Impact of chemical cleaning on properties and functioning of polyethersulfone membranes

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Abstract

In water treatment processes, membrane cleaning is of paramount economic and scientific importance. Traditionally, ultrafiltration membranes fouled with organic matter are cleaned with hypochlorite, an operation that usually results in complete restoration of the initial flux. Although the cleaned membranes are deemed suitable for continued operation, membrane integrity may have been damaged (manifested as holes in the membrane skin) by the cleaning process. To assess the degree of chemical resistance of polyethersulfone (PES)-based membranes, the membranes were fouled with bovine serum albumin and cleaned with various concentrations of sodium hypochlorite. The properties of pristine, fouled, and cleaned membranes were compared by spectrochemical analysis, mechanical testing, microscopy imaging, and streaming potential and permeability measurements. Our results suggest that cleaning does have a major impact on the performance and properties of PES membranes. Effective removal of the foulant from the membrane surface resulted in more severe fouling and increased electronegativity of the cleaned membrane. The increased electronegativity was related to chain scission of the polymer, leading to the formation of phenyl sulfonate. The deterioration in the mechanical strength of hypochlorite-treated membranes indicated a loss of membrane integrity. The transmembrane streaming potential technique provided information on membrane pore size, cleaning efficiency, and membrane integrity.

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1. Introduction

Chemical cleaning of ultrafiltration (UF) polymer membranes is a widely accepted procedure aimed at minimizing flux loss due to irreversible fouling. Although there are five categories of cleaning chemicals (caustic, oxidants/disinfectants, acids, chelating agents, and surfactants [1]), hypochlorite remains a popular choice because of its availability, reasonable price, and capacity to prevent biofouling via efficient cleaning and biosanitation. A new class of UF membranes made of cellulose triacetate (CA), polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile (PAN), or polyvinylidifluoride (PVDF) exhibit enhanced chemical resistance and, as such, they are treated with hypochlorite at water treatment facilities as a part of routine clean-in-place operations. Although the cleaned membranes are considered suitable for continued use, they may have suffered damage, which is manifested as holes in the membrane skin [2]. Previous reports on the effect of hypochlorite treatment on UF membranes indicated a flux increase in NaOCl-treated membranes [3,4]. This increase was explained by Wolff and Zydney [5] in terms of a direct relationship between membrane pore size and bleach treatment duration. Reported changes in streaming potential [6] and increased hydrophilicity of hypochlorite-cleaned membranes were considered advantageous, provided that the UF membranes do not react with the hypochlorite blends [3].

A variety of novel instrumental tools have recently been introduced to the field of UF membrane surface characterization to complement conventional flux, contact angle, and streaming potential measurements. The new techniques, which include X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and atomic force microscopy (AFM), facilitate the investigation of membrane morphology at length scales spanning a few nanometers to hundreds of micrometers [7]. XPS is a surface-sensitive technique that measures the elemental composition (except H)
and provides chemical binding information for the top 1–5 nm of the surface region. ATR-FTIR spectroscopy penetrates to greater depths (from <200 nm to >1 μm) depending on, among other factors, the incident wave number and the incident angle [8]. Although less quantitative than XPS, ATR-FTIR provides significant qualitative detail about the types of functional groups, making it a highly complementary method to XPS. AFM produces micrograph images of the membrane surface together with its corresponding physical properties, such as topography and interatomic forces.

