Cleaning and ageing effect of sodium hypochlorite on polyvinylidene fluoride (PVDF) membrane

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Abstract
Many membrane suppliers recommend sodium hypochlorite (NaOCl) as cleaning agent. Despite the popularity of this chemical for membrane cleaning, there is still a lack of publications regarding NaOCl short- and long-term effect on fouling removal. To properly conduct this cleaning study (i.e. obtaining the required level of reproducibility and confidence), a rigorous methodology was proposed and applied in this paper. The results indicated that cleaning efficiency varied between single and cyclical (i.e. repeated fouling/cleaning cycles) cleanings: While 1% of NaOCl provided 95% efficiency in single cleaning, only 87% removal efficiency was observed during cyclical cleaning. As expected, foulant was found to be more difficult to remove during cyclical cleanings. The potential effect of NaOCl on polymeric materials ageing has drawn attention and recent studies have been dedicated to assess the impact of its exposure on numerous membrane materials. Still, the effect of NaOCl on polyvinylidene fluoride (PVDF, commonly used in membrane material for water and wastewater treatment) is discussed in limited references only. Under accelerated cleaning conditions (2% NaOCl), Fourier transform infrared (FTIR) analysis showed chemical changes in membrane functional groups of the PVDF flat sheet membrane, indicating possible ageing effect. This ageing study also revealed that PVDF membrane exhibited a two-step-degradation mechanism: first, the removal of its surface modification substance, followed by the increase of its relative hydrophilicity. These results were confirmed by X-ray photoelectron spectroscopy (XPS), FTIR spectroscopy, contact angle and hydraulic measurements.

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1. Introduction

In membrane technology in general, and membrane bioreactors (MBR) in particular, fouling remains the most significant factor limiting the cost effectiveness of their use for water and wastewater treatment. The deposition of unwanted materials on the membrane surface results in filtration downtime and higher energy requirements for membrane operation. With fouling remaining an inevitable phenomenon, membrane cleaning is generally performed regularly, even when careful design and adequate pretreatment processes have been implemented to the filtration system. Common practice in MBR, for example, is to perform weekly maintenance cleanings, and intensive cleanings every 6–12 months, with sodium hypochlorite (NaOCl) and acids as common cleaning agents [1].

The efficiency of chemical agents during the cleaning process depends on numerous parameters which could be divided into three groups: chemical properties of the cleaner (i.e. nature, concentration, pH and temperature), membranes characteristics (material, hydrophobicity, nature and extend of fouling layer) and cleaning operating conditions (duration, frequency and cross-flow velocity). Previous studies have reported the relative influence of many of these parameters on cleaning efficiency [2–13]; however, the interactions between these parameters remain more difficult to assess.

Longer duration of cleaning does not always correlate linearly with greater cleaning results and the different cleaning methods used in the industry generally result in a wide range of optimum cleaning times. In reverse osmosis (RO), increase in membrane cleaning time from 15 to 60 min showed little improvement with sodium hydroxide (NaOH), while cleaning efficiency increased by almost two fold when ethylenediaminetetraacetic acid (EDTA) was used for 60 min [4]. Depending of the nature of the cleaner, temperature has also a significant effect on the cleaning process. EDTA cleaning efficiency of RO membrane fouled by whey was doubled when the temperature was raised from 20 to 40 °C [5]. However, cleaning at high temperature may not always be possible due to membrane material limitation and/or higher energy costs [6]. Because of the complexity of the interactions between the

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parameters defining cleaning conditions, this study solely focuses on the effect of the cleaning agent concentration.

Depending on membrane materials and feed characteristics, NaOCl has been shown to provide a wide range of cleaning performances. Full flux recovery was obtained when 0.4% concentration of NaOCl was used on Norit Xiga hollow fibre membrane fouled with surface water [7]. Complete cleaning of polyethersulfone (PES) membrane used to filter bovine serum albumin (BSA) was also obtained with NaOCl concentrations ranging between 0.01 and 0.5% [11]. Other studies also investigated the efficiency of NaOCl when combined with other cleaning chemicals. For example, NaOCl, at 0.015%, was combined with sodium hydroxide (NaOH) and protease to clean polysulfone membrane fouled with soy extract at 50 °C [8]. Seventy percent of flux recovery was attributed to NaOH, while NaOCl contributed another 20% flux recovery. For polyvinylidene fluoride (PVDF) membrane fouled with biomass, 0.05% NaOCl mixed with NaOH as part of the alkali treatment, followed by nitric acid (HNO₃), resulted in 77% flux recovery [9]. Recent publication found that 0.1% NaOCl provides the best result for MBR cleaning when compared to different enzymes, acids and hydrogen peroxide [10].

