Almost all remaining HS were removed during membrane filtration. Compounds smaller than HS (i.e. building blocks and LMW acids and neutrals) were also removed by the membranes. The combined process removed more than 95% of incoming TOC (average TOC after membrane filtration was 0.6 ppm).

Removal of NOM by the membranes also caused an increase in TMP. The TMP was recovered effectively after chemical cleaning (Figure 4).

The LC-OCD data can be used to quantify the contribution of HS in all water samples throughout the whole treatment steps. UV absorbance at 254 nm is tightly related to the measured content of HS (Figure 5). This is consistent with earlier findings (Erlandsson et al. 2012) and allows for quantification of the amount of HS that may be flocculated from the incoming raw water using absorbance values only. High precision measurement of absorbance in the membrane permeate will help to indicate problems with the incomplete separation of HS during membrane failure.

Data collected from August 2013 to July 2014 (Figure 6) showed that more than 85% of dissolved organic carbon (DOC) in the sand filtered water was removed by the membranes (from 4.4 to 0.6 mg/L), with less than 2% difference in removal efficiency throughout the 12 months’ operational period. HS, which accounted for 53 (±3) % of the hydrophilic chromatographic DOC, also reduced from 2.33 (±0.14) mg/L in the sand filtered water to 0.19 (±0.03) mg/L in the membrane filtrate, indicating membranes’ stable performance on the rejection of organic matters.

The extensive NOM characterisation of various water samples from the existing treatment process and the membrane pilot (Keucken et al. 2014) indicated a relationship between biopolymers and DOC. As shown in Figure 7(a) biopolymers with larger molecular weight were removed proportionally over the rapid sand filters and completely removed by the membrane module. On the other hand, it was found that the building blocks could not be removed by rapid sand filtration. The proportional retention behaviour by the membrane module is consistent with the specified molecular weight cut-off (MWCO) of the membrane (500–700 Da) (Figure 7(b)).

Mechanical properties

Tensile strength analysis and independent samples t-tests showed that the Young’s Modulus of the top and bottom were higher than that of reference (virgin membrane) sample indicating that the samples became stiffer after multiple filtration/cleaning cycles while the middle sample’s Young’s Modulus was statistically unchanged (Figure 8(a)). No significant changes in the force required to fracture the membrane were observed from the tensile strength analysis (Figure 8(b)) and subsequent t-tests showed no statistical differences in breaking force amongst the four samples at a 95% confidence interval. Thus, it can be concluded that this increase in Young’s Modulus caused by multiple filtration/cleaning cycles did not have an impact on the membrane’s mechanical strength. It should be noted that during the pilot trials, chemical cleaning was carried out using a solution of pH 12.4. A previous study by Causserand et al. (2008) suggested that no change to the mechanical properties of the membranes could be observed at this pH.
because the hypochlorite solution at pH 12 would contain hypochlorite ion (OCl⁻) only, which has less oxidising potential compared with the hypochlorous acid.

**Hydrophilicity and surface roughness**

Lumen (feed) side average contact angle increased from 62.06° (±4.51°) to 69.73° (±2.37°), 70.16° (±5.45°), and 66.56° (±4.02°) for the top, middle, and bottom samples, respectively, indicating that the membrane’s lumen surface became less hydrophilic after prolonged operation and cleaning. Comparison of the contact angle also showed that the top, middle and bottom sections had similar hydrophilicity and wettability.

An increase in lumen side surface roughness was observed for the top, middle and bottom sections when
compared with that of the reference membrane sample with the $R_q$ value, increasing from 10.6 nm for reference sample to 18.6 nm for the sample collected from the top section of the module. Bottom section samples had a relatively lower roughness ($R_q = 15.4$ nm) compared with samples from the top and middle sections. This trend was also observed for the calculated average roughness (Figure 9 and Table 2). Increase in roughness could indicate the possibility of the enlargement of pore size (Arkhangelsky et al. 2007).

An significant increase in shell side surface roughness was observed for the top, middle and bottom sections when compared with that of the reference membrane sample (Figure 10) with the $R_q$ value increasing from 23.5 nm for reference sample to 28.1 nm, 35.6 nm, and 62.9 nm for the sample collected from the top, middle, and bottom section, respectively. The shell side surface also exhibited a higher roughness than the lumen side surface, which is due to the higher porosity (Figure 10).

### Chemical degradation

The ATR-FTIR spectra of the virgin and aged membrane samples are shown in Figure 11, and the peak assignments for PES membranes are given in Table 3.

Different mechanisms of NaOCl attachment on PES membranes have been proposed, including chain scission and formation of phenyl sulfonate (Arkhangelsky et al. 2007), or the chain scission of the PES polymeric backbone into two parts with one end terminated by a sulfonic acid group and other part terminated by a phenyl chloride group (Yadav et al. 2009). None of this was observed on the current membrane samples as similar peaks were detected at their corresponding functional group's wavelengths. A significant change in the broad peak at around 3,400 cm$^{-1}$, which was the hydrogen bonding stretching vibration, was observed. This could be attributed to the residual glycerol and water in the reference sample. The
ATR-FTIR results suggested that samples were chemically identical and that no degradation to the membrane samples’ polymer material composition occurred.