Most membrane characterization efforts have focused on reverse osmosis membranes, and, as a result, very little work has been done on UF membranes. The scientific literature, however, does contain some preliminary reports regarding the possible deformation of UF membranes after hypochlorite treatment: chain breaking in PSf molecules after extended exposure to hypochlorite was observed by Rouaix et al. [9] and Gaudichet-Maurin and Thominette [10], and the oxidation of CA, leading to the formation of various end groups, such as carboxyl, aldehyde, and ketone, was reported by Gitis et al. [11]. There is very little information in the literature on the effect of hypochlorite cleaning on PES membranes, mainly because PES membranes are considered highly tolerant to oxidants (>250,000 mg h/L for chlorine) and to a wide pH range between 2 and 12. Among the few reports that have appeared, Wienk et al. [3] described the gradual dislodging of polyvinyl pyrrolidone (PVP), used in the initial casting of PES membranes as a pore former and hydrophilizer, but such an effect was viewed as an advantage by Qin et al. [12], who reported a five-fold increase in membrane flux and a narrowed pore size distribution after the hypochlorite treatment. Thominette et al. [13] reported a decrease in elastic elongation of PES membranes exposed to hypochlorite solution. Kuzmenko et al. [14] reported that effective oxidation with free chlorine resulted in complete restoration of the initial flux but caused more severe fouling after each cleaning. Although reports on PES membranes portray the hypochlorite treatment as a safe and recommended procedure needed to increase flux and minimize fouling, the contradictory reports on PSf and CA membranes imply that the integrity of PES membranes will be impaired, despite their stability in hypochlorite solutions.

At water treatment facilities the addition of free chlorine is performed to either prevent the biofouling by back flushing of 1 min with 2–8 mg/L of NaOCl, or to clean the membrane surface from foulants by soaking in 20–400 mg/L free chlorine for approx. 1 h. Although at treatment plant the membranes are most of the time in contact with water and just periodically with chlorine, the combined effect of oxidation can be expressed as total dose (concentration × contact time) of hypochlorite. The applicability of Ct concept to polymer oxidation was shown [2] on chlorine cleaning of CA membranes. In the current study the PES membranes were dipped into solutions containing 150 mg/L free chlorine in continuous manner and left to soak. The experiments were performed at constant temperature and pH to pertain the oxidizing potential. The chosen pH of 7.2 is that at which the concentrations of hypochlorous and hypochlorite ions are equal. As oxidizing potentials of the two are different (1.49 V versus 0.94 V, respectively) the more significant degradation in membrane properties is expected with HOCl. Recent reports [9,15] indicate that changes in pH alter the mechanical strength of UF membranes when lower mechanical strength was observed at lower pH. It was decided to perform the study in conditions where presence of both forms of free chlorine cannot be neglected.

The current study thus aims to systematically compare the physicochemical properties of pristine and hypochlorite-treated PES membranes. The main question addresses whether the gradual alteration of microscopic properties of the membrane surface, such as hydrophilicity and surface charge, affects the performance of PES membranes. The current study showed that hypochlorite treatment does, in fact, affect the performance and surface properties of PES membranes. These findings have important implications for the design of chemical cleaning protocols for PES membranes used for surface water treatment.

2. Experimental

2.1. Membrane degradation experiments

PES membranes manufactured by Sterlitech Corporation (Kent, WA, USA) and Microdyn-Nadir GmbH (Wiesbaden, Germany) with molecular weight cut-offs (MWCO) of 20 and 10 kDa, respectively, were used. The membranes were supplied as flat sheets and were stored dry under ambient conditions. The PES polymer comprises phenylene rings connected by alternate sulfonyl (SO2) functional groups and ether (–O–) linkages (Fig. 1). The sulfonyl groups confer rigidity (with a high glass transition temperature) and, together with the ring structures, chemical resistance and relative hydrophobicity. The ether linkages make the polymer less hydrophobic and more flexible, hence more amenable to processing.

The membranes were characterized by conventional techniques – measurements of flux, contact angle, streaming potential, tensile strength at break, and pore size distribution – and by XPS, ATR-FTIR, and AFM. Each piece of membrane was thoroughly rinsed with deionized water at 50 °C by shaking it at 1.66 Hz (100 rpm) on a mechanical shaker for 1 h before the experiment. The fouling experiments were performed as previously described a 150-mL stirred cell [14]. In brief, the feed comprised a solution of 0.3 g of bovine serum albumin (BSA) per liter of phosphate buffer solution (pH 7.2). The fouling experiments were performed at 25 ± 1 °C and 1 × 105 Pa (1 bar) nitrogen pressure for 30 min, i.e., sufficient time for the filtration of 50 mL of the feed suspension through the membrane.

