Characterization of fouled membranes from a membrane enhanced biological phosphorus removal system

Z. Geng and E.R. Hall
Department of Civil Engineering, The University of British Columbia, Vancouver, Canada, V6T 1Z4
(E-mail: zgeng@civil.ubc.ca; ehall@civil.ubc.ca)

Abstract Characterization of fouled membranes is the first step towards a good understanding of membrane fouling nature and thus formulating effective engineering measures for fouling prevention and control. In this study, fouled membrane fibres collected from a pilot scale membrane enhanced biological phosphorus removal (MEBPR) process were systematically examined. Several analytical tools, including scanning electron microscopy (SEM), conventional optical microscopy (COM), energy dispersive X-ray (EDX) microanalysis, matrix assisted laser desorption/ionization – mass spectrometry (MALDI-MS) analysis, and conventional chemical analysis techniques were used. The results indicated that membrane fouling in the MEBPR process was mainly of an organic nature, and most extractable foulants were carbohydrates and humic or humic-like substances. Unlike in other wastewater treatment membrane bioreactors, microbial growth on fouled membranes was not substantial, probably due to the vigorous aeration applied and the strong hydrodynamic conditions within the membrane pore structure. After a period of sludge filtration, membrane surfaces became more hydrophobic and the resultant hydrophobic interactions between the fouled membranes and mixed liquor constituents might have accelerated the fouling process.

Keywords Carbohydrates; EPS; humic or humic-like substances; membrane fouling; membrane enhanced biological phosphorus removal (MEBPR) process

Introduction
It is well known that membrane fouling is an inherent problem that has restricted the environmental application of membrane technologies. Understanding the characteristics of foulants and fouled membranes is crucial for exploring the nature of membrane fouling and formulating effective strategies for fouling prevention and control. Previous investigations of membrane fouling revealed that, depending on the water treated and the membrane process used, natural organic matter (NOM), biofouling in the form of microbial growth and/or synthesis of extracellular polymeric substances (EPS), and even inorganic precipitates (i.e. struvite) all could play an important role in deterioration of membrane performance (Ridgway and Flemming, 1996; Cho et al., 1998; Choo et al., 2000).

As a new application of membrane technology in wastewater treatment, the membrane enhanced biological phosphorus removal (MEBPR) process, which encompasses an anaerobic zone, an anoxic zone and an aerobic zone in series, is receiving increasing attention. However, the studies that have been initiated on the MEBPR-type processes mostly focused on the effect of membrane operation on biological phosphorus (Bio-P) removal (Adam et al., 2003). No research has been reported on the specific features of fouling in this type of membrane application. To date, it is not known whether microbial growth is significant on the membrane surfaces in the MEBPR process, just as in many other wastewater treatment membrane bioreactors. It is also unclear what material tends to accumulate on the membrane surfaces. Additionally, since anaerobic environment tends to preserve ammonia and phosphate, it is anticipated that inorganic fouling such as...
the formation of struvite (MgNH₄PO₄·6H₂O) may coexist with biofouling due to the possible accumulative effect of the anaerobic zone in the MEBPR process.

To address these research issues, membrane fouling in a pilot scale MEBPR system was investigated in this study with respect to the characteristics of foulants and fouled membranes. The objective of the study was to characterize fouled membranes, determine the extent of inorganic fouling, identify and quantify the major fouling-causing substances, and gain insight into the nature of membrane fouling in the MEBPR-type processes.

**Methods**

**The MEBPR process**

Figure 1 is a schematic of the pilot scale membrane enhanced biological phosphorus removal process utilized in the present study. The three compartments of the membrane bioreactor, i.e. the anaerobic (A), anoxic (B), and aerobic (C) compartments, operated with liquid volumes of 0.23, 0.59, and 1.31 m³, respectively. The membrane module was submerged in the aerobic compartment and the permeate was collected via a vacuum pump. Air was supplied in this compartment in a cyclic mode of 10 second ON and 10 second OFF with an aeration rate of 20–26 m³/h. The influent was from a municipal wastewater source and contained about 110 mg/L suspended solids (SS), 330 mg/L total COD, 2.7 mg/L phosphate phosphorus (PO₄-P), 26 mg/L ammonia nitrogen (NH₄-N) and 1.3 mg/L magnesium (Mg). The latter three suggested a possibility of struvite precipitation due to their relatively high concentrations.

The MEBPR experimental program was designed with two consecutive runs during the period March 2003–June 2004. In Run I, the sludge retention time (SRT) was set at 12 days and the hydraulic retention time (HRT) was 10 hours. In Run II, the SRT was unchanged but the HRT was reduced to 7 hours. The mixed liquor suspended solids (MLSS) in the aerobic zone ranged from 3.3 g/L in Run I to 4.1 g/L in Run II. Overall, the MEBPR process worked well in both experimental runs. The average concentration of total COD in the effluent was below 30 mg/L, total phosphorus below 1.0 mg/L, and ammonia nitrogen less than 0.2 mg/L.

**Membrane operation**

A custom-built ZeeWeed membrane filtration module (Zenon Environmental Inc., Oakville, Ontario, Canada) with a surface area of 11.9 m² was used in the MEBPR system. The module consisted of bundles of hollow fibres with a nominal membrane pore size of 0.04 μm. The hollow fibres encompassed two parts: an outer membrane skin and an inner fabric support. The former was made of polyvinylidene fluoride (PVDF) and its surface was neutral and hydrophilic. The membrane module was operated in a cyclic mode of

![Figure 1](https://iwaponline.com/wst/article-pdf/54/10/169/431007/169.pdf)
9 minutes and 30 seconds of suction followed by a 30 second backflushing with permeate. The flux was constant at each experimental run: 23 L/m²·h in Run I and 33 L/m²·h in Run II.

**Analytical methods**

All fouled membrane fibres analyzed in the present study were sampled from the membrane module of the MEBPR process at the ends of filtration runs at which time the biological process was operating under pseudo-steady state conditions and the maximum allowable transmembrane pressure (10 psi or 69 kPa) had been reached. Such collected membranes were thus defined as “completely fouled membranes”. They were first rinsed with deionised distilled water (DDW) to remove scum. Then, the outer membrane skin was peeled off from the inner fabric support, and both the outer skin and the inner support were cut into small pieces (≈5 mm) for the following analyses. Virgin membranes were used as a control.

**Microscopic study.** The samples for scanning electronic microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis were prepared according to a microwave SEM processing protocol (BIF, 2003). The processed slices of outer membrane skin and inner fabric support were then placed under a Hitachi S4700 SEM for high resolution imaging. To study the effect of fouling on the hydrophobicity of membrane surface, the contact angle between a water droplet and a fouled or virgin membrane surface was measured using a conventional optical microscope (COM), as described in the modified sessile drop method (Cho et al., 1998).

**Extraction of membrane foulants.** Samples of sliced membrane skin and inner support, of a total length of 1.8–2.0 m, were soaked in 9.0 mL of 0.1 mol l⁻¹ NaOH solution. After sonication (Aquasonic Model 550HT, VWR) at 40°C for 1 hour, the solution was neutralized with 3.0 mL of 0.15 mol l⁻¹ H₂SO₄. The resultant liquid was then collected as the membrane foulant extract.

**Conventional chemical analysis.** The extracted membrane foulants were analyzed in terms of such gross parameters as total Kjeldahl nitrogen (TKN), total phosphorus (TP), and total organic carbon (TOC) as described in Standard Methods (APHA et al., 1995). EPS were also measured on the foulant extract, of which carbohydrates were determined according to Frølund et al. (1996), proteins and humic or humic-like substances were quantified using the modified Lowry method (Jahn and Nielsen, 1995).

**MALDI-MS analysis.** To gain more information about the membrane foulants, the foulant extracts from both the outer membrane skin and the inner fabric support were submitted to the UBC chemistry lab for a matrix assisted laser desorption/ionization–mass spectrometry (MALDI-MS) analysis. Bruker Biflex IV, a time-of-flight mass spectrometer equipped with MALDI ion source, was used to analyze the samples, and 2,5-dihydroxybenzoic acid (DHB) and α-cyano-4-hydroxycinnamic acid (CHCA) were chosen as the matrices, respectively.

