Application of nanoscale probes for the evaluation of the integrity of ultrafiltration membranes

Vitaly Gitisa,*, Roy C. Haughtb, Robert M. Clarkc, Jenny Gund, Ovadia Lev

a Department of Biotechnology and Environmental Engineering, Ben-Gurion University of the Negev, Beersheva 84105, Israel
b Water Quality Management Branch, Water Supply and Water Resources Division, National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268, USA
c Environmental Engineer and Public Health Consultant, 9627 Lansford Cr., Cincinnati, OH 45242, USA
d Laboratory of Environmental Chemistry, Faculty of Science, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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Abstract

The consequences of chemical cleaning of ultrafiltration membranes should not be interpreted solely in terms of flux recovery. It is important to evaluate the nature of the interactions between the cleaning agent and the membrane surface and to determine whether the introduction of the agent acts solely to improve the flux recovery or whether it also alters the membrane skin layer. Despite the important consequences of this information, only very limited data have been reported to date about the permeability-treatment relationships. Studies on membranes have mainly considered changes in streaming potential, FTIR spectra and hydrophobicity of the membrane surface. The present report uses an additional tool, probes of gold nanoparticles or dye-labeled MS2 bacteriophages, to trace gradual disintegration of the membrane skin layer during chemical cleaning. The new type of probe allowed us to follow two-stage deformation kinetics of the membranes during oxidative cleaning. The first stage involved the formation of holes with an average diameter of 20–30 nm, and the second stage, the rapid growth of the holes, leading to disintegration of the skin layer. The two-phase transition was followed using bubble-point measurements, ATR-FTIR spectroscopy, and SEM micrography. A second aim of the current article is to demonstrate the usefulness of a newly introduced tool—monodispersed nanoprobes—to trace membrane damage.

Keywords: Ultrafiltration membranes; Drinking water; Chemical cleaning; Nanoparticles; Flux

1. Introduction

One of the main barriers to the operation of ultrafiltration (UF) membrane processes for the treatment of drinking water is irreversible fouling by natural organic matter (NOM). Membrane fouling, i.e., the accumulation of certain constituents of the feed water on the surface of the membrane or in the membrane matrix, causes a decline in membrane flux. Four categories of membrane fouling are generally recognized according to the type of fouling materials: (a) inorganic fouling/scaling, (b) particulate deposition (collodion fouling), (c) microbial adhesion and growth (biofouling), and (d) organic molecule adsorption (organic fouling) [1]. Among these, organic fouling is believed to be the most significant factor contributing to flux decline in UF treatment facilities for water sources containing relatively high NOM. In general, the term NOM is attributed to organic compounds originating from the breakdown of organisms and plant material in the environment. Progress in instrumental analysis has enabled each detectable organic molecule in a NOM sample to be classified in terms of molecular weight into: (a) a low-molecular-weight group of small hydrophilic acids, proteins and amino acids, (b) a medium-molecular-weight group of fulvic and humic polymers, and (c) a high-molecular-weight category comprising organic polymers such as humines, polypeptides, and carbohydrates [4].

Organic fouling is governed by three main mechanisms related to both the foulant and the membrane surface: size exclusion, electrostatic forces and hydrophobic/hydrophilic interactions. The surface charge of the membrane is conferred by either ionic (-SO3−, -N(Et)3+) or ionisable (-NH2, -COOH) functional groups on its surface. Due to deprotonation of ionisable groups in the pH range of typical natural waters, most membranes appear
to have a negative net surface charge. In the case of a neutral polymeric surface, adsorption of colloids, particles, and dissolved organic matter typically carrying negative charges at the pH of natural water also results in a negatively charged surface. Therefore, electrostatic repulsion between the membrane skin and the negatively charged NOM prevents membrane fouling. At the same time, hydrophobic interactions based on van der Waals attraction between NOM and the membrane constitute a major driving force for affinity of NOM to the membrane surface. The balance between size exclusion, the electrostatic repulsion force and hydrophobic adhesion determines the outcome of membrane fouling, as well as the efficiency of chemical cleaning.