Cleaning experiments were performed by soaking pieces of the fouled PES membranes in deionized water (MilliQ purity) containing free chlorine, 150 mg/L in Petri dishes with closed

![Fig. 1. Molecular structure of polyethersulfone.](image-url)
lids. Commercially available bleach (Unilever Best Foods Israel, 15 g/L free chlorine) was used as the hypochlorite source. The concentration of free chlorine in the stock solution was determined by the 4500-Cl B iodometric method [16]. Fresh solutions were prepared daily. Chlorination was performed at a constant pH of 7.2, corrected if necessary with concentrated HCl and NaOH solutions. The membranes were immediately rinsed with deionized water after they had been soaked for various times to give doses (concentration $C \times$ exposure time $t$) of free chlorine of 10 or 100 g h/L.

2.2. Methods of characterization

2.2.1. X-ray photoelectron spectroscopy

XPS analyses were performed with a PHI-5000C ESCA system (Perkin-Elmer) with Al Kα radiation as the X-ray source (1486 eV). The electron flood gun was operated at an energy setting of 3 eV to compensate for membrane surface charging. The membrane sample was directly pressed to a self-supported disk (10 mm × 10 mm), mounted on a sample holder, and then transferred into the analyzer chamber. The whole spectrum (0–1200 eV) was recorded four times for each sample.

2.2.2. ATR-FTIR spectroscopy

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 and subtracted from the appropriate background spectra) were recorded at 25 °C. The instrument was purged with dry nitrogen to prevent atmospheric moisture from interfering with the spectra. Samples taken from the membranes and stored in water were blotted with clean filter paper to remove excess liquid and then dried in air. Finally, to complete the drying process, they were placed in a desiccator over P$_2$O$_5$ for 2 h. The samples were then clamped to the ATR crystal.

2.2.3. Streaming potential

The streaming potential was measured in the stirred cell by pumping a KCl solution through the membrane pores, i.e., the flow was directed perpendicular to the membrane active layer (Fig. 2). To this end, the membrane cell was remodeled to include a salt bridge between the electrodes on the feed and the permeate sides of a membrane cell, in a setup similar to that used by Pontie et al. [17]. The membrane sample was placed above a PTFE spacer (0.2 mm in thickness) with the membrane skin-layer facing the flow channel (200 mm × 74 mm). The electrolyte solution was forced through the membrane by static pressure given by nitrogen. Gas pressure was set by a precision regulator equipped with a digital pressure display (IR2000-FO2 and ISE40, respectively, SMC Corporation, Tokyo Japan) at a range of 0–2 × 10$^5$ Pa (0–2 bar) and with a 0.01 × 10$^5$ Pa (0.01 bar) accuracy. The electrical potential difference was measured between the feed and permeate by opening the back-pressure valve, thus allowing the feed electrolyte to vacuum soak into a vial containing an electrode. Such a setup allows the electrodes to be kept separate from the cell and prevents the electrokinetic effects that arise from the convective hydrodynamic movement of the electrolyte near the electrode surface.

For streaming potential measurements, the membrane was equilibrated by soaking it in a 0.001 mol/L KCl solution overnight. Measurements were performed for 0.5, 1, 10 and 50 mM KCl at pressures of 0.5 × 10$^5$ and 1 × 10$^5$ Pa (0.5 and 1 bar) in the pH range 3–10.5 (at pH values higher than 10.5, the electrode is unstable; at pH measurements lower than 3, solution conductivity will be too large and will affect the measurement). Measurements were conducted with Ag/AgCl reference electrodes (model 723/733, Metrohm Ltd., Switzerland) and a high impedance digital multimeter (EDM 2347, Escort, Taiwan). The asymmetry potential of the electrode pair was less than 1 mV.

The streaming potential values for pristine and fouled membranes were calculated from four measurements for each KCl strength/pressure combination by applying the Helmholtz-Smoluchowski equation (Eq. (1)):

$$\xi = \frac{\Delta E}{\Delta P \epsilon_0 \kappa}$$

where $\Delta E$ is the potential difference across the membrane, $\Delta P$ the applied pressure, $\kappa$ the dynamic viscosity of the electrolyte, $k$ the conductivity of bulk electrolyte, $\epsilon$ the dielectric permittivity of water, and $\epsilon_0$ is the permittivity of vacuum.