**Results and discussion**

**Surface morphology of fouled membrane fibres**

Direct examination of fouled membranes using a microscopic technique is usually the most straightforward method for exploring the nature of fouling. Figures 2(a)–(d) are SEM images of virgin and completely fouled membranes. It is evident that virgin
membrane surfaces had a relatively homogeneous, cross-linked and porous structure (Figures 2(a)). In contrast, completely fouled membrane surfaces were quite heterogeneous. As expected, bacteria were observed on the fouled membranes (Figures 2(b)). However, unlike some literature reports (Ridgway and Flemming, 1996; Liao et al., 2004), the microbial colonies were scattered sparsely and were not dominant over the fouled membrane skins. Among the many microscopic observations made in the present study, only a very few indicated bacterial growth. The majority of the membrane area was covered with a layer of material (Figure 2(c)), which had a porous structure similar in appearance to that of the virgin membrane surface (Figures 2(a)). This porous foulant layer could also be seen surrounding bacterial colonies as illustrated in Figures 2(b). The observed void space of the foulant layer seemed to be slightly less than that of the membrane substratum. This was probably because, as filtration proceeded, some of membrane pores were clogged with fine colloids or blocked with adsorbed foulants, resulting in a decrease in the total filtration area. The adjacent foulant thus accumulated, expanded and eventually covered the membrane surface, forming a porous layer of foulants under the repeated suction and backflushing. On the other hand, the vigorous aeration in the aerobic zone of the MEBPR process and the strong hydrodynamic shear conditions within the membrane module apparently made microbial attachment so difficult that only a few bacteria could adhere to the membrane surfaces.

Figure 2(d) is the SEM image of the inner fabric support of completely fouled membrane fibres. Like the outer membrane skin, the inner fabric support was also fouled after a period of filtration, as a result of frequent backflushing with permeate that contained soluble organic substances. X-ray microanalyses by SEM-EDX showed that the membrane foulants, either on the outer skin or on the inner support of membrane fibre, were mainly organic carbon compounds (Table 1). Compared to the virgin PVDF membrane, the surfaces of the two completely fouled membrane skins, which were sampled at different times, were found to contain more carbon and oxygen and less fluorine. Since the fluorine detected by EDX very likely originated from the membrane material itself (PVDF), due to
the penetration of x-rays through the foulant layer to the membrane substratum, it was deduced that carbon was the backbone element of the membrane foulants. On the other hand, struvite (MgNH₄PO₄·6H₂O), one of important foulants in the anaerobic membrane processes (Choo et al., 2000), was not detected on the fouled membranes in the present MEBPR study. Although the influent characteristics and the presence of the anaerobic environment in the MEBPR process suggested the possibility of struvite formation, the strong oxidation conditions and the Bio-P uptake mechanism in the MEBPR aerobic compartment made the PO₄-P and NH₄-N concentrations as low as about 0.54 mg/L and 0.47 mg/L, respectively, in the membrane filtration zone. These concentrations were far below the solubility product of struvite and thus did not favour its precipitation (Doyle and Parsons, 2002).

Composition of membrane foulants
The specific composition of membrane foulants was further revealed through conventional chemical analysis, and the results are presented in Table 2. It was noted that, for both pilot plant runs, the key extractable foulants were organic carbon compounds such as carbohydrates and humic or humic-like substances, which are the primary components of EPS. Nitrogen-containing compounds and phosphorus-containing compounds were present in minor amounts, and in particular, no measurable amount of protein was detected in the foulant extract. Evidently, these results are very consistent with the previous SEM examination and x-ray microanalysis. In addition, it was also concluded from Table 2 that the amounts of foulant extracted from the completely fouled membranes of the two experimental runs were approximately the same, considering the possible variation associated with membrane sampling, storage, foulant extraction and the laboratory analysis errors. This implies that the process design and operating conditions imposed here did not significantly affect the total amount of foulants that caused the TMP to reach the operating limit, or, which led to a complete fouling. One meter of completely fouled membrane fibre skin carried about 1,100–1,800 µg of carbohydrates (220–360 mg/m²)

Table 2

<table>
<thead>
<tr>
<th>Run time</th>
<th>Sample</th>
<th>Amount of extracted foulants, µg/m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TKN</td>
</tr>
<tr>
<td>Jul.9-Oct.2, 2003</td>
<td>outer skin</td>
<td>28 (17)</td>
</tr>
<tr>
<td>Run I</td>
<td>whole fibre</td>
<td>60 (9)</td>
</tr>
<tr>
<td>Mar.7-Apr.27, 2004</td>
<td>outer skin</td>
<td>78 (3)</td>
</tr>
<tr>
<td>Run II</td>
<td>inner support</td>
<td>31 (2)</td>
</tr>
</tbody>
</table>

Note: a. “whole fibre” means that the outer skin of membrane fibre was not peeled off and both the outer skin and the inner support were processed as a whole; b. “-” means that the measurement result was below the method detection limit (MDL). The MDL of TP and protein was 3 and 90 µg/m, respectively; c. The values in parentheses indicate standard deviation
and 400–800 µg of humic or humic-like substances (80–160 mg/m²) extractable in a basic solution.