Chemical cleaning, often termed cleaning-in-place (CIP), comprises depressurization of a membrane module, followed by consecutive soaking of the membranes in solutions of bases, acids, surfactants, or oxidizing agents. Acids and bases are used to hydrolyze the foulants, and surfactants serve to solubilize the organic fouling layer for effective flushing or backwashing. A sharp pH change has not been proven to be an effective procedure to minimize organic fouling [5]; therefore, the standard procedure is the introduction of an oxidizing agent. Application of oxidizing agents serves the dual goal of depressing microbiological activity on the membrane skin layer and oxidizing the NOM, thus increasing the negative charge of the organic matter and the repulsion forces between the NOM and the membranes. Under intense conditions, introduction of oxidants such as free chlorine and hydrogen peroxide results in cleavage of the organic foulants and the generation of ketones, aldehydes and carboxylic acids. The existence of these functional groups generally increases the hydrophilicity of the parent compounds and reduces the adhesion of fouling materials to membranes. Oxidation CIP calls for optimization of the reaction time and the concentration of the oxidizing agent. More rigorous oxidation facilitates better cleaning, but it is achieved at the expense of skin layer deformation. Little is known about the interactions between membrane surfaces and the chemicals and the possible complications of these interactions. This point is worthy of attention, particularly in the light of the common practice of assessing the results of chemical cleaning in terms of the restoration of the initial flux and the decrease in trans-membrane pressure. No subsequent evaluation of membrane surface integrity is performed, and the tools for such an evaluation are limited.

As mentioned above, the search for an optimal combination of cleaning agents [6,7] and best operating conditions [8] currently relies on the recovery of flux as the main indicator of efficient cleaning. It has been found that maximizing the concentration gradients of the cleaning chemicals and using strong oxidants or extreme pH values result in better restoration of the initial flux. Thus, in practice, the concentrations of cleaning chemicals are usually as high as 0.1% NaOH and 100 ppm free chlorine. Only a few studies have addressed the adverse effects of intensive chemical cleaning on the membrane surface [9,10,11]. In these studies, data collected for virgin, fouled and cleaned membranes were compared in terms of contact angle, streaming potential and attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy measurements. Valuable information on the morphologies of virgin, fouled and clean membranes as a function of the CIP treatment may also be obtained from electron microscopy [12,13]. Most studies have found that application of cleaning agent results in a slight increase in hydrophilicity of the cleaned membrane and a slight decrease in the absolute values of streaming potential towards the isoelectric point. No significant changes in the FTIR spectra have been found, and none of the studies has reported the kinetics of deformation of the membrane skin layer following “effective” chemical cleaning.

As will be shown in the current paper, chemical cleaning is accompanied by a change in membrane surface chemistry and a gradual deterioration of membrane integrity. Application of chlorine results in the formation of holes with inner diameters comparable to those of pathogenic viruses. As was reported previously, a single integrity breach might significantly reduce the log removal value (LRV), defined as \( \log_{10}(C_0/C_{at}) \), for Bacillus subtilis and MS2 viruses [14,15]. Such a breach is barely detectable with current integrity tests, but it could certainly lead to viral contamination of tap water after extensive membrane treatment. Thus, the development of a sensitive test to assess whether a membrane module is intact or whether its integrity has been compromised is critical for membrane filtration systems. In our companion paper, we reported the development of sensitive probes for monitoring membrane integrity. Small changes in the pore size cut off of the membranes were detected by the introduction of a probe comprising either fluorescent-dye-labeled MS2 bacteriophages or a gold nanoparticle suspension [16]. In the current study on the evaluation of these nanopores, we delineated two stages in the dynamics of the deformation of the membrane skin layer. The obtained results were confirmed by SEM micrography and ATR-FTIR spectroscopy. Breaches in membrane integrity were detected as early as the first appearance of small holes with an average diameter of 20 nm. With our probes, we were able to detect an early breach at a Ct level of 5 g/L h, a value three times lower than breach detection by the bubble point method, which detected breaches only after application of an oxidizing agent at a Ct level of 18 g/L h. To detect a breach at such a Ct level with the bubble point method, we would need to apply an additional pressure of 10 bars, a value four times larger than the maximum pressure permitted by membrane manufacturers.