2.2.4. Sieving tests

The molecular determination of UF pore size distribution was performed by measuring membrane rejection of polyethylene glycols (PEG) with different molecular weights. Solutions of PEG were preferred to solutions of dextrans or polystyrenes because of the low susceptibility of PEG to conformational variations in response to changes in temperature and pH. The
monodispersivity (the ratio of the weight-average molecular mass to the number-average molecular mass) of the PEGs is reported to be in the 1.1–1.2 range by the manufacturer (Sigma–Aldrich Co.). Additionally, polydispersed synthetic polymers such as PEG show negligible interactions with PES membranes.

A separate rejection test was performed for each of eight PEG molecules (molecular masses of 300, 600, 2000, 3350, 6000, 10,000, 20,000, and 35,000 Da, Sigma–Aldrich) and three polyethylene oxide (100, 200 and 600 kDa, Fluka GmbH, Germany) polymers. The influent polymer solution (3 g/L of deionized water) was transferred through a PES membrane at a constant pressure of 0.506625 \times 10^5 Pa (0.5 atm). The effluent concentration was determined by a combustion-infrared method on a total organic carbon analyzer Apollo 9000 TOC analyzer (Tekmar Company, Cincinnati, OH). The rejection coefficient was determined from the rejection coefficient-hydraulic radius plot, where

\[ R = \left( 1 - \frac{C_{i,p}}{C_{i,0}} \right) \times 100\% \]  

(2)

where \( C_{i,p} \) is the concentration of polymer of molecular mass \( i \) in the permeate (mg/L), and \( C_{i,0} \) is the concentration of polymer of molecular mass \( i \) in the feed (mg/L).

The Stokes radius of macromolecules that served for sieving experiments was determined from their diffusivities in a solution by using the following approximation [18]:

\[ r (\text{nm}) = 0.078 M^{0.33} \]  

(3)

where \( M \) is the molecular weight of the polymer molecule.

Pore size distribution was obtained using a log-normal probability density function [19]:

\[ f(d_p) = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left( -\frac{1}{2} \left( \frac{\ln(d_p/\mu_p)}{\ln\sigma_p} \right)^2 \right) \]  

(4)

where \( d_p \) is the pore diameter (m), \( f(d_p) \) the solute separation, \( \mu_p \) the geometric mean pore diameter (m), and \( \sigma_p \) is the geometric standard deviation of the membrane. The function parameters were determined from the rejection coefficient-hydraulic radius plot, where \( \mu_p \) was calculated as \( d_50 \) corresponding to \( f=50\% \) and \( \sigma_p = d_{90}/d_{50} \).

2.2.5. Contact angle, permeability and flux measurements

Contact angle was measured with a goniometer (Rame-Hart, CA) using the sessile drop method to determine an index of membrane hydrophobicity. In this test a \(~20\ \mu\text{L}\) drop of deionized water was placed on the dried membrane surface with a microsyringe, and the air–water–surface contact angle was measured within 10 s. Contact angle measurements were performed in triplicate using separate pieces of membrane. As a measure of membrane permeability, pure water flux was determined by filtration of deionized water for 30 min at \( 1 \times 10^5 \text{ Pa} \) (1 bar) \( \text{N}_2 \) pressure. Then the deionized water was shifted to the feed solution to carry out the experiment.

2.2.6. Atomic force microscopy

AFM images were obtained on a Dimension 3100 instrument (Digital Instruments-Veeko, Santa Barbara, CA) using silicon nitride DNP tips (Digital Instruments-Veeko) with nominal spring constants of 0.32 N/m. The contact mode was employed, which makes use of ‘hard core’ repulsive (but very short range) interactions between the tip and the surface. A strip several microns wide was first scanned in the dry state. The tip was then disengaged without moving the sample, the fluid cell was filled with water, and the same area was imaged under liquid. To obtain the closest possible correspondence between the dry and wet images, it was typically necessary to correct the lateral offset (X–Y) a few times until satisfactory correspondence was obtained. Each image represents a 0.5 \( \mu\text{m} \times 0.5 \mu\text{m} \) scan area.