So far, no study has appropriately investigated the optimum operating conditions for which NaOCl would provide the best cleaning effect on membranes. This is partly due to the small number of rigorous methods used in membrane cleaning studies, for which the characteristics of the membrane before and during the filtration and cleaning periods have to be closely assessed and monitored [14]. Before the cleaning process itself, it is crucial for the new membranes and for the fouling protocol to be fully characterized and for the hydraulic performances to remain within a reasonably small range from one experiment to another. As a result, the various chemical cleaning protocols can be applied on membranes of similar characteristics, and the efficiency of the cleaning could therefore be properly assessed on the same baseline. Only then, can the reproducibility of the fouling/cleaning experiments be fully assessed, legitimizing the study.

There are also insufficient reports on the cleaning efficiency of chemical agents (NaOCl in particular) during repeated fouling/cleaning cycles; and it is expected that the cleaning efficiency of NaOCl may shift after a number of cleaning episodes. In this paper, results from a rigorous study will be presented for the assessment of the optimum NaOCl cleaning concentration in both single and multiple cycles.

Although widely used as membrane cleaning agent, NaOCl has been long suspected to cause harm to the membrane [15–20]. The oxidizing properties of NaOCl and its elevated working pH have the potential to damage membranes over their lifetimes. A number of publications have been dedicated to the investigation of the ageing effect of NaOCl on membranes. For example, polysulfone membranes exhibited some damage, following NaOCl treatment, as evidenced by enlargement of the membrane pores and lower membrane elongation [18–20]. Studies by Kwon and Leckie [17] and Arkhangelsky et al. [16] show that NaOCl treatment caused chlorination and changes in hydrophilicity in polyamide RO membranes. Increasing membrane surface hydrophilicity due to NaOCl cleaning was also reported for polyether sulfone (PES) material [16–17,21]. However, chemicals agents are not always the culprit. An autopsy of ultrafiltration (UF) membrane from wastewater treatment system showed that the membrane damage and rapid fouling was caused by mechanical forces rather than halogen attack [22].

PVDF membrane is widely applied in membrane industry, especially for MBR applications. One of the aims of this study is to observe the changes occurring in PVDF membrane properties due to ageing and its effect on membrane hydraulic performances. Ageing was first performed through membrane soaking in NaOCl solution and high concentration was chosen to accelerate the study. Other factor, such as temperature or pressure, which may impinge on membrane ageing, was not investigated in this study.

2. Methods and materials

2.1. Membrane and ageing procedure

In this study, Durapore® membrane was used (flat sheet PVDF from Millipore™ with nominal pore size of 0.22 μm). During the ageing experiment, the membrane was soaked in 1% NaOCl solution for period of 1–21 weeks. NaOCl (originally at 12.5%) was obtained from Ajax Finechem Pty Ltd. Iodometric titration was performed to assess NaOCl concentration. Due to NaOCl concentration deterioration over time, the ageing solution was changed every 2 days to maintain constant concentration. After the ageing process, the membrane was washed with MilliQ water and its resulting hydraulic resistance was measured.

2.2. Filtration and cleaning

Filtration was performed using a cross-flow module with, channel height and width of 2.5 and 0.25 cm, respectively; the membrane effective area was 27.5 cm². Before the beginning of filtration, initial resistance of the membrane (Rm) was measured by clean water test. Filtration runs were performed under constant flux of 30 L·m⁻²·h⁻¹ until trans–membrane pressure (TMP) of 50 kPa was reached. The model solution was prepared with 3.5 g/L of sodium alginate and 2 g/L of BSA for the single cleaning, and 1 g/L of alginate + 1 g/L of BSA for the other experiments. Flow rate of the feed was 0.11 L/min. These model solutions and operating conditions were chosen to allow accelerated fouling of the membrane. After filtration, rinsing was performed for 2 min using MilliQ water with the same flow rate as the feed. Cleaning was then carried out for 10 min using 1% of NaOCl. A further water rinsing (4 min) was conducted after the cleaning step to remove the residual foulant and cleaning agent. Clean water tests were performed after the filtration, rinsing and cleaning steps to assess the hydraulic resistances of the fouled, rinsed and cleaned membranes (Rfouled, Rsed., and Rcleaned), respectively. Cleaning efficiency was calculated as described in Eq. (1):

\[ \text{Overall cleaning efficiency (OCE)} = \frac{R_{\text{fouled}} - R_{\text{cleaned}}}{R_{\text{fouled}}} \times 100\% \]  

(1)

The average and standard deviation values obtained during the repeatability tests are reported in Table 1. The presented data were obtained from 23 runs using 3.5 g/L of alginate and 2 g/L of BSA in the feed solution. Rm of virgin membrane was found to be 6.8 ± 0.8 × 10¹⁰ m⁻¹. Fouling increased the membrane resistance approximately tenfold of its initial value, while rinsing process reduced around 20% of the resistance increase (Table 1).

2.3. Characterization methods

The ageing effects of the cleaning agent on the membrane were analysed with different techniques. Attenuated total reflection (ATR)–Fourier transform infrared (FTIR) spectroscopy with

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average</th>
<th>Standard deviation</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_m) (10¹⁰ m⁻¹)</td>
<td>6.8</td>
<td>0.8</td>
<td>12</td>
</tr>
<tr>
<td>(R_{\text{fouled}}) (10¹⁰ m⁻¹)</td>
<td>71.6</td>
<td>8.7</td>
<td>12</td>
</tr>
<tr>
<td>(R_{\text{sed.}}) (10¹⁰ m⁻¹)</td>
<td>58.8</td>
<td>5.3</td>
<td>9</td>
</tr>
<tr>
<td>Fouling duration (min)</td>
<td>52.9</td>
<td>7.5</td>
<td>14</td>
</tr>
<tr>
<td>Rinsing efficiency (RE) (%)</td>
<td>17.8</td>
<td>2.9</td>
<td>16</td>
</tr>
</tbody>
</table>
diamond window was used with spectra recorded between 400 and 4000 cm\(^{-1}\) (Nicolet 5700—Smart Orbit, Thermo Scientific). Sample was vacuum dried to eliminate water molecules which may interfere the IR reading. X-ray photoelectron spectroscopy (XPS, Escalab220i-XL, Thermo Scientific) was also used to identify the chemical changes within the membrane (C1s = 285.0 eV was used as energy reference). Physical changes were observed by field emission scanning electron microscope (FESEM) (Hitachi S900). Sample was vacuum dried and chromium coated prior to imaging process. Membrane pore size was measured using capillary flow porometer (Porous Material, Inc) with the sample being vacuum dried prior to analysis. Contact angle (KSV, CAM200) was performed by sessile drop technique on humid sample to assess membrane hydrophilicity. Preliminary analysis indicated that no significant change was observed in terms of contact angle measurements between dry and humid samples.

3. Results and discussions

3.1. Assessment of cleaning efficiency

3.1.1. Single cleaning

The cleaning efficiency of NaOCl on the fouled membrane was assessed over a wide range of concentrations (0–5 g L\(^{-1}\)). Each test was conducted with a new membrane filtering alginate/BSA under controlled environment. Results indicated that membrane cleaning by water rinsing (i.e. no NaOCl) was responsible for the removal of 43% of the hydraulic resistance due to fouling (Fig. 1). With 0.01% NaOCl, the resistance removal increased to 64% and larger cleaning efficiencies were obtained for higher NaOCl concentrations. As expected, higher concentrations of NaOCl showed higher ability to oxidize and remove foulants from the membrane. Within the investigated concentration range, maximum cleaning efficiency reached 95% with 1% NaOCl. Higher concentration (5%) did not improve the cleaning efficiency; it even led to slightly lower efficiency of 93%.

The optimum NaOCl concentration of 1% obtained in this study can be considered to be relatively high compared to the recommendations given for most of membrane cleaning applications; yet this was not enough to fully recover the membrane initial resistance value (\(R_m\)). This could have been caused by the high concentration of feed solution being used. Previous study using NaOCl indicated flux recovery up to 104% [11] with BSA 0.3 g/L as feed solution for PES membrane. In the present study, the BSA concentration alone was 2 g/L (plus 3.5 g/L of alginate), which could explain the more severe fouling observed. NaOCl acts as an oxidizer and foulants on the membrane were chemically degraded by NaOCl, which were then removed from the membrane surface by the aid of the continuous cross-flow of the solution.

SEM pictures of cleaned membranes were taken to observe potential changes on membrane surface due to NaOCl cleaning (Fig. 2). Large flocs of fouling materials could be observed in the membrane cleaned by water only, indicating the limited efficiency of rinsing. A lesser amount of foultant was visible on the membrane cleaned with 0.05 and 0.3% of NaOCl. For membrane cleaned with 1% NaOCl, most foulant seems to have been removed from the surface, explaining the 95% cleaning efficiency. Foulant left in the membrane was most likely located inside the pores and were not characterized by SEM observation.

3.1.2. Cyclic cleaning

Consecutive cleanings of flat sheet PVDF membrane were carried out to assess the effect of repetitive cleaning cycles on the membrane hydraulic properties and structures. In these experiments, model solutions were used at a lower concentration (1 g/L alginate + 1 g/L BSA) compared to previous single cleaning experiments. Lower concentration of foulants was expected to result in longer filtration time before the system reaches the critical TMP of 50 kPa, indicating the end of the run. Fig. 3 shows the overall cleaning efficiencies (OCEs) for membrane with cyclical cleanings. OCE was obtained by comparing \(R_m\) and final \(R_{cleaned}\) after four cycles. Similar to the trend obtained in the single cleaning (Fig. 1), higher concentration of NaOCl provided better cleaning efficiency, with 0.01% of NaOCl resulted in an OCE of 48%. The OCE values increased until the optimum value of 87% was reached with 0.5% of NaOCl. Higher concentration of NaOCl (1 and 2%), did not produce higher OCE. This shows that in longer run, 0.5% of NaOCl was sufficient to provide optimum cleaning.

For a given NaOCl concentration, the cleaning efficiency values obtained during the individual cyclical cleaning experiments were constantly lower than those of single cleaning, except for 0.5%. In the case of the 0.1% NaOCl for example, cyclical and single runs resulted in OCE of 71 and 80%, respectively. It is important to mention that, although higher concentration of foulants was used in the single cleaning trials, better cleaning performances were obtained in those tests. This is probably due to the short time required for the filtration system to reach the TMP critical value of 50 kPa, which was 53 min in average. During this small filtration time, fouling is expected to only weakly attach on the membrane and not to participate to significant pore blocking. These results therefore revealed the more strongly attached fouling layer building up over consecutive filtration/cleaning cycles. Not only the remaining fouling materials from the previous run may accelerate the formation of further deposition, but the consecutive filtration episodes may participate to fouling compaction, making the layer denser and more difficult to remove.

The FTIR spectroscopy was performed to analyse the changes in the function groups of the membrane resulting from the membrane interactions with NaOCl and the foulants (Fig. 4). Each peak illustrates a specific type of molecular vibration (i.e. symmetric, asymmetric, twisting, wagging, bending, or rocking) [24].

