

**CHEMICAL AND THERMAL STABILITY STUDIES OF
HYDROPHOBIC AND HYDROPHILIC POLYVINYLIDENE
FLUORIDE (PVDF) MEMBRANES IN ALKALINE
ENVIRONMENTS**

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ABSTRACT

This research work has highlighted the effects of alkaline solution towards PVDF stability at the typical concentrations used in membrane cleaning and membrane contactor processes such as gas absorption using alkaline solution. In the first part of the study, PVDF membranes treated with two types of strong alkali, sodium hydroxide (NaOH) and potassium hydroxide (KOH) at different concentrations, temperatures and treatment times. The virgin and treated membranes were analysed using FESEM, DSC, FTIR, pure water flux measurement and tensile test. PVDF membrane was found to experience changes in its intrinsic properties following exposure towards alkaline solution. For 120 minute treatment at 50 °C, the nominal elongation values decreased to 75% and 73% for membrane immersed in 0.2 M KOH and NaOH, respectively. The results demonstrated that PVDF membrane can be attacked and degraded upon exposure, even to a low concentration of 0.01 M alkaline solution, the concentration that is commonly applied in membrane contactor applications and cleaning. The findings from this study also suggested that PVDF membrane is more vulnerable to NaOH solution as compared to KOH solution. In membrane cleaning study, all cleaning conditions failed to achieve complete flux restoration except for the membrane cleaned at the extreme condition (concentrated chemical, high temperature and longest cleaning period) with cleaning efficiency (C_e) was measured to be more than 1. Increased water flux over the virgin membrane value signifies the alteration in membrane properties subsequent to a cleaning process. Overall, NaOCl was observed to be more efficient in removing protein (BSA) particles than NaOH; however, it causes a further decline in membrane stability. The efficiency of protein filtration was compromised during the use of cleaned membrane where it gave lower protein retention. This phenomenon is mainly linked to membrane hydrophilicity and pore structure in which the cleaned membrane results in a poor performance for protein rejection.

ABSTRAK

Penyelidikan ini difokuskan untuk mengkaji kesan penggunaan alkali terhadap kestabilan PVDF pada kepekatan yang biasa digunakan dalam proses pembersihan membran dan proses membran penyentuh seperti penyerapan gas menggunakan alkali. Dalam bahagian pertama kajian, membran PVDF dirawat dengan dua jenis alkali kuat iaitu natrium hidroksida (NaOH) dan kalium hidroksida (KOH) pada kepekatan, suhu dan masa rawatan yang berbeza. Membran dirawat dan kemudiannya dianalisa menggunakan FESEM, DSC, FTIR, pengukuran fluks air tulen dan ujian ketegangan. Membran PVDF didapati mengalami perubahan dalam ciri-ciri intrinsik selepas didedahkan dengan larutan alkali kuat. Untuk rawatan selama 120 minit pada suhu 50 °C, nilai pemanjangan nominal menurun kepada 75 % dan 73 % bagi membran yang direndam dalam 0.2 M KOH dan NaOH. Hasil analisa menunjukkan bahawa membran PVDF boleh diserang oleh alkali apabila didedah, walaupun pada kepekatan yang rendah iaitu 0.01 M, kepekatan yang sering digunakan dalam aplikasi membran penyentuh dan pembersihan membran. Hasil kajian juga mencadangkan bahawa kestabilan membran PVDF lebih terjejas apabila didedahkan pada NaOH berbanding KOH. Dalam kajian pembersihan membran, semua keadaan pembersihan gagal mencapai pemulihan fluks yang lengkap kecuali membran yang dibersihkan dalam keadaan yang ekstrem (kepekatan tinggi, suhu yang tinggi dan tempoh pembersihan paling lama) dengan kecekapan pembersihan (C_e) direkodkan melebihi 1. Peningkatan fluks air melebihi membran asal menandakan perubahan dalam sifat-sifat membran selepas proses pembersihan. Secara keseluruhan, NaOCl lebih berkesan dalam membersihkan zarah protein (BSA), bagaimanapun ia menyebabkan penurunan ketara pada tahap kestabilan membran. Kecekapan dalam proses penapisan protein telah terjejas semasa menggunakan membran yang telah dibersihkan di mana ia memberikan kualiti penapisan yang lebih rendah. Fenomena ini adalah sebahagian besarnya

dikaitkan dengan ciri-ciri hidrofilik pada membran dan struktur liang pori di mana hasil analisa menunjukkan membran yang telah dibersihkan merekodkan prestasi yang lemah bagi penapisan protein.

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CHAPTER 1: INTRODUCTION

1.1 Research Background

In separation process, the demand for new technologies is necessary in order to meet stringent product quality requirements, adhere to stricter environmental laws, achieve energy optimisation and reduce operational costs. Membrane technology has progressed from being a research interest to an established separation technology. Due to its simplicity, flexibility, lower costs and ease to operate, membrane technology are gaining popularity and offers a competitive alternative to conventional separation techniques. Membrane technology has a huge potential to be applied over a wide array of industrial applications such as wastewater treatment, chemistry, food and beverages, pharmaceuticals, and biotechnology.

One of the main aspects of membrane technology is the materials used for making membrane. Until now, polymer remains as a major basic material for making membranes. Polymeric membranes are considered to be more economical than other membranes due to their ability to be easily spun into hollow fibres or spiral wound modules because of their flexibility and solution processability. Among the emerging membrane materials is polyvinylidene fluoride (PVDF). PVDF offers better characteristics in comparison to their organic polymer counterpart mostly due to its outstanding properties such as high mechanical strength and toughness, high hydrophobicity and high chemical resistance against a broad range of chemicals. In addition, it is a thermoplastic that holds flexibility due to amorphous phase as well as thermal stability due to the crystalline phase.

A common application of PVDF membranes includes separation and filtration processes. Its excellent hydrophobic property has made it a preferred option as a membrane material in the membrane contacting system such as for gas absorption process and membrane distillation. PVDF application in membrane contactor was proven to be efficient to remove toxic gases that are harmful to humans and the environment. Attributed to its high mechanical stability, hydrophilic PVDF membrane is suitable for water and wastewater treatment which are regularly subjected to high pressure as well as a fairly harsh environment. There has been a great caution in the prolonged exposure to such extreme conditions which can lead to the need for frequent membrane replacements. Besides, membrane costs have gone down drastically from its early days of application; however, it remains as a major cost factor in membrane application and is a concern for many users of membrane technology.

1.2 Problem Statement

In recent years, the application of hydrophobic PVDF membranes in non-dispersive gas absorption and hydrophilic PVDF (modified) membrane for water filtration has attracted considerable interest among the research community. Generally, hydrophobic PVDF membrane system was shown to be effective in removing gases with sodium hydroxide (NaOH) as a liquid absorbent, while the application of hydrophilic PVDF membrane for water and wastewater treatment has drawn significant attention due to their high mechanical strength. Despite the successfulness of membrane for filtration process, one major drawback is fouling phenomenon. Membrane fouling could be eliminated by cleaning process where NaOH is also frequently used as a cleaning agent. Many of these applications involve the use of the fairly harsh environment such as high pH and prolonged period of exposure to chemicals which can be detrimental to the membrane material itself. It is uncertain whether the contact of

PVDF membrane with chemical would alter the structure of the membrane, which then leads to the decline in membrane stability.

So far, studies of PVDF membrane often discussed and evaluates overall system performance rather than to look at what happen to the stability of the membrane material after continuous usage in harsh application. For instance, the main findings of membrane contactor studies always reported on the gas removal efficiency instead of describing the changes in the membrane stability upon exposure to chemicals. Meanwhile, in membrane cleaning studies, it is also insufficient to portray the cleaned membrane properties solely by its flux recovery, as it does not disclose the chemical, thermal, and mechanical properties of membrane in detail. This is because the membrane could be undergoing deterioration throughout the exposure to alkaline solution.