2.2.7. Tensile strength at break measurement and scanning probe microscopy studies

The experiments were conducted with Universal Mechanical Tester UMT-2 (CETR, Campbell, CA, USA) at the manufacturer’s laboratories, as described in a separate publication [20].

3. Results and discussion

3.1. X-ray photoelectron spectroscopy

XPS experiments were conducted to determine the surface composition of membrane samples and demonstrate their relative changes upon chemical treatment (Fig. 3). The XPS spectrum of the pristine PES membrane (upper curve) showed that the membrane is composed of sulfur [3.7 at.\% (2p at 170 eV) and (2s at 234 eV)], carbon [50.4 at.\% (1s at 284.6 eV)], nitrogen [5.9 at.\% (1s at 403 eV)], and oxygen [37.2 at.\% (1s at 537 eV) and 1.5 at.\% (2s at 28 eV)]. Hydrogen was not included in the spectrum since XPS cannot detect hydrogen.

A well-pronounced N peak was present in the spectra of both pristine and BSA-fouled membranes, but the peak was absent in the NaOCl-treated membrane. The origin of this peak is probably the nitrogen-containing, nonionic, water-soluble polymer PVP, which is added to the original membrane blend as a spacer.
Table 1
Elemental content concentrations in pristine and hypochlorite-treated PES membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (at.%)</th>
<th>S (at.%)</th>
<th>O (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>50.4</td>
<td>6.7</td>
<td>38.7</td>
</tr>
<tr>
<td>10 g h/L</td>
<td>51.3</td>
<td>8.5</td>
<td>38.6</td>
</tr>
<tr>
<td>100 g h/L</td>
<td>52.2</td>
<td>9.3</td>
<td>38.5</td>
</tr>
</tbody>
</table>

Fig. 4. Proposed mechanism of NaOCl attack on PES membrane.

and hydrophilicity promoter. In the course of the cleaning experiments this polymer is washed as the filtration progresses, as may be seen from the absence of the N peak in the NaOCl-cleaned membrane. The slight increase in nitrogen concentration (to 7%) in the BSA-fouled membrane may be attributed to the two amine bonds in the protein structure. The spectrum of the NaOCl-cleaned membrane shows that a small quantity of chlorine was bound to the membrane surface [0.4 at.% (2p at 1.6 eV)].

An examination of the concentrations of elemental C, S, and O on the membrane surfaces indicates that in response to hypochlorite cleaning carbon and sulfur increased and oxygen decreased (Table 1). The elevated concentrations of sulfur and carbon in the upper part of the PES membrane may indicate partial scission of the sulfonyl Ph–S bond. In the presence of sufficient hypochlorite the possible mechanism is shown in Fig. 4. The reaction occurs through an intermediate step in which phenyl sulfinate PhSO$_2$ dissociates into PhSO$_2^-$ followed by the formation of PhSO$_3^-$ [21].

3.2. ATR-FTIR spectroscopy

The ATR-FTIR spectra of the pristine PES membrane and of PES membranes treated with doses of 10 and 100 g h/L chlorine are shown in Fig. 5, and the peak assignments [22] are given in Table 2. The strong bands at 1650 and 1578 cm$^{-1}$ represent aromatic bands characteristic of the PES membrane [8]. The sharp absorption peaks at 1150 cm$^{-1}$ were ascribed to the symmetric vibration of the SO$_2$ group, and the distinct peaks at 1241 cm$^{-1}$ to C–O–C vibrations. The intensity of the peak at 1485 cm$^{-1}$, attributed to C–S vibration, was lower in the chlorine-treated PES membranes than in the pristine membrane, which indicated a weakening of the C–S bond, as required by the formation of phenyl sulfonate.