Table 2 reports the identification of the main chemical groups detected in Fig. 4, some of them being spectrum specifically characterising PVDF material. The FTIR spectra were analysed with the high resolution Hummel polymer and additives spectrum library (software available with the FTIR program) and indicated
that approximately 76% of the spectra matched with PVDF for all samples. This confirmed the overall membrane nature and also revealed the presence of additional chemicals used as membrane coating agents. Peaks at 1069 and 1401 cm\(^{-1}\) represent CH\(_2\) wagging while the 838 cm\(^{-1}\) peak characterises “CH out of plane and deformation and CH\(_2\) rocking” [25]. Spectra at 763 cm\(^{-1}\) originates from PVDF skeletal bending, while 795 and 840 cm\(^{-1}\) result from CH\(_2\) rocking [26]. These specific peak values slightly vary from a study (i.e. 767, 796, 855, 978, and 1072 cm\(^{-1}\) in [27]) to another (i.e. 764, 795, 839 and 976 cm\(^{-1}\) in [26,28]). However, most of the membranes tested in this study provided similar peaks with slight differences in the percentage of reflectance. The membrane cleaned with 2% NaOCl was the only sample for which the 1729 cm\(^{-1}\) peak was not clearly detected.

Peak at 1729 cm\(^{-1}\) represents the carbonyl group (C=O), which could originate from polyvinylpyrrolidone (PVP). PVP has been studied as additive in various membrane fabrications [29–35] and has been found to increase membrane hydrophilicity [30,34]. When
added to PVDF material, PVP is expected to bond through H-F elimination, nucleophilic addition and hydrogen interaction, resulting in the attachment of −OH group and the substitution of an −F group [32]. The carbonyl group could also originate from proprietary additives used by the membrane manufacturer. A patent made by Wang [36] for Millipore™ stated that membrane hydrophilicity was increased by the creation of an interpenetrating polymeric network using crosslink hydrophilic resin. Suitable monomers used for the hydrophilic resin included hydroxyalkyl acrylates or methacrylates [36], all featuring carbonyl and hydroxyl groups [37–38].

With Millipore™ membrane being used in this study, the carbonyl is more likely to derive from polyhydroxyacrylates or methacrylates instead of PVP, and more advanced analysis would be required to confirm the exact nature of the hydrophilic modifier substance. Still, the damaging effect of the cleaning agent on the membrane chemical properties was clearly revealed during the cyclical cleaning test, through the elimination of C＝O, and will be studied in details in the following section.

3.2. Ageing effect of NaOCl

To assess the ageing effect of NaOCl, the analysis of aged membrane was conducted and divided into two sections. Firstly, the membrane filterability was analysed through the assessment of the membrane hydraulic performances. Secondly, changes in the chemical and physical characteristics were characterized by FTIR, XPS, contact angle and pore size measurement.

3.2.1. Changes in membrane filterability

The effect of membrane ageing due to NaOCl in membrane filterability was assessed in terms of intrinsic membrane hydraulic resistance (Rm) for the membranes aged up to 18 weeks (Fig. 5). The initial Rm values for membrane batch used in the ageing test averaged $5.2 \times 10^{10}$ m$^{-1}$ for virgin membrane, and significantly increased up to $188 \times 10^{10}$ m$^{-1}$ after 2 weeks of ageing. After 4 weeks of ageing, Rm decreased and continued to decline until it reached $4 \times 10^{10}$ m$^{-1}$ at 18 weeks ageing. The Rm values for membranes aged more than 11 weeks were consistently slightly lower than those of the virgin membrane.

In a second series of experiments, the aged membranes were used in consecutive fouling/cleaning cycles, identical to those reported in Section 3.1.2. The OCE values calculated at the end of the four cycles are reported in Fig. 6. The repetitive use of NaOCl on the aged membrane (now fouled by BSA and alginate) resulted in significant changes in cleaning efficiencies. Non-aged membrane cleaned with 1% NaOCl resulted in 98% OCE. However, for 2-week-aged membrane, the OCE value decreased to 49%, before increasing...
for membranes aged longer than 2 weeks. The similarity in the pattern implied that changes in \( R_m \), which were caused by the ageing process, also affected membrane OCE. Membranes aged from 1 to 6 weeks showed fluctuating pattern of OCE, which might be caused by the initial changes in hydrophilicity and elimination of the surface modification substance. However, after few weeks of ageing, the membrane seems to reach stable condition as the OCE values were relatively constant from week 11 onwards.