**MALDI-MS analysis**

As an effective tool for mass analysis of peptides and proteins, carbohydrates, oligonucleotides, and polymers (Fenselau, 1997), matrix assisted laser desorption/ionization – mass spectrometry (MALDI-MS) was used to supplement the characterization of membrane foulants. An example of MALDI mass spectrums obtained in the present study is shown in Figure 3, in which the abundance of analyte ions (a.i.) is plotted against mass-to-charge ratio (m/z). The constant mass intervals (162) between the adjacent major peaks clearly indicated a polymer fragment with a mass of 162, suggesting that a polymeric substance was present in the foulant extract. Since most of the peaks appeared in the low m/z range (500–2,000) and no peaks with m/z exceeding 3,000 were detected, the foulants assessed by MALDI-MS were primarily polymers with small molecular weights (MW). These might be the oligosaccharides or low MW humic or humic-like substances as measured in the conventional chemical analysis (Table 2). Given that the membranes used in this study had a nominal molecular weight cut off (MWCO) of about 100,000 daltons, these detected small MW foulants were retained on the membranes not because of their molecular sizes, but as a result of other fouling mechanisms such as organic adsorption.

It should be pointed out that no protein was detected in the MALDI-MS analysis, which was in agreement with the chemical analysis results presented in Table 2. However, the extraction efficiency for organic nitrogen was only about 5–10% in this study. It must be assumed that the extraction efficiencies for other foulants may also have been modest. In this regard, the MALDI-MS technique may have been restricted by the low concentration of the foulant extract, and hence it may have been unable to reveal other important information on the membrane foulants.

**Effect of fouling on membrane hydrophobicity**

The contact angle between a membrane surface and a water droplet on the surface is indicative of the hydrophobicity of the membrane surface material. The larger the angle, the more hydrophobic the surface is assumed to be (Cho *et al.*, 1998). In the present

![Figure 3](https://iwaponline.com/wst/article-pdf/54/10/169/431007/169.pdf)
study, measurements of contact angle were performed on both virgin membranes and the completely fouled membranes sampled from different sites of the membrane module at the end of the filtration run from March 7 to April 27, 2004. The results are summarized in Table 3. The statistical analysis of the results indicated that the fouled membranes were less hydrophilic than the virgin membrane ($\alpha = 0.05$), as shown by their increased contact angles. From the previous foulant analysis results (Table 2), it is known that the extractable membrane foulants consisted primarily of carbohydrates and humic or humic-like substances. Since the former tends to be hydrophilic and the latter is essentially hydrophobic, the hydrophobicity of fouled membranes is thus determined by the combined effect of the two major constituents. As a result, the surface of the fouled membrane fibres in the MEBPR process appeared to be less hydrophilic than that of the virgin fibres after over one month of sludge filtration. This probably in turn accelerated the fouling process by facilitating the hydrophobic interactions between the fouled membrane surfaces and the hydrophobic substances in the MEBPR mixed liquor and caused an exponential rise in TMP as filtration runs progressed.

### Conclusions

Different from the observations reported for many other wastewater treatment membrane bioreactors, microbial growth on membrane surfaces was minimal in the MEBPR process studied here, and was most likely limited by the vigorous aeration applied around the membranes. Instead, the fouling in the MEBPR system was predominantly expressed as accumulation of a porous layer of substances on the membrane surfaces and in the membrane pore structures. In particular, it is characterized with the following features.

1. Membrane fouling in the MEBPR process was mainly of an organic nature. Precipitation of struvite was not found in the fouled membrane structure, probably because of the strong oxidation conditions and the Bio-P uptake mechanism in the MEBPR aerobic zone.

2. Carbohydrates and humic or humic-like substances, the key EPS components, were the major extractable foulants. A change in the operating conditions, such as a reduction in HRT, did not have significant effect on the amount of foulants that led to a complete fouling.

3. Filtration of activated sludge increased the hydrophobicity of membrane surfaces. This may have facilitated the hydrophobic interactions between the foulant layer and mixed liquor constituents that may then have accelerated the fouling process.

4. Filterable substances with small MW were able to cause membrane fouling via adsorption.

### Acknowledgements

This work was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC). Technical and financial aid from Zenon Environmental Inc., Stantec Consulting, and Dayton and Knight Ltd. is also acknowledged.

**Table 3** Comparison of contact angles between virgin and completely fouled membranes

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>Number of measurements</th>
<th>Average contact angle</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin membrane</td>
<td>8</td>
<td>51.5</td>
<td>5.6</td>
</tr>
<tr>
<td>Completely fouled membrane (1)</td>
<td>8</td>
<td>61.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Completely fouled membrane (2)</td>
<td>8</td>
<td>59.8</td>
<td>4.9</td>
</tr>
</tbody>
</table>
References