3.3. Streaming potential and sieving

Measurements of transmembrane streaming potential require that conditions for the Helmholtz-Smoluchowski approximation of the Poisson-Boltzmann equation for strong electrolytes are met, i.e., that the pore size is larger than the Debye length $\kappa$. Fig. 6 shows the pore size distribution function calculated on the basis of the retention values obtained from sieving experiments. A Gaussian distribution was obtained with a hydrodynamic mean diameter of 3.2 nm and a tail for pore size values larger than 12 nm, a size usually not encountered in normal distributions. The 8 nm value was approximated as a MWCO of 20 kDa, which is the MWCO value claimed by the manufacturer (Sterlitech Corp.). The distribution displayed in Fig. 6 suggests that to obtain meaningful streaming potential values, the Debye length of the membrane pore walls should not exceed 4 nm.

For our system, the Debye length decreased exponentially from 28.5 nm at 0.1 mM KCl to 0.9 nm at 0.1 M KCl (Table 3). The 4-nm limit corresponds to a 5 mM KCl concentration, meaning that the transmembrane streaming potential should be

Table 2
Assignment of the relevant IR bands in the range of 1800–800 cm$^{-1}$

<table>
<thead>
<tr>
<th>IR band (cm$^{-1}$)</th>
<th>Range given in the literature [22]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1650</td>
<td>1620–1680</td>
<td>Aromatic stretching vibrations</td>
</tr>
<tr>
<td>1578</td>
<td>About 1580</td>
<td>Aromatic systems</td>
</tr>
<tr>
<td>1485</td>
<td>1460–1550</td>
<td>C–S stretch</td>
</tr>
<tr>
<td>1241</td>
<td>1275–1200</td>
<td>C–O–C</td>
</tr>
<tr>
<td>1150</td>
<td>1160–1120</td>
<td>SO$_2$ stretching</td>
</tr>
</tbody>
</table>

Fig. 6. Pore size distribution function of PES-20 membranes.
Table 3
Calculated values of the Debye length

<table>
<thead>
<tr>
<th>KCl (mM)</th>
<th>Debye length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>28.46</td>
</tr>
<tr>
<td>0.5</td>
<td>12.7</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>4.02</td>
</tr>
<tr>
<td>10</td>
<td>2.84</td>
</tr>
<tr>
<td>50</td>
<td>1.27</td>
</tr>
<tr>
<td>100</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The relative dielectric permittivity of KCl was taken as 70 [25].

measured with an electrolyte having an ionic strength of 10 mM or higher. Experimental confirmation was obtained from streaming potential measurements for KCl concentrations of 0.5, 1, 10 and 50 mM (Fig. 7A). Streaming potential measurements were performed at pH values ranging from 3 to 10.5. None of the four curves crossed the pH axis, probably because the isoelectric point of PES is located at superacid conditions. However, it is not possible to determine the isoelectric point under such conditions, since they do not fall within the pH range for chemical stability provided by the manufacturer. All the PES membrane samples were negatively charged, and as the pH became more alkaline, the absolute values of the streaming potential measured in 10 mM KCl increased from $-5 \text{ mV}$ at pH 3 to $-12 \text{ mV}$ at pH 10.5, in keeping with the findings of Wang et al. [23]. Since PES has no dissociated functional groups, specific ion adsorption is the only possible process for the formation of surface charge, i.e., the initial charge can be attributed to the adsorption of hydroxyl ions on the PES membrane surface.

In the pH range of 3–10.5, streaming potential absolute values obtained for 10 and 50 mM KCl solution were significantly lower than those for 1 and 0.5 mM solutions. With Debye length smaller than pore size, the membrane allows partial transfer of both chloride and potassium and ceases to function as an electronegative barrier. For 1 and 0.5 mM solutions the UF membranes exhibited charge-selective behavior and contributed to the gap in KCl concentrations between the feed and permeate sides of the membrane.

A similar set of measurements were performed after soaking the membrane samples in aqueous chlorite solutions (pH 7.2) at dosages of 20–120 g h/L (Fig. 7B). Chemical treatment increased the negative charge on the membrane. The streaming potential dropped from $-11 \text{ mV}$ for a pristine membrane to $-22 \text{ mV}$ for a membrane treated with 120 g h/L of free chlorine. A possible explanation for the increased electronegativity is the partial scission of the Ph–S bond and formation of charged PhSO$_3^-$ compounds as explained in Section 3.1. The measurements performed with 1 and 10 mM of KCl produced almost identical results, in contrast to the results shown in Fig. 7A, where the streaming potential measured with 1 mM KCl at pH 7.2 was much more negative. We therefore conclude that oxidation with hypochlorite resulted in a gradual enlargement of membrane pore size.