### Table 3

<table>
<thead>
<tr>
<th>Ageing duration (weeks)</th>
<th>Total C (%)</th>
<th>Total O (%)</th>
<th>Total F (%)</th>
</tr>
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<tbody>
<tr>
<td>New</td>
<td>57.7</td>
<td>12.6</td>
<td>29.7</td>
</tr>
<tr>
<td>1</td>
<td>53.1</td>
<td>4.7</td>
<td>42.2</td>
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<td>2</td>
<td>51.2</td>
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<td>46.1</td>
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<td>7</td>
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<td>1</td>
<td>49.6</td>
</tr>
<tr>
<td>18</td>
<td>51</td>
<td>0.4</td>
<td>48.6</td>
</tr>
<tr>
<td>21</td>
<td>50.1</td>
<td>1.3</td>
<td>48.7</td>
</tr>
</tbody>
</table>

3.2.2. Changes in membrane chemical and physical characteristics

Table 3 shows the XPS results of the virgin and aged membranes. Virgin membrane contains carbonyl groups in addition to common PVDF elements which are carbon (C) and fluorine (F). For 1-week-aged membrane, there was a significant decrease in peak intensity of O from 12.6 to 4.7%. This number decreased further to 2.7% for 2 weeks ageing. With longer ageing duration, the peak intensity for oxygen (O) was decreased to 1% or less, implying the elimination of the carbonyl groups.

As mentioned before, some of these groups belong to the surface alteration substances used by the manufacturer to make the membrane more hydrophilic [36–38]. Therefore, XPS results confirmed that after NaOCl ageing, the surface modification substances were eliminated. To further support this hypothesis, contact angle measurements were performed with humid samples. Since the ageing process was found to eliminate surface alteration substances, membrane hydrophilicity was expected to decrease (Fig. 5). Virgin membrane was found to have contact angle of 29° and contact angle value for 1-week-aged membrane slightly decreased compared to virgin membrane. However, for 2-week-aged membrane, contact angle increased more than twice to 65°, which implies that the membrane became significantly more hydrophobic. From this point, contact angle decreased with increasing ageing time until it reached 8° for 21 weeks. Except for 1-week-aged membrane, the trend obtained in those tests matched the finding from resistance value. Following the rapid removal of the surface modification substance, NaOCl treatment was responsible for the consecutive increase of the membrane hydrophilicity.

Two consecutive phenomena caused by NaOCl treatment were proposed in order to explain the observed changes in \( R_m \) values. A fraction (or the whole) of the coating agent used by the membrane manufacturer was first removed from the polymeric surface, making the membrane highly hydrophobic, resulting in the observed increase in \( R_m \) values. Then, the membrane hydrophilicity increased resulting in the decrease in \( R_m \), during the ageing period of 3–18 weeks. Previous studies of ageing and cleaning have shown that the hydrophilicity of PES membranes was increased with NaOCl treatment, which resulted in partial ionization of membrane surface and pore enlargement [16,21]. Membrane cleaning by NaOCl was also found to cause increase in hydrophilicity of polyamide membrane [17]. In this same study, hydrophilicity was observed to increase as NaOCl concentration was raised from 0.1 to 2 g/L. To investigate this hypothesis, further analyses were performed to examine the physical and chemical characteristics of the membrane.

FTIR spectroscopy was performed to further assess the changes occurring in the membrane functional groups. Results obtained during the ageing testing (Fig. 7) were similar to those previously reported in Fig. 4, and most of the peaks (apart from the 1729 cm\(^{-1}\), carbonyl peak) were still present after 18 weeks of ageing. The carbonyl peak indeed disappeared within the first week of ageing at 1% NaOCl. This can be compared to the behaviour obtained for the four fouling/cleaning cycles carried out at 2% NaOCl (Section 3.1.2). During these ageing experiments, chemical modification was observed in the early stage of ageing and extended contact time between the membrane and the cleaning agent did not seem to significantly affect the membrane function groups any further.

Besides the loss of the carbonyl peak, a weak hydroxyl peak can be observed in the virgin and 1-week-aged samples at roughly 3300 cm\(^{-1}\) (Fig. 7). These functional groups most likely impart the hydrophilic character to the PVDF membranes. As these functional groups are destroyed, the membrane becomes more hydrophobic, as seen by the increase in the contact angle measurements in Fig. 5. Thus, the increase in contact angle can be directly linked to the loss of the hydrophilic modifiers to the PVDF surfaces due to the ageing process.