The conclusions drawn from ATR-FTIR spectroscopy were cross-confirmed by measuring the changes in the mass of the sample as a function of temperature using...
TGA. The TGA profiles of the all four samples have identical decomposition profiles indicating the absence of chemical degradation of the polymer material (Figure 12). The plot of percentage mass loss as a function of temperature for all the tested samples exhibited a two-step degradation mechanism. The mass loss due to decomposition of the material started at around 450 °C, with major mass loss occurring between 500 to 560 °C followed by a second degradation stage occurring between 630 to 650 °C. The weight loss patterns for all the test samples were very similar to the reference membrane sample suggesting the absence of any potential chemical degradation of the polymer material. However, the decrease in mass was observed at around 280 °C, for the reference membrane sample, can be attributed to the residual glycerol preservative agent present in the sample, with glycerol having a boiling point of 290 °C.

**Surface morphology**

The lumen and shell side surfaces as well as cross-sections of the hollow fibre samples were microscopically analysed for any signs of damage by high resolution SEM. Not any significant defects, cracks, or deposits (foulants) were observed on the shell side surface sample (at ~×1,000 magnification) and cross-sections (at ×800 magnification) (Figure 13).

SEM images of the lumen side surface showed that the lumen surface of the top, middle and bottom samples were visibly rougher compared with the reference sample's
surface (Figure 14). This observation is consistent with the results obtained via AFM analysis. At a magnification levels of ∼×1,000, tiny cracks were observed on all samples. It should be noted that these cracks could be caused by sample preparation and were unavoidable given the necessity for the samples to be cut to expose the lumen side surface for analysis.

Table 3 | Assignment of the relevant IR bands in the range of 1,800–1,100 cm⁻¹ (Arkhangelsky et al. 2007; Beller et al. 2000)

<table>
<thead>
<tr>
<th>IR band (cm⁻¹)</th>
<th>Range given in the literature</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,642</td>
<td>1,620–1,680</td>
<td>Aromatic stretching vibrations</td>
</tr>
<tr>
<td>1,578</td>
<td>About 1,580</td>
<td>Aromatic systems</td>
</tr>
<tr>
<td>1,485</td>
<td>1,460–1,550</td>
<td>C-S stretch</td>
</tr>
<tr>
<td>1,320</td>
<td>1,310–1,350</td>
<td>SO₂</td>
</tr>
<tr>
<td>1,298</td>
<td>1,050–1,300</td>
<td>SO₂</td>
</tr>
<tr>
<td>1,241</td>
<td>1,200–1,275</td>
<td>C-O–C</td>
</tr>
<tr>
<td>1,148</td>
<td>1,120–1,160</td>
<td>SO₂ stretching</td>
</tr>
<tr>
<td>1,105</td>
<td>1,085–1,125</td>
<td>C-O stretching vibration</td>
</tr>
</tbody>
</table>
A further analysis on the elemental composition was conducted using EDS. Similar spectra with three elements, carbon, oxygen, and sulphur, were obtained for all samples analysed (Figure 15). Given that EDS detected no other elements, it can be concluded that there were neither signs of fouling on the lumen side surface of all the membrane fibre samples nor traces of CIP by-products further reinforcing the conclusion that the cracks were caused by sample preparation and not by chemical ageing.

CONCLUSIONS

A total of 12 months’ operational data were collected from a pilot plant located at Görvälnverket water treatment plant (WTP) in Sweden. The DOC removal efficiency was significantly improved by 87.8% using the hollow fibre membrane filtration when compared with the existing treatment (floculation, sand filtration and granular activated carbon) currently used in the WTP. A membrane autopsy was conducted on samples obtained from the top, middle and bottom sections of the module. Autopsy results showed that no substantial changes were detected for samples obtained from the different sections of the aged membrane.

Figure 12 | TGA profiles of membrane samples.

Figure 13 | SEM images of shell side surface and cross-sections of the hollow fibre samples: (a) shell side surface of virgin membrane; (b) shell side surface of the aged membrane; (c) cross-section of the virgin membrane; and (d) cross-section of the aged membrane.
**Figure 14** | SEM images of the lumen side surfaces of: (a) top; (b) middle; (c) bottom; and (d) reference.

**Figure 15** | EDS spectra of the lumen side surfaces.
and were very similar to the reference sample. Membrane ageing was the main cause for the minimal changes in the Young’s Modulus and the lumen surface’s contact angle. However, the effects of these changes would have an insignificant impact on the membrane’s overall integrity and performance. Therefore, it can be concluded that the hollow fibre membranes are reliable and capable of providing safe drinking water for the northern part of the Swedish capital of Stockholm.

REFERENCES


First received 19 August 2015; accepted in revised form 9 November 2015. Available online 26 November 2015