2. Materials and methods

Seven types of UF flat-sheet membranes of typical material and size range for UF water treatment applications were used in this study, i.e., cellulose acetate (CA-0.5, CA-5, CA-10), cellulose ester (CE-20), polyvinylidene fluoride (PVDF-55) and polyethersulfone (PES-15, PES-20). All the membranes were commercially available integrally skinned asymmetric membranes that differ in terms of their chemical and mechanical stability and of their resistance to organic fouling. The detailed properties of membranes used in the current study can be found in Gitis et al. [16].

ATR-FTIR spectra were recorded on a Nicolet spectrometer (model 5PC, Thermo Electron, Waltham, MA, USA). The ATR accessory contained a ZnSe crystal (25 mm × 5 mm × 2 mm) at a nominal incident angle of 45°, yielding about 12 internal
reflections at the sample surface. All spectra (100 scans at 4.0 cm\(^{-1}\) resolution) were recorded at 25 °C. The instrument was purged with dry nitrogen to prevent spectral interference of atmospheric moisture. Samples that had been taken from the membranes and subsequently stored in water were blotted dry with clean filter paper to remove excess liquid and dried in air and in a desiccator over P\(_2\)O\(_5\) for 2 h. The samples were then clamped to the ATR crystal.

Scanning electron microscopy (SEM) (Hitachi S-4100) on a 1 μm\(^2\) surface area was employed to visualize the degree of membrane integrity.

Flux reduction studies were performed by filtration of a solution containing 0.3 g/L bovine serum albumin (BSA, Sigma–Aldrich) at 2 bar additional pressure in the batch UF filtration unit described in the companion paper [16]. BSA is a 67-kDa molecular weight protein having an isoelectric point at pH 4.8, as measured with ZetaPlus (Brookhaven Instruments Corporation, Holtsville, NY, USA) zeta potential and particle size analyzer equipped with a 30 mW 657 nm laser (Hamamatsu Photonics K.K., Hamamatsu City, Japan). The protein was dissolved in deionized water, and the pH was adjusted to 7 with 0.01 M NaOH. The permeate flow rate was measured by weighing the permeate collected over fixed time intervals and plotting the masses against time from the start of the run.

Cleaning of the membrane was performed with commercially available bleach NaOCl (18 g/L free chlorine) at concentrations of 20, 40, 70 and 400 mg/L or with 0.3% NaOH (Frutarom, Israel). Introduction of NaOH raised the pH to 11. Oxidation with hypochlorite was performed at pH 6.8. In some tests, the pH was adjusted with dilute HCl (J.T. Baker Chemical Co., Phillipsburg, NJ) or NaOH to the desirable value. Concentration of free chlorine in the soaking solution was determined by the 4500-Cl B iodometric method I [17] using the following relationship:

\[
\text{Cl}_2 \text{ mg} \text{ as Cl}_2/\text{ml} = \frac{A \times (0.01 \times 35.45)}{\text{ml sample}}
\]

where \(A\) = ml titrating solution; 0.01 = normality of Na\(_2\)S\(_2\)O\(_3\); 35.45 = molecular weight of chlorine. Titration of the blank showed that there was no free chlorine in the deionized water.