In addition to chemical changes of the membrane, the mean pore diameters of the aged membranes were measured to examine any changes of pore sizes due to the ageing process. Analysis was performed using capillary flow porometer and the results can be observed in Fig. 8. The results obtained showed that new membrane has an average pore of 0.187 μm (lower than the pore size value given by the membrane supplier at 0.22 μm). Pore size was increased to 0.211 μm for 1-week-aged membrane, and the value decreased after 2 weeks of ageing to 0.162 μm, which was smaller than new membrane. For ageing of 4 and 6 weeks, membrane pore size experienced increase to 0.193 μm. Comparing pore sizes of new membrane, membrane aged for 2 weeks, and membrane aged for 4 and 6 weeks, the trend followed previous hypothesis of the loss of hydrophilicity. The decrease of the pore size might again be due to elimination of the surface modifier. As the hydrophilic surface modifier is destroyed, due to the ageing process, voids and gaps in the membrane surface would occur yielding increases to membrane porosity and surface heterogeneity. Initially, this could result in a lowering of the average pore size, and according to the Wenzel equation [39] which relates the surface composition and heterogeneity to that of the contact angle of the material, result in a further increase in the contact angle of the membrane. However, as significantly more modifier is destroyed, the pore size will increase so that now capillary flow will increase, for contact angles less than 90°, and the overall resistance of the membrane will decrease, trend that

![Fig. 7. FTIR spectrum for virgin and aged (from 1 to 18 weeks) membranes.](image-url)
are observable in Fig. 5. Thus, the deterioration of the hydrophilic additives of the PVDF membrane material by NaOCl during the ageing process is responsible for both the initial resistance and contact angle increase and subsequent decrease after 2 weeks of ageing.

4. Conclusions

Based on the presented results, it can be confirmed that NaOCl is able to remove most of the irreversible fouling on the membrane. Higher concentration of NaOCl resulted in larger cleaning efficiency until an optimum value is reached. Optimum cleaning concentration depends on the type of foulant, membrane material and operating conditions of the filtration and cleaning. In this study, optimum cleaning for single cleaning was achieved with 1% NaOCl, resulting in 95% OCE.

Cyclical cleanings were performed to analyse the effect of repetitive NaOCl exposure on membrane performances. There was no significant difference between fouling durations of cycles one to four. This indicated that there was no interaction between residual foulant and the membrane which fastened consequent fouling. From the OCE data, 0.5% of NaOCl was found to provide the highest cleaning efficiency. It appeared that residual foulant was more difficult to remove in cyclical filtration. At high concentration of NaOCl (2%), FTIR spectrum showed that the surface modification substance used in membrane manufacturing was eliminated, indicating the ageing effect of NaOCl on the PVDF membrane.

Ageing process was also demonstrated by the decrease of the hydraulic resistance following NaOCl treatment. XPS and FTIR analysis showed that NaOCl eliminated the surface modification substance from the membrane. For room temperature ageing, total analysis showed that NaOCl eliminated the surface modification substance from the membrane. Following NaOCl treatment, XPS and FTIR showed that the surface modification substance was obtained after 2 weeks. Following NaOCl treatment, XPS and FTIR showed that the surface modification substance was obtained after 2 weeks. Following NaOCl treatment, XPS and FTIR showed that the surface modification substance was obtained after 2 weeks. Following NaOCl treatment, XPS and FTIR showed that the surface modification substance was obtained after 2 weeks. Following NaOCl treatment, XPS and FTIR showed that the surface modification substance was obtained after 2 weeks.

Results showed that NaOCl could cause ageing on membrane after prolonged exposure and changes in membrane chemical groups, hydraulic performances, mechanical properties and physical structures were observed. Considering the high NaOCl concentration and long ageing duration applied in this study, it could be concluded that the PVDF membrane tested remained reasonably resistant to NaOCl ageing. Nevertheless, continuous contact with this cleaning agent was capable of reducing the membrane initial hydrophobicity.

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