The enlargement was verified with solute tests and virus filtration experiments. The results of solute tests are plotted in Fig. 8 as percentage polymer retention of versus its molecular weight. A significant increase in polymer retention after chemical cleaning was observed for all the solutes starting with 3% retention of PEG with molecular weight of 200 Da. Application of 120 g/L h free chlorine resulted in 100% retention of polymers with molecular weight of 20 kDa and higher. The straight conclusion of the observed tendency is that hypochlorite treatment results in significant narrowing of membrane pores. The observation is supported by previous reports [3,12] of a tight pore size distribution after the hypochlorite treatment.

Arylsulfonate groups however are known to react with polyethylene glycols to form amorphous matrix [24]. It is pos-

![Fig. 7. Plots of streaming potential of PES-20 membrane vs. (A) pH and (B) NaOCl concentration for a pristine membrane (●) and at KCl concentrations of 1 mM (○) and 10 mM (▼).](image-url)

![Fig. 8. Solute separation of pristine and chlorine-treated membranes.](image-url)
sible that Ph-SO$_3^-$ end groups formed after the cleaning have an increased affinity to PEGs and the performed solute tests resulted in adsorption of PEGs on the membrane surface. That possibility was verified with filtration experiments performed with bacteriophages MS2, phi X 174 and T4 [18]. A significant reduction in viral retention after hypochlorite cleaning was observed. Based on viral experiments and streaming potential measurements we conclude that oxidation resulted in a gradual enlargement of membrane pore size beyond the 9 nm diameter value. As a result, we propose that streaming potential measurements with electrolytes of different ionic strengths could constitute an additional method for the characterization of membrane pore size distribution, particularly in the absence of a reliable technique for the direct measurement of pore size.

3.4. Contact angle and permeability measurements

Hydrophilicity or wettability of the PES membrane was evaluated from measurements of the contact angle between the membrane surface and the air/water interface (Fig. 9). The finding that the contact angle decreased with increasing chlorination contradicts previous assumptions [3] that dislodging the PVP would lead to increased contact angle values. Again, one possible explanation is the partial ionization of the membrane surface due to the formation of phenyl sulfonate, PhSO$_3^-$ (charged compounds are usually more hydrophilic than uncharged compounds). The increased hydrophilicity of cleaned membrane can also be explained by formation of bigger pores due to membrane degradation. Increased porosity could be responsible of spreading out of the drop by capillarity.

The initial permeability of the PES-20 membrane was $50 \pm 1 \times 10^{-5}$ L/m$^2$ h Pa ($50 \pm 1$ L/m$^2$ h bar) and increased to $60 \times 10^{-5}$ L/m$^2$ h Pa ($60$ L/m$^2$ h bar) after each chlorine treatment [14] (Fig. 10). The observed increase may be related to two parallel phenomena, ionization of the membrane surface, due to the partial scission of the Ph–S bond, and dislodging of PVP, leading to increased pore diameter. Thus, each consecutive cleaning leads to higher pure water flux and a higher degree of BSA fouling. Treated membranes exhibited an increased tendency to fouling with rising hypochlorite concentration. The moderate fouling of 10% for 1 g/L free chlorine was hardly comparable to the 30% fouling observed when the clean-in-place was performed with 5 g/L.

3.5. Atomic force microscopy

AFM images of the active surface layers of pristine and chlorine-treated PES membranes are shown in Fig. 11. Both images were taken of the same scan area of 0.5 μm × 0.5 μm. Roughness, which is calculated as the peak-to-valley distance (the distance between the highest data point and the lowest data point of the surface), was 14.5 nm for pristine and 9.8 nm for NaOCl-cleaned membranes. We assumed a direct relationship between the size of the sink leading to the membrane pore and the pore size. A bigger sink, then, probably indi-
Fig. 11. AFM images of the surface of the active layer of pristine (A) and chlorite-treated (B) PES membranes. Images are 5 μm × 5 μm.

cates a larger pore size. Although qualitative, the scans suggest that the average size of sinks in chlorine-treated membranes is larger which, in turn, may be indicative of correspondingly larger pore sizes in chlorine-treated membranes, as was observed via streaming potential measurements and virus filtration tests (Section 3.3).