There is a noteworthy information that PVDF polymer or film can be attacked and degraded upon exposure to alkaline environment. In general, the interaction of PVDF membranes with alkaline solution often found in membrane contactor and during membrane cleaning where NaOH is used as absorbent and cleaning agent, respectively. Limited studies were found in the investigation of the effect of alkaline solutions, particularly at mild condition (e.g. low chemical concentration and shorter exposure period) toward PVDF membrane stability. Earlier studies have focused mainly on one type of alkaline solution which was NaOH. There has been no detailed investigation on the comparison of PVDF membrane characteristics treated using different alkaline solutions. It is also worth mentioning that earlier works were performed under extreme condition in which high alkaline concentrations were used, either in the absence or presence of a catalyst at a longer exposure time.

The understanding about membrane technology requires an on-going research because currently there is insufficient information on the issues related to membrane

material such as membrane stability and ageing phenomenon. Observation of the changes in membrane stability is vital since membrane is a key component in membrane systems. The exposure towards chemicals could negatively affect the properties of the membrane. For example, a decline in membrane properties might cause a failure in membrane modules that affects the whole operation of membrane systems. More thorough and continuing research on this issue is crucial for a better understanding on the effects of chemical exposure towards PVDF membrane properties. Therefore, there is a need to conduct an investigation in this area in order to develop better materials and better operation procedures since the membrane can be a significant cost factor in membrane systems. In this work, the main aim is to study the effects of exposure to the different types of alkaline solution at mild condition on PVDF membrane stability and performance.

1.3 Research Objectives

This study was aimed to investigate the chemical and thermal stabilities of PVDF membrane in alkaline environments at a relatively mild condition (i.e. at lower concentration and shorter treatment period). Two types of experimental works were proposed. The first part involved the exposure of an alkaline solution to the hydrophobic PVDF membrane by a simple immersion. Secondly, the effect of chemical cleaning on hydrophilic PVDF (modified) membrane properties was investigated. In general, the objectives of this study were as follows:

1. To study the stability and performance of hydrophobic PVDF membranes exposed to alkaline environments.
2. To study the effects of chemical cleaning towards the properties and performances of the hydrophilic PVDF membranes.
3. To investigate the effects of treatment time, alkaline concentration and temperature towards the changes in PVDF membrane properties.

1.4 Scope of Study

1. In essence, this study is divided into two parts. In the first part of this study, the hydrophobic PVDF membranes were immersed in two types of strong alkali solution, which were NaOH and KOH. The second part involved the application of a strong oxidant (NaOCl) and a strong alkali (NaOH) as cleaning agent for membrane cleaning process.
2. Commercial membranes were used in both parts of the study. Hydrophobic PVDF membrane with average pore size of 0.45 μm was used in the first part of the study. Hydrophilic (modified) PVDF membrane with 100K molecular weight cut-off (MWCO) was employed in the membrane cleaning study.

1.5 Outline of Thesis

Chapter 1: Introduction

This chapter encompasses the introduction of the research background, objectives, scope of study and the outline of the thesis.

Chapter 2: Literature Review

This chapter provides an overview of polyvinylidene fluoride (PVDF) as membrane material. Several stability issues of PVDF membrane are discussed and examples of situations in which PVDF is in contact with alkaline environments is elaborated.

Chapter 3: Materials and Methods

This chapter demonstrates descriptive information about equipments and experimental techniques. Analytical procedures to examine the alteration in PVDF membrane characteristics following exposure to alkaline environments are presented.

Chapter 4: Results and Discussions

This chapter provides the experimental outcomes with a detailed discussion.

Chapter 5: Conclusion and Recommendations

The final chapter of the thesis is to conclude the overall findings in this study and recommends several potential studies for further investigation.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

According to a review of the scientific literature, the common examples of commercialized polymeric membrane materials are cellulose acetate (CA), polyamide (PA), polyimide (PI), polysulfone (PS), polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE) and poly(vinylidene fluoride) (PVDF). For over 50 years after its introduction, PVDF has gained significant interest as a preferred membrane material because of its remarkable mechanical and thermal stability along with its inertness against a range of chemicals (Hashim et al., 2011a; Khayet et al., 2002). These significant characteristics make it appropriