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A systematic assessment method for the investigation of the PVDF membrane stability

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ABSTRACT

This article reports the systematic assessment method for membrane stability using a hydrophilic polyvinylidene fluoride (PVDF) membrane. In this study, bovine serum albumin, fouled PVDF flat-sheet membranes were cleaned with sodium hydroxide (NaOH) and sodium hypochlorite (NaOCl). The effects of repeated chemical cleaning on membrane water flux recovery and the PVDF membrane intrinsic properties were investigated. The virgin and cleaned membranes were characterised by water flux measurement, field emission scanning electron microscopy, tensile test, Fourier transform infrared, contact angle measurement and protein rejection performance. As expected, higher cleaning efficiency was achieved when using higher concentration and extended cleaning time with NaOCl showing better performance compared to NaOH. It was found that the use of chemical cleaning agent for fouling control has an impact on membrane integrity and shortens their lifespan. Their declining functionality is normally associated with ageing; a term meant to describe changes in physical parameters and a declined stability.

Keywords: PVDF membrane; Stability; NaOH; NaOCl; Degradation

1. Introduction

Water and wastewater treatment is essential to produce clean water that is harmless for human use as well as for industrial applications. The removal of contaminants, such as suspended solids, bacteria, viruses, minerals (heavy metal components) and other chemical pollutants such as dyes, is compulsory to guarantee the high quality of water that could be safely released to the environment and consumed by humans [1–3]. Various methods have been applied to treat water, such as coagulation, flocculation, adsorption with activated carbon or biosorbent, electrochemical methods and filtration process [4–6]. The increasing demand for fresh water supply and more efficient water treatment method drove the development of new technology. Today, membrane technology has developed to become the most preferable method for separation processes. Its application could be found in gas separation, non-dispersive gas absorption, general filtration process, purification and fractionation processes, seawater desalination and others [7,8].

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Membranes should possess excellent mechanical strength, thermal stability and chemical resistance, which depend on the material of construction. In recent years, polyvinylidene fluoride (PVDF) appeared as a favourite membrane material given by its excellent properties, such as high mechanical, chemical and thermal stability [9,10]. Nowadays, the hydrophilic PVDF membrane is used in micro and ultrafiltration separation, for example in pharmaceutical industries, water or wastewater treatment, food and beverage industries and others [11–13]. This is mainly due to various advantages, such as low cost, good flux, low energy consumption, range of pore sizes, simple up-scaling and the continuous separation ability [14–16]. However, fouling is inevitable during the membrane filtration even though various fouling control measures had been taken. Membrane cleaning is the primary method to restore membrane flux and permeability, and has been considered as a must to extend membrane lifespan. There are several types of membrane cleaning, such as physical and chemical cleaning [17,18]. Physical and chemical cleaning is used to remove reversible and irreversible foulant, respectively. Until now, sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) are the two most common cleaning agents to help recover membrane water flux due to their availability, economical price and relatively high efficiency [8,19–23].

The exposure to harsh chemical environment has long been suspected to be detrimental to PVDF [24]. Several researchers have reported the vulnerability of PVDF membrane towards alkaline environments, though their main intention is to study the degradation mechanism [25–28]. In our recent study, we too showed that the effects of alkaline environment towards PVDF membrane properties could be observed upon exposure to a mild condition [21]. Not until recently, a more comprehensive study on the effects of chemical exposure towards membrane characteristics has attracted significant attention. Previously, the effects of membrane cleaning towards PVDF membrane was mainly discussed in terms of their flux recovery with less detailed assessment on the alteration in membrane properties. Other factors, such as physicochemical properties of the membrane, should also be investigated in order to completely understand the impacts of chemical exposure towards the stability of PVDF membrane. A number of analytical tools are currently available that could be used to detect, assess and understand the degradation process, and the changes in membrane integrity. Most of these techniques are destructive in nature and are adopted in laboratory-scale studies to explain the fundamentals of membrane degradation and to assess membrane integrity post membrane operation.

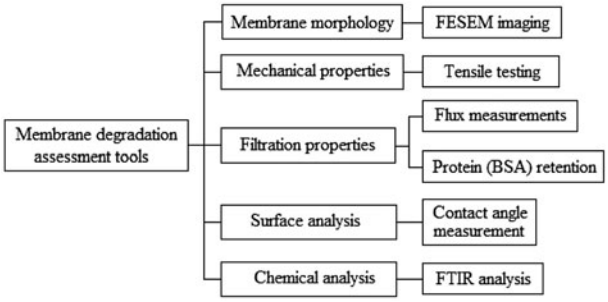

Fig. 1. Membrane degradation assessment tools.

To our knowledge, there is a lack of studies that thoroughly assesses the potential damage to PVDF membranes caused by the cleaning agent. It is predicted that the cleaning process would alter the properties of PVDF membrane and the cleaning efficiency will vary after several cycles of membrane operation. Therefore, the aim of this paper is to systematically study the effects of cleaning processes on the intrinsic nature of PVDF membrane by frequently used cleaning agents, NaOH and NaOCl. The repeated fouling and cleaning process was executed to mimic the real industrial application, where the membrane is subjected to cyclical operation. We propose various analytical techniques as depicted in Fig. 1 in order to systematically study the changes in the properties of PVDF membranes.

2. Experimental

2.1. Materials

Flat-sheet hydrophilic PVDF membrane with 120 kDa molecular weight cut-off (MWCO) was purchased from Sterlitech Corporation (USA). It is to be noted that the method for fabricating the hydrophilic (modified) PVDF membrane could not be disclosed as it is regarded as proprietary information by the suppliers. NaOH was supplied by R&M Chemicals (Malaysia). NaOCl solution (4.99% available chlorine) and bovine serum albumin (BSA) were obtained from Sigma-Aldrich (Malaysia). Ultrapure water (Milli-Q) with resistivity of 18.2 MΩ was used for preparing solutions and rinsing purposes throughout the study.

2.2. Methods

PVDF membrane was soaked in the Milli-Q water for at least one day prior to experimental work. All filtration experiments were performed at room condition (25 ± 2˚C) using a cross-flow filtration module, TR-32

(Solteq, Malaysia) and transmembrane pressure (TMP) of one bar. The membrane effective area was 40.1 cm^2. The filtration module used in this work is depicted in Fig. 2.

The membrane cleaning procedures:

(1) initial water flux measurement for 40 min;
(2) membrane fouling experiment using 0.3 g/L BSA solution for 40 min filtration time;
(3) membrane physical cleaning (via forward flush) for 10 min;
(4) chemical cleaning process at conditions as shown in Table 1;
(5) rinsing with pure water for 15 min;
(6) cleaned membrane water flux measurement for 40 min; and
(7) another cycle of fouling and cleaning experiment was done by repeating step 2 until 6.

All fouled membrane was cleaned in place (CIP method), in which during membrane cleaning process, the fluid (i.e. ultrapure water and chemical solution for physical and chemical cleaning, respectively), was allowed to flow along the fouled membrane. The cleaning process was performed at room temperature (25 ± 2˚C), whereas it is common to clean at an elevated temperature to increase the kinetics of the process. This is to minimise the potential damage to the PVDF membrane. It is worth mentioning that the main focus of this work is to study the potential degradation of PVDF membrane following cleaning process based on various assessment tools. Subsequent to cleaning experiment, the membrane was removed from the module and allowed to dry at room condition prior to membrane characterisations.

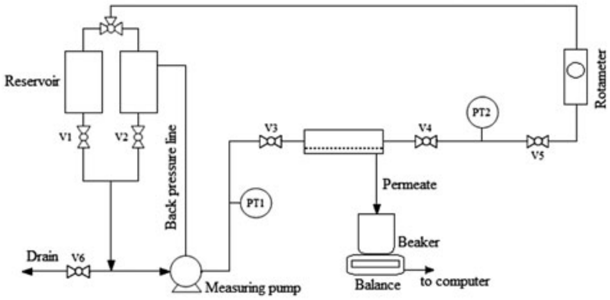

Fig. 2. Schematic diagram for cross-flow filtration unit (Solteq TR-32, Malaysia).

Table 1
Parameters for chemical cleaning process

Cleaning agent	Concentration (*M*)	Time (min)
NaOH	0.01 and 0.1	20, 40 and 60
NaOCl	0.01 and 0.1	20, 40 and 60

2.3. Membrane characterisations

The flux of ultrapure water (Milli-Q) across the membrane was determined by TMP of one bar after a steady reading was obtained. The performance of NaOH and NaOCl as cleaning agents is evaluated by determining their cleaning efficiency. Cleaning efficiency (C_e) is defined as the ratio of the cleaned membrane flux (J_c) to the virgin water flux (J_v) and described in the following equation:

$$\text{Cleaning efficiency } (C_e) = \frac{J_c}{J_v} \tag{1}$$

Morphology of PVDF membrane was examined using Auriga field emission scanning electron microscopy (FESEM) (Carl Zeiss Microscopy, USA). The dried membrane was coated with gold for 30 s prior to analysis to enhance its conductivity. FESEM images were taken at a range of magnifications. The mechanical properties of virgin and cleaned PVDF membranes were tested by measuring the maximum elongation using Instron 5569 (USA). The experiment was carried out at room condition with the elongation speed of 50 mm/min and load range of 10 kN. The test was performed in accordance with ASTM D882. Membrane sample with a gauge length of 8 cm was securely clamped at both ends and subject to elongate until it breaks at maximum elongation.

Surface chemical composition changes of PVDF membrane were studied through attenuated total reflectance. Fourier transform infrared spectrometer (ATR–FTIR). The spectra were collected using a Nicolet iS10 Thermo Scientific (USA), where all spectra were recorded in the wavelength range from 650 to 4,000 cm^{-1} by accumulating 32 scans set with 4 cm^{-1} resolution. The surface analysis was conducted with Dataphysics OCA-15 plus (DataPhysics, USA) for contact angle measurement. An approximately 20 μl drop of deionised (DI) water was placed onto the membrane surface using a microsyringe and air–water–surface contact angle was measured immediately within 10 s. The measurement was repeated at five different spots to obtain the average values and to reduce the error. The protein rejection was measured in accordance to Bradford assay method [29]. The concentration of BSA in the permeate was determined and the protein rejection was calculated using the following equation:

$$\text{BSA rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

where C_p and C_f are the BSA concentration in the permeate and in the feed, respectively.

3. Results and discussion

3.1. Flux measurement and cleaning efficiency

Fouled membrane was first cleaned by means of physical cleaning via forward flushing. This cleaning process achieved approximately 30% of cleaning efficiency. For that reason, chemical cleaning is required to remove the irreversible foulant that attached to the membrane surface by means of chemical reactions. Although physical cleaning only resulted in relatively lower removal efficiency, it is carried out before chemical cleaning to loosen the physically attached particles on the membrane surface that could possibly be removed via flushing. The cleaning efficiency using either NaOH or NaOCl was determined by varying the concentration of the cleaning agents and cleaning times.

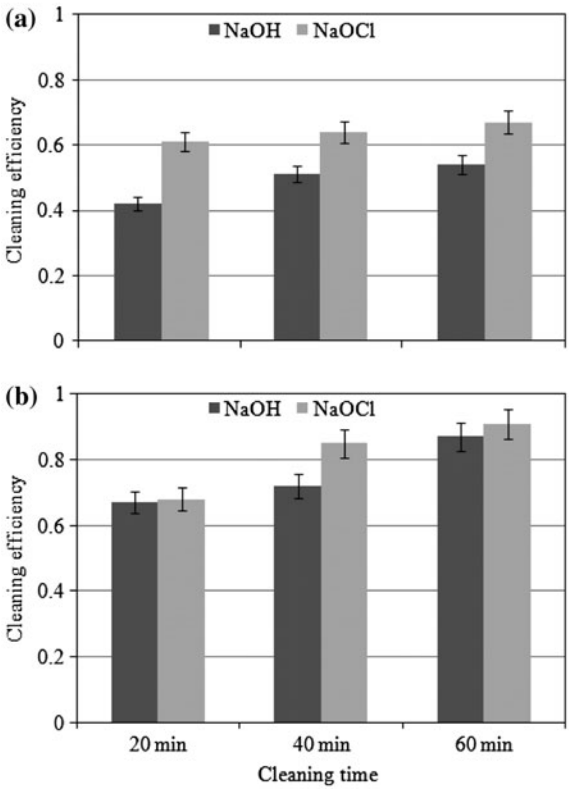

Fig. 3. Cleaning efficiency for membrane cleaned with (a) 0.01 M and (b) 0.1 M at different cleaning time.

From Fig. 3, for chemical concentration of 0.01 M, NaOH showed the average cleaning efficiency below 60%, regardless of the cleaning time while NaOCl showed relatively higher cleaning efficiency. When applying higher chemical concentration of 0.1 M, the increase in efficiency for both cleaning agents became significant. NaOCl achieved the highest cleaning efficiency of 91% for 60 min cleaning time, while NaOH cleaned membrane showed 87% efficiency.

As shown in Fig. 4, the performance of the first time cleaned membrane (cycle 1) and the second time cleaned membrane (cycle 2) was comparable. The reason is due to same cleaning protocol was applied to the fouled membrane. It is noteworthy to mention that there was only a slight decrease in cleaning efficiency for the second time cleaning process. This could be attributed to the changes in the membrane surface properties. From contact angle measurement, the membrane became less hydrophilic after the exposure to chemicals. Further discussion on contact angle measurement is discussed in Section 3.4. The decrease in cleaning efficiency for the second time cleaning cycle is also believed to be due to part of the protein adsorbed in the inner layer of the membrane did not completely removed by the cleaning agent.

Generally, a better cleaning efficiency was recorded with higher concentration of chemical agents. It is generally known that oxidants and alkaline solutions can remove organic foulants effectively. In comparison, hypochlorite showed better performance than an alkaline solution in removing BSA from the surface of PVDF membrane. The observed cleaning performance met our expectations and was in good agreement with previous literatures [24,30]. As a whole, it was found that membrane cleaning at room condition did not completely recover membrane water flux even with the application of relatively higher concentration and longer cleaning period.

3.2. Morphology of PVDF membranes

The surface characteristics of the virgin and cleaned membranes were examined by FESEM analysis. From Fig. 5(a)–(c), it could be observed that some protein particles adsorbed or deposited on the membrane surface. This indicated that cleaning with 0.01 M NaOH and 0.01 M NaOCl for 20 min could not completely remove the foulant from the membrane surface. Almost no trace of foulants could be observed on the membrane cleaned using 0.01 M NaOCl at a longer cleaning time as shown in Fig. 5(d).

The images of membrane cleaned using higher chemical concentration are shown in Fig. 6. Subsequent chemical cleaning with 0.1 M of NaOCl

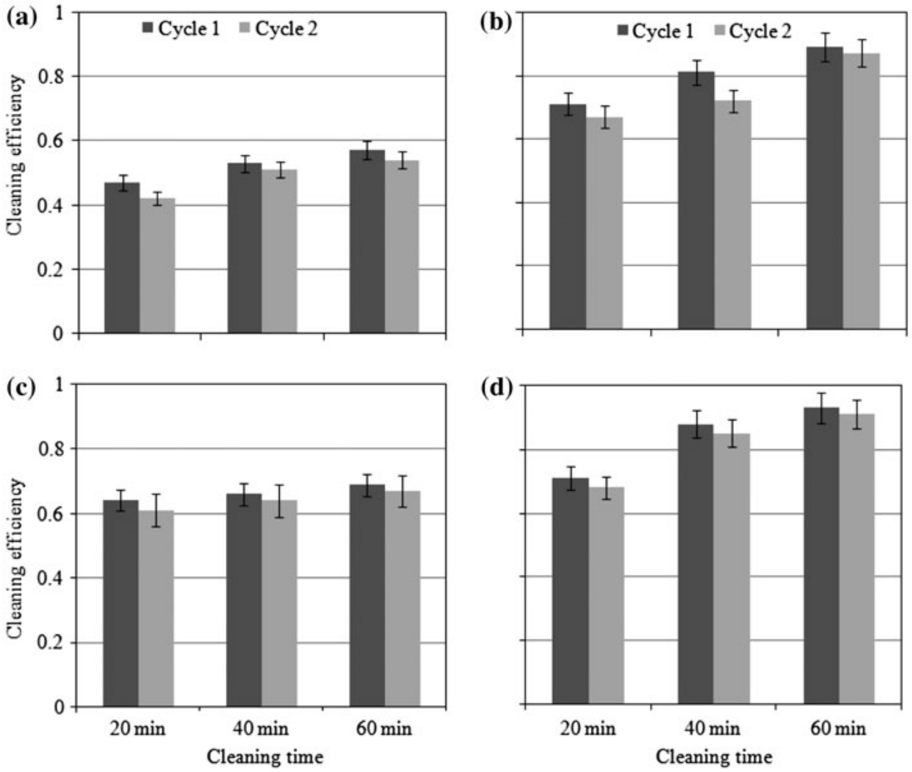

Fig. 4. Cleaning efficiency using (a) 0.01 M NaOH, (b) 0.1 M NaOH, (c) 0.01 M NaOCl and (d) 0.1 M of NaOCl for the first and second cleaning cycles.

removed most of the foulants from the membrane surface as shown in Fig. 6(c) and (d). On the other hand, the FESEM images of NaOH cleaned membrane (Fig. 6(a) and (b)) showed that there are still protein particles deposited on the surface. A lesser amount of foulant was visible on the membrane cleaned at a longer cleaning time. This trend was expected, as we predict that the longer cleaning time will result in better removal efficiency. In comparison, NaOCl was found to be a better cleaning agent as shown by its efficiency to remove foulant deposited on the membrane. It is to be noted that no significant change in membrane pore size as indicated by the scale of FESEM images. Although cleaning with chemicals showed high potential in removing foulants from the membrane surface, the cleaning process was unable to completely restore membrane water flux. A reasonable explanation is that the foulant left in the membrane was most likely located inside the pores and were not characterised by FESEM analysis.

3.3. Tensile test

The alteration in membrane mechanical strength was evaluated via tensile testing. Since the broken membrane can be regarded as the main reason for failure in membrane modules and operation of membrane systems, the flexibility of membranes is significant to represent the extent of mechanical strength [31]. Generally, a flexible membrane can sustain higher elongation compared to brittle membrane. In this particular work, nominal elongation was chosen to be the parameter to represent the membrane's mechanical properties. It is defined as a ratio of elongation of the cleaned membrane to the elongation of virgin membrane. It is essential to have a measure of the mechanical strength of membranes that have been subjected to fouling and chemical cleaning. The nominal elongation of cleaned membrane at different cleaning parameters is shown in Fig. 7.

For both chemicals, the extension of membrane was found to decrease with the increment in chemical concentration and cleaning time. Membrane cleaned with NaOCl was observed to exhibit relatively poor flexibility than the NaOH cleaned one. Membrane subjected to 0.1 M NaOCl cleaning for 60 min experienced a drastic decline in flexibility, which indicated the most severe reduction in mechanical properties. This trend was also observed previously, in which the mechanical strength was inversely proportional to the

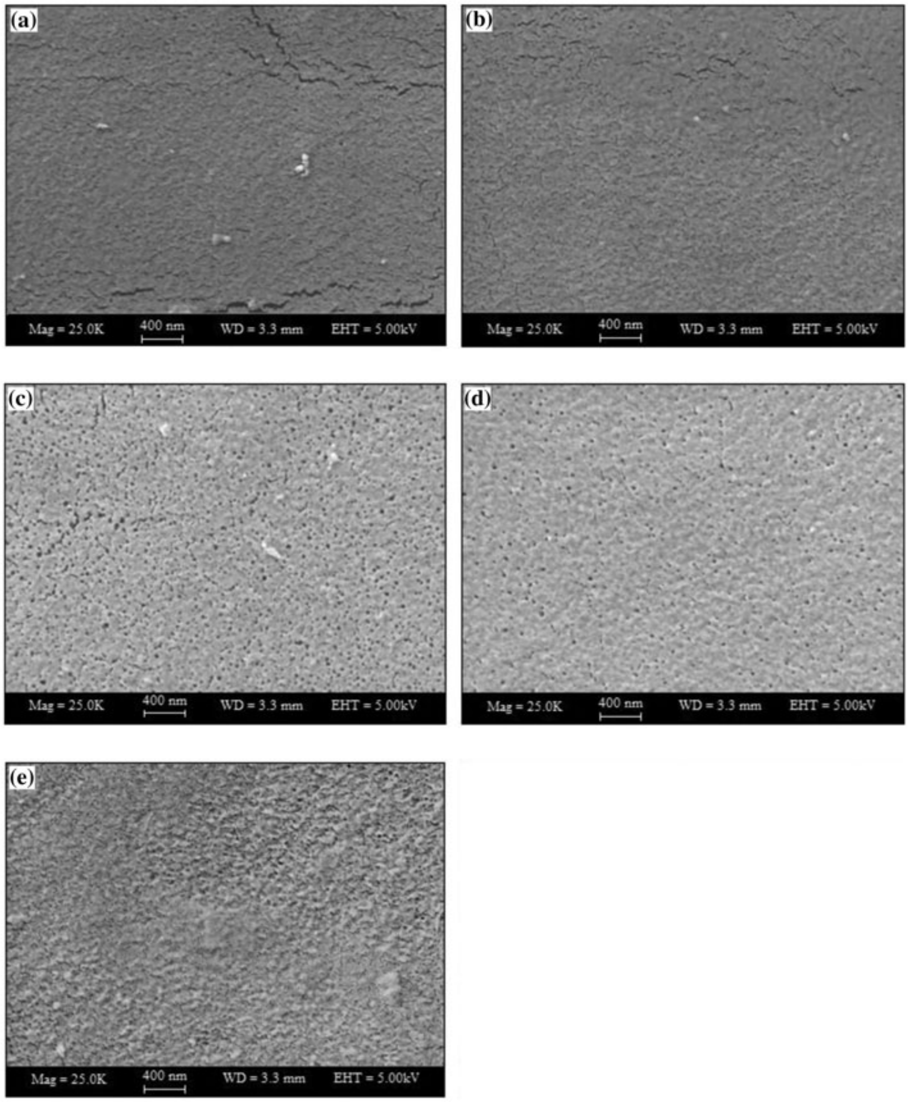

Fig. 5. FESEM images at 25,000 magnifications for membrane cleaned with 0.01 M of (a) NaOH for 20 min, (b) NaOH for 60 min, (c) NaOCl for 20 min, (d) NaOCl for 60 min and (e) virgin membrane.

cleaning time and concentration of the cleaning agents used [31]. It has been proposed that these changes are due fundamentally to the reactions between the cleaning agents and some specific functional groups. In accordance with Lovinger [32], the reduction in nominal elongation is linked to the chain breaking of membrane materials exposed tobelieved to be attributed chemicals. Chain breaking on membrane polymer influences continuing deterioration of the membrane layer and as a result, the interaction between polymer molecules is weakened and becomes easier to fracture. Particularly for PVDF, the membrane degradation is attributed to the loss of hydrogen fluoride (HF), or defined as dehydrofluorination reaction.

This phenomenon is hostile given that the membrane itself is the major component in the membrane system. The membrane should be able to withstand an attack by the chemical to avoid from deteriorating during operation. Overall, the cleaned PVDF membranes displayed a reduction in its mechanical strength, in which it became brittle upon contact with chemical, where oxidising properties of NaOCl have more potential to cause damage on the membrane as compared to NaOH. Reduction in nominal elongation manifests the decline of membrane's mechanical strength, thus it is recommended that the alternatives to NaOCl and NaOH as cleaning agents for PVDF should be considered.

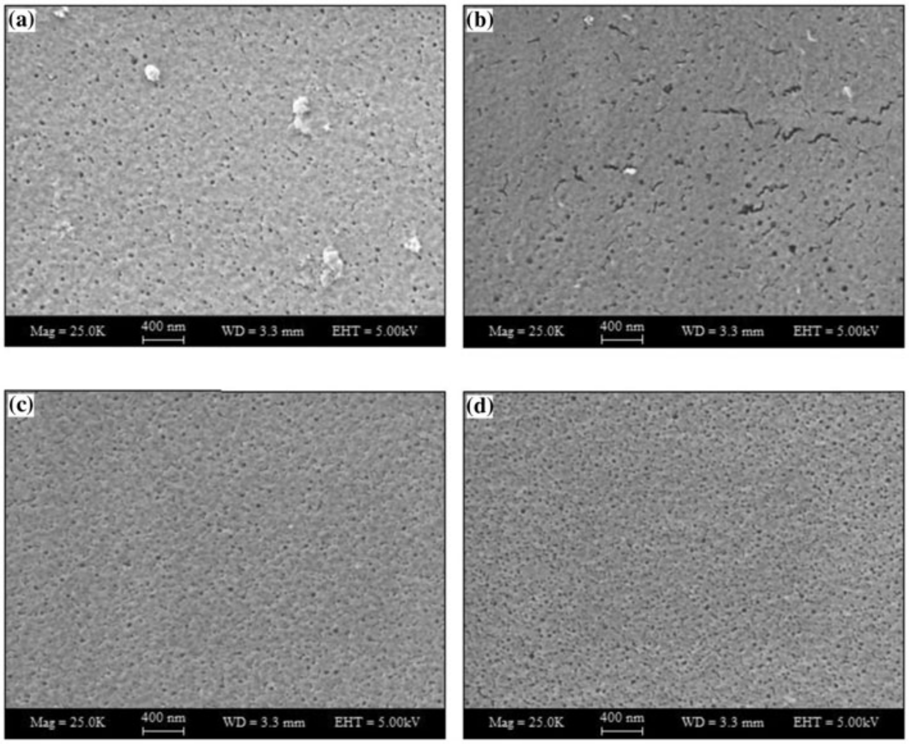

Fig. 6. FESEM images at 25,000 magnifications for membrane cleaned with 0.1 M of (a) NaOH for 20 min, (b) NaOH for 60 min, (c) NaOCl for 20 min and (d) NaOCl for 60 min.

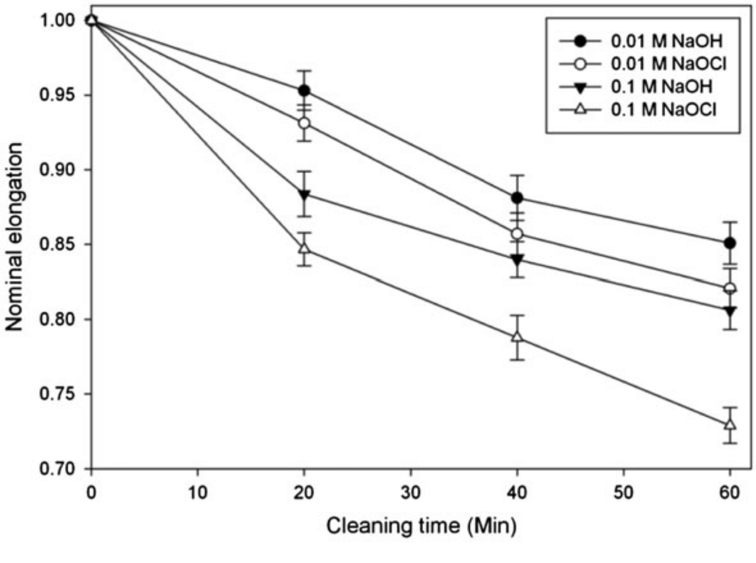

Fig. 7. Nominal elongation for membranes cleaned with NaOH and NaOCl at different concentration.

3.4. Surface chemical analysis

FTIR analysis was used to analyse the changes in the chemical functional group of PVDF membrane following the cleaning process. The common characteristic bands for PVDF membrane appeared at 762, 796, 875, 974, 1,070 and 1,181 cm^{-1}, which is similar to PVDF film containing α-phase, whilst several other peaks detected at 841, 1,274 and 1,403 cm^{-1} are believed to be attributed by the β-phase [31,33]. The occurrence of dehydrofluorination process is mainly indicated by the occurrence of the peaks at a range from 1,590 to 1,650 cm^{-1} assigned for carbon–carbon double bond, from 1,700 to 1,800 cm^{-1} assigned for carbonyl bond and 2,100 cm^{-1} representing the carbon–carbon triple bond [27,31,34].

The alteration in chemical composition of PVDF membrane following chemical cleaning could be detected by the emergence of peaks representing carbon–carbon double and triple bond [25]. From Fig. 8, there were no new peaks appearing in the spectra of cleaned membranes. This indicated that the polymer surface chemistry did not change significantly. However, it is important to mention that the degradation on PVDF membrane could not only occur on the surface but also in the inner layer as well. The apparent change in relative intensity was observed for the peak at approximately 1,710 cm^{-1} assigned to the C=O functional group. The relative intensity of this peak for cleaned membrane was reduced significantly as compared with the virgin membrane. In general, we could observe that the peak strength decreased with the increase of cleaning times.

It is commonly known that there are several functional groups that contribute to membrane hydrophilicity, such as hydroxyl, carbonyl and carboxyl functional groups. PVDF-based membranes are often modified with proprietary additives to improve their hydrophilicity and flux properties. Particularly in this study, we anticipated that the peak representing carbonyl bond (C=O) is due to the presence of blended-in additives. This additive is responsible for the hydrophilicity of the PVDF membrane and this assumption is in line with earlier studies [30,35]. As carbonyl group is one of the functional groups that contribute to the hydrophilicity of the membrane, the decline in its intensity signifies reduced surface hydrophilicity. This result was in good agreement to contact angle measurement (Section 3.5), where membrane was found to become less hydrophilic upon chemical cleaning process.

3.5. Contact angle measurement

Alteration of membrane surface properties was analysed using contact angle measurement. In principle, the contact angle is a parameter to indicate the surface hydrophobicity and hydrophilicity. The higher the contact angle, the higher the hydrophobicity of the membrane surface. The membrane that has a contact angle of less than 90° is classified as hydrophilic. In

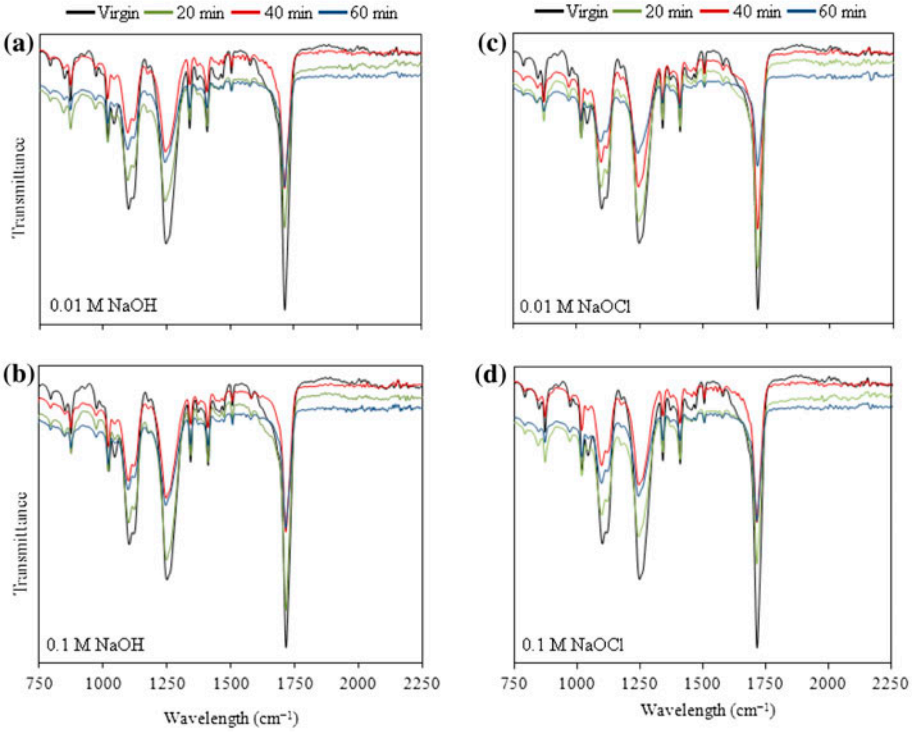

Fig. 8. FTIR spectra for PVDF membrane cleaned with (a) 0.01 M NaOH, (b) 0.1 M NaOH, (c) 0.01 M NaOCl and (d) 0.1 M NaOCl for different cleaning time.

Table 2
Contact angle of virgin and cleaned PVDF membranes

	Contact angle (°)			
	NaOH		NaOCl	
Concentration (*M*)	20 min	60 min	20 min	60 min
0	68.97 ± 0.38	68.97 ± 0.38	68.97 ± 0.38	68.97 ± 0.38
0.01	69.72 ± 0.45	70.73 ± 0.62	69.93 ± 0.44	70.97 ± 0.39
0.1	71.70 ± 0.52	72.75 ± 0.37	73.20 ± 0.65	75.63 ± 0.40

this work, the contact angle for virgin PVDF membrane was measured to be 68.97°, indicating that it is a hydrophilic membrane. Table 2 summarises the contact angle for cleaned membranes. In general, the measurement of contact angle showed that the cleaned membranes either with NaOH or NaOCl had become less hydrophilic represented by the increment in contact angle values. In comparison, the change in membrane hydrophilicity was more significant for NaOCl cleaned membranes than those cleaned by NaOH.

It was previously reported that effective chemical cleaning increases the hydrophilicity of the membrane, thus allowing higher water flux for the same applied pressure [22,30]. Nevertheless, the results obtained in our study showed that the membrane became less hydrophilic following the cleaning process. The changes in contact angle values were related to the membrane surface modification that was probably caused either by the chemicals, foulants or both [36]. Besides, the alteration in membrane surface hydrophilicity may also be due to the changes in the membrane structure or its composition. Hydrophilic PVDF membrane is typically fabricated via modification techniques, either material blending (addition of additives into casting solution) or surface modification (coating or grafting) [37]. Blending method is the preferable method as it involves a straightforward and simple modification process during membrane fabrication.

Following membrane cleaning, the employed chemicals are believed to degrade the hydrophilic surface additives from the membrane, resulting in an expected more hydrophobic surface. It is assumed that functional groups, such as carbonyl groups, impart the hydrophilic character of PVDF. The observation of increased contact angle values can be linked to the membrane becoming less hydrophilic upon cleaning. As discussed in Section 3.4, the relative intensity of the peak representing carbonyl bonds reduced following the exposure towards chemical, which indicate reduced hydrophilicity. This signifies that the PVDF membrane was unable to retain its hydrophilicity upon contact with either NaOH or NaOCl as revealed by the increased contact angle values. In addition, the decline in membrane hydrophilicity may also be caused by the deposition of BSA on the membrane surface. During the adsorption of particles on the membrane surface, the hydrophilicity of the material increases, when the adsorbed molecules are more hydrophilic than the material or otherwise it will decrease. Since BSA is naturally hydrophobic, the deposited BSA that remained on the membrane surface had caused the membrane to be less hydrophilic.

3.6. Protein rejection

The changes in PVDF membrane filtration characteristic following chemical cleaning were determined by the protein rejection study. The protein separation was conducted using 0.3 g/L of the BSA model protein solution. It is anticipated that the virgin PVDF membrane will result in the best rejection performance. The overall results for protein rejection by the virgin and cleaned membranes are shown in Table 3. As expected, the virgin membrane recorded the highest rejection performance of approximately 94.8%. Following the cleaning process, all cleaned membranes recorded a decreased rejection performance. The reduction in separation efficiency became more significant as higher concentration chemical is used for membrane cleaning at prolonged cleaning period.

The reduced separation performance by the cleaned membrane was due to the alteration in membrane morphology and surface properties. Earlier works explained that the BSA rejection mechanism is adsorption governed by membrane hydrophilicity. The increased rejection performance increases with the increment in membrane hydrophilicity [36]. Nevertheless, we found that in this study, the rejection performance was reduced when using cleaned membrane. From contact angle measurement, our membrane became less hydrophilic upon cleaning process and this could be the reason of the declined in the cleaned membrane performance.

Table 3
Protein rejection performance of virgin and cleaned PVDF membranes

	Protein rejection (%)			
	NaOH		NaOCl	
Concentration (*M*)	20 min	60 min	20 min	60 min
0	94.76 ± 0.45	94.76 ± 0.45	94.76 ± 0.45	94.76 ± 0.45
0.01	86.56 ± 0.65	78.74 ± 0.70	82.19 ± 0.71	73.61 ± 0.69
0.1	85.01 ± 0.58	77.93 ± 0.59	73.19 ± 0.87	72.04 ± 0.62

Table 4
Impacts of chemical cleaning towards PVDF membrane using various analytical tools

Analytical tools	Changes	Remarks
Flux measurement	↓	Chemical cleaning conditions used in this study were unable to completely restore membrane water flux and permeability
FESEM analysis	≈	Pore sizes of cleaned and virgin membrane are comparable
Tensile test	↓	Reduction in nominal elongation indicated the increased membrane rigidity and/or lower flexibility
FTIR analysis	↓	Reduction in the relative intensity of peak corresponded to the blended-in additive that led to membrane becoming less hydrophilic
Contact angle	↑	Reduction in the membrane hydrophilicity
Protein rejection	↓	Cleaned membranes exhibit poorer separation performance than virgin membrane

3.7. Assessment of PVDF membrane degradation

Stability issue of PVDF membrane has attracted a significant interest among researchers in recent years. Despite having excellent properties, such as high chemical, thermal and mechanical stability, PVDF was alleged to be vulnerable towards alkaline environments. Investigation on the degradation of PVDF membrane in alkaline environments has been documented by several researchers [31,38]. Nevertheless, earlier studies were mainly focused on the degradation mechanism of alkaline attack towards PVDF membrane; therefore, extreme treatment conditions were applied (i.e. relatively high concentrations, temperature or with the presence of catalyst) [25–28]. PVDF membrane exposed to NaOH solution is known to endure degradation, due to chemical attack by hydroxide ions. It has been proposed that the degradation mechanism is mainly caused by the dehydrofluorination process, which leads to the formation of carbon–carbon double bond and the incorporation of oxygen-contained group to the polymer. This mechanism has been discussed thoroughly elsewhere [25,26]. These double bonds are inclined to be chemically attacked by NaOH and NaOCl. Meanwhile, we believed that the membrane degradation caused by hypochlorite was contributed by its high oxidising properties. In solution, hypochlorite produces several by-products and one of them is hypochlorous acid, which is a powerful oxidising agent. Besides, hypochlorite can also form radicals, and PVDF membrane ageing could possibly be associated with the radicals attack. The alteration of PVDF membrane properties after being exposed to hypochlorite is intimidating, since NaOCl is currently being widely used as cleaning agent.

In practice, membranes need to be monitored regularly to ensure their integrity. We examined the alteration in PVDF membrane properties prior and subsequent to the cleaning process. The effects of chemical cleaning of the structure of the PVDF membrane were detected by most of the analytical indicators, as summarised in Table 4. From the analysis via different “assessment tools”, the cleaned membrane properties was observed differed from the virgin one. PVDF membrane was found to be susceptible to these chemicals, even in a mild cleaning condition (i.e. low concentration and shorter cleaning time). The overall results revealed that although membrane cleaning with chemical could potentially remove foulants from its surface, it causes a decline in membrane stability. This is hostile since membrane as a major component in the membrane system should possess excellent stability against various chemical and could withstand high pressure operation.

4. Conclusion

In this work, we assessed the changes in PVDF membrane properties following the repetitive filtration and cleaning cycles using a systematic study. PVDF membrane degradation upon exposure to chemical cleaning agents was studied using various analytical techniques. In general, both NaOH and NaOCl showed their potential to remove irreversible foulants, yet all cleaning conditions applied in this study failed to completely recover the membrane water flux and permeability. The deterioration in the mechanical strength of chemical cleaned membranes indicated a loss of membrane integrity. The surface and chemical analysis indicated that the hydrophilic PVDF membrane was unable to sustain their hydrophilicity, whereby the blended-in additive was subjected to chemical attack. Besides, repeated filtration and cleaning cycle of membrane showed a reduction in cleaning efficiency of the subsequent cleaning cycle. NaOCl was identified to be a better cleaning agent, but it is more detrimental to PVDF membrane as compared to NaOH. To conclude, as NaOH and NaOCl were found to exert negative impacts on PVDF membrane characteristics, it is suggested that another substitute should be considered to extend membrane lifespan.

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