The bubble point test was performed with the specially designed assembly shown in Fig. 1. A 20 cm × 20 cm piece of the commercial membrane under investigation was placed on a horizontal surface, and a circle was cut out with a sharp metal ring. The 3.2 cm\(^2\) round piece of membrane was placed on a 2-cm diameter metal-free filter (A-424, Upchurch Scientific, Oak Harbor, WA, USA) and held tightly between two frits (A-346, Upchurch Scientific). The liquid was introduced from the upper side of the set-up. Wetting was performed with water and a 60:40 isopropanol:water solution for hydrophilic and hydrophobic membranes, respectively. The frit assembly, held by nuts (A-510, Upchurch Scientific), was tightly screwed into a PEEK fluoropolymer body so that the Teflon tube coming out of the N\(_2\) cylinder delivered the gas straight to the membrane surface. The loose end of the tube was immersed into a 50-ml beaker filled with water so a stream of nitrogen bubbles coming through the skin layer of the membrane could easily be visualized. A pressure was applied in the range of 1–10 bars, with an accuracy of 0.01 bar, by a Precision Regulator IR2000-FO2 equipped with a digital pressure display ISE40 (both from SMC Corporation, Tokyo, Japan). The precision regulator was placed downstream of a regular nitrogen pressure regulator and nitrogen cylinder.

3. Results and discussion

Fig. 2 shows reduction in flux due to fouling of the membrane surface with 0.3 g/L BSA. The three curves on the plot are for a virgin cellulose ester membrane CE-20, and for CE-20 membranes pretreated with 40 ppm aqueous chlorine and 300 ppm sodium hydroxide. Application of a concentrated solution of sodium hydroxide resulted in an increase of the pH to 10, which is the upper limit of the chemical stability range recommended by the manufacturer [18]. Oxidation with hypochlorite ion kept pH 7.4 practically neutral. As a result of the chemical pretreatment, the flux through the precleaned membrane was higher than that of the virgin membrane. It is usually argued

Fig. 2. Filtration of BSA by clean and chemically treated CE-20 membranes.
that CIP operation results in either enhance electrostatic repulsion by a drastic change in the pH values, or in oxidation of the organic compounds into more hydrophilic residuals [9]. In the current study, an additional reason, the deterioration of membrane integrity, was also taken into account. The majority of the study was performed studying oxidation with aqueous chlorine as a cleaning agent that offers complete recovery of the initial flux [5].

Fig. 3 presents the FTIR spectrum of the initial cellulose ester membrane after it had been soaked in deionized water to remove preservatives (usually glycerin). As can be seen, practically no peaks were detected for wave numbers above 2000 cm\(^{-1}\). The spectral features of the membrane in the area of 1800–800 cm\(^{-1}\), along with literature assignment of the bands [19], are given in Table 1. The small peak at 3400 cm\(^{-1}\) was attributed to the non-hydrogen bonded O-H stretching vibration of water molecules. We believe that the residual band is due to residual water molecules retained in membrane pores. This claim is indirectly supported by analyzing the same band in the spectra of the destroyed membranes given in Fig. 4. The disintegrated membrane had a more pronounced band, which might indicate that a larger number of water molecules had been retained inside the pores.

The disintegration process was clearly illustrated by the gradual deterioration of the characteristic cellulose peaks, as shown in Fig. 5, which shows the spectra for the 800–2000 cm\(^{-1}\) region. The FTIR spectra were obtained for a clean membrane (Fig. 5a), a membrane treated with 5 g/L h NaOCl (Fig. 5b) and a membrane treated with 18 g/L h NaOCl (Fig. 5c). The initial spectrum (Fig. 5a) exhibited the following characteristic intense bands: 1760 cm\(^{-1}\) for O-C=O vibrations, 1630 cm\(^{-1}\) for O-H vibrations, 1440 cm\(^{-1}\) for CH\(_2\) symmetric vibrations, 1340 cm\(^{-1}\) for C-H vibrations, 1230 cm\(^{-1}\) for O-C=O vibrations, and 1050 cm\(^{-1}\) for C-C vibration [20]. The above-described spectra were compared with the spectrum of the initial BSA solution (Fig. 6). BSA is a heteropolymer formed by a chain of 50–500 amino acids, linked together by peptide bonds. The protein is constructed

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**Table 1** Assignment of the relevant IR bands in the area of 1800–800 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>IR band (cm(^{-1}))</th>
<th>Range given in the literature(^a) (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1780</td>
<td>1725–1750</td>
<td>Strong O=(\cdots)O vibration</td>
</tr>
<tr>
<td>1630</td>
<td>1600–1635</td>
<td>Medium O=(\cdots)H vibration of adsorbed water</td>
</tr>
<tr>
<td>1630–1670</td>
<td></td>
<td>Strong: CH(_2) stretching vibration (after oxidation)</td>
</tr>
<tr>
<td>1440</td>
<td>1440</td>
<td>CH(_3) symmetric vibration</td>
</tr>
<tr>
<td>1340</td>
<td>1340–1380</td>
<td>C=O vibration</td>
</tr>
<tr>
<td>1230</td>
<td></td>
<td>C=O vibration</td>
</tr>
<tr>
<td>1050</td>
<td>1030–1320</td>
<td>C=(\cdots)= C stretching vibration</td>
</tr>
</tbody>
</table>

\(^a\) University of Potsdam.
from just 20 amino acids, which share a common “backbone” but are distinguished by their chemically diverse “sidechains”. Each amino acid backbone contains polar amino (C-N and N-H) and carbonyl (C=O) groups with characteristic 1570–1580 and 1630–1670 cm⁻¹ bands, respectively, which give a definite indication of the presence of BSA on the membrane surface [21]. From the absence of the characteristic peaks at 1570–1580 cm⁻¹ in each of the three membrane spectra, we could assume that BSA was absent from the membrane surface and thus allocated the 1630 cm⁻¹ peak to the O-H vibrations of adsorbed water. A gradual deterioration in the intensity of the following three peaks was observed: The intensity of the peak at 1760 cm⁻¹ changed from 1.2 for the clean membrane, through 0.2 for the membrane treated with 5 g/L h NaOCl, to 0 for the membrane treated with 18 g/L h NaOCl. Similar trends were observed for the peaks at 1440 cm⁻¹ (0.1, 0.05, 0) and at 1230 cm⁻¹ (1.3, 0.2, 0). The bands are attributed to O-C=O, C-O and CH degradation vibrations. We also observed larger half-width peaks at 1630 and 1050 cm⁻¹, corresponding to the OH of adsorbed water and C=C bonds, respectively. The peak at 1630 cm⁻¹ could possibly be attributed to the carbonyl C=O group, but the resolution of the available equipment did not enable us to distinguish between C=C bonds and OH vibrations. It is thus likely that the possible pathways of cellulose oxidation include formation of various end groups, such as carboxyl COOH, aldehyde –CHO, and ketone C=O.

Changes in membrane morphology were visualized by SEM for the same type of cellulose ester membrane after the following four treatments of increasing degrees of severity: an undestroyed membrane, a membrane treated with 5 g/L h Ct contact value, a membrane treated with 18 g/L h Ct contact value, and a disintegrated membrane after exposure to 63 g/L h Ct (Fig. 7A–D, respectively). The 25 nm black spots visible in Fig. 7B may be attributed to the oxidation of cellulose by free chlorine. Further soaking of the membrane in chlorine solution resulted in partial peeling off the skin membrane layer, occurring at concentrations of 18 g/L h and higher (as depicted in Fig. 7C). The round parts on the membrane surface are attributed to the disintegrated skin layer. The complete disintegration that occurred at Ct values of 63 g/L h and higher (Fig. 7D) was visible as separate pieces of skin layer of various sizes from 70 to 200–300 nm on the membrane support. The final stage of total disintegration was also discernable visually in terms of the change of color from white to yellowish and by the peeling off the membrane skin layer. The nanoprobes described in the companion paper, i.e., gold nanoparticles and dye-labeled MS2 bacteriophages, were used to study the kinetics of membrane disintegration. Membrane integrity was compromised by soaking the membranes

![Fig. 7. Scanning electron micrographs of CE-20 membranes: clean membrane (A), membranes treated with NaOCl at Ct levels of 5 (B), 18 (C) and 63 g/L h (D).](image-url)
in hydrochloric acid solutions for various times periods. The kinetics of disintegration were studied by removing the soaked membranes from the solution, washing them for 30 min with deionized water, mounting them in the membrane cell and introducing a solution of gold nanoparticles or dyed MS2 bacteriophages. The results are shown in Figs. 8–10.

Fig. 8 presents the first set of experiments performed on polyethersulfone membrane PES-20 and on cellulose membranes CA-0.5, CA-5, CA-10 and CE-20. No detectable levels of gold were observed for the untreated membranes and for the membranes that had been soaked in the 70 mg/L free chlorine solution for 1, 2, 4, 12, or 24 h. The solution pH had been kept at constant at 7.3–7.4, ensuring equal concentrations of HOCl and OCl\(^-\) ions. After 48 h of treatment, the CE-20 membrane exhibited approximately 0.1% leakage of the gold probe solution into the permeate. At Ct levels of 5 g/L h, all four cellulose membranes showed some degree of disintegration, i.e., 0.55–1% leakage. The trend continued for all four types of cellulose membranes for cleaning intervals of 72–120 h, with the gold concentration varying between 0.6 and 1.5%. That level corresponds to 5 g/L h Ct value with first appearance of the black pinholes on the SEM micrograph (Fig. 7B). After 120 h of oxidation, corresponding to a Ct value of 10 g/L h, the concentration of gold in the permeate increased to 4–6% of the initial probe. This massive leakage was linked to the first signs of membrane disintegration depicted in Fig. 7C for 18 g/L h Ct contact value.

In Fig. 8, the areas of undetectable gold levels, a plateau of small concentrations in the permeate, and the complete disintegration of the membrane were designated as areas I–III, respectively. No signs of disintegration of the polyethersulfone membrane PES-20 were depicted. The experiments with PES-20 membrane were continued up to 50 g/L h without any detectable concentrations of gold in the permeate.

Fig. 9 presents the results of studies of the kinetics of disintegration for CE-20 membranes at different concentrations of NaOCl (Fig. 9A) and different pH levels (Fig. 9B). Application of 20 and 70 mg/L free chlorine resulted in virtually the same level of gold transition. Higher concentrations of free chlorine, such as 400 mg/L (Fig. 9A), caused faster destruction of the membrane skin layer and earlier appearance of gold nanoparticles in the permeate. Experiments performed at pH 5–7 gave almost similar results, but the pattern of deterioration was completely different for the pH 8.5 treatment (Fig. 9B). At this pH, the percent of gold nanoparticles in the permeate was consistently higher, as can be seen from Fig. 9. The observed phenomenon can be attributed to the low chemical stability of cellulose membranes at this pH value, as was already mentioned above.

A similar trend in membrane deterioration upon contact with aqueous chlorine was also observed for CA-5 and CE-20 membranes when fluorescent-dyed MS2 bacteriophages were used as the integrity probes (Fig. 10). The fluorescein-5-isothiocyanate (FITC)-labeled MS2 bacteriophages used as the probes were prepared in accordance with the procedure detailed in the
4. Conclusions

In this study, we demonstrated a new method for following changes in UF membrane integrity, which may expedite faster and more accurate measurements than those available currently. The proposed methodology provides a novel method for on-line monitoring of virus removal to comply with stringent regulations for drinking water treatment. This approach may provide a unique advantage for immediate detection of possible membrane site deficiencies. Application of the method for day-to-day operation might serve as a key to determining filtration efficiency in a particular size domain.

The established base line of filtration disintegration as a function of chemical cleaning should be expanded for various cleaning protocols and agents, acids as well as bases. Our preliminary results suggest that further investigation of membrane integrity is necessary, starting with bench-scale dead-end modules and continuing with tests of semi-pilot hollow-fiber UF capillaries driven in both cross-flow and dead-end modes.

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