3.6. Tensile strength at break measurement

As the treatment dose increased from 0 (pristine) to 50 g h/L of free chlorine, the tensile strength at break of the PES-20 membrane decreased from 16.4 to 11.6 MPa (Fig. 12); elongation at break decreased from 4.55% to 3.85%, and Young’s modulus values declined from 130 to 90 MPa [20]. The results thus indicate that membrane mechanical strength deteriorated as treatment dose increased.

3.7. Discussion

UF membranes made of PSf, PES, PVDF and CA are considered highly chlorine-tolerate. The total concentration of free chlorine that can be applied for membrane cleaning is as high as 250 g, and up to that level the membrane is considered chemically and mechanically stable. Recent reports however indicate that the membrane’s polymer structure changes upon the oxidation with free chlorine, and the alteration occurs at levels sufficiently lower than the 250 g. Two recent studies on PSf membranes [9,10] point on structural changes as total chlorine concentration reaches 1 g threshold. In one study [10] the changes of the polymer structure were linked to membrane mechanical strength, and it was shown that after 1 g free chlorine threshold the membrane mechanical strength deteriorates.

The current research indicates that the chlorine treatment of PES membranes lead to enlarged pore sizes as depicted by AFM, transmembrane streaming potential and contact angle methods; and more charged membrane as depicted by streaming potential and contact angle measurements. Our explanation of the observed is a partial scission of C–S bond that leaded to loss of polymer integrity. The microscopic changes in polymer structure were well pronounced at macroscopic levels. The mechanical strength of chlorine-cleaned membranes became lower as the total chlorine concentration increased. More significant flux drop was observed after chemical cleaning with increased hypochlorite dose.

The reported scission of C–S bond and alteration of macroscopic membrane characteristics occurred at hypochlorite concentrations falling within the safety margins recommended for UF membrane operation. Noticeably the current study was performed at rather accelerated conditions where the PES membranes were challenged with 150 mg/L HOCl, and membrane fouling was performed by filtration of solution containing 0.3 g/L BSA protein only. At water treatment plants the chlorine in the cleaning solution is primarily used for disinfection and the residual chlorine may attack the membrane material. The total of 250 g is probably addressing both disinfection and possible membrane oxidation side effect, when in our study a significant portion of HOCl was devoted toward membrane degradation. It will be desirable to determine the precise characteristics of membrane integrity and the extent of chlorine concentration that can be used for UF membrane cleaning. Without having that information the water treatment sites should periodically check for membrane integrity, and not to assume that the membrane will remain intact within the given chlorine safety margins. After all, the first signs of membrane disintegration were observed at 1 g free chlorine total [10], and at levels of 5 g chlorine total the membrane ceases to serve an effective virus removal barrier [2].
4. Conclusions

A systematic study of PES membrane degradation in bleach solutions was undertaken by comparing the properties of cleaned and pristine membranes. The results of conventional testing and of advanced spectroscopy studies indicated that the cleaning process substantially affects the subsequent performance and surface properties of the PES membrane. The chemical cleaning of PES membranes appeared to dislodge the PVP component from the membrane matrix, causing decreases in contact angle and flux values and an increase in pore size. Thus, each successive cleaning of the PES surface led to increasingly severe fouling and more significant flux drops.

Other testing methods revealed additional shortcomings of the chemical cleaning process. XPS and ATR-FTIR spectroscopy findings suggest possible chain scission of ether sulfone, with the formation of phenyl sulfonate. The resultant deterioration in the mechanical strength of chemically cleaned membranes may cause a much earlier loss in membrane integrity than that stated by the manufacturer. Although chain scission in the PES molecules affected the mechanical and textural properties of the membrane at the microscopic scale, the phenomenon was not reflected in permeability measurements. Additional microscopic tools should therefore be used to assess the degree of integrity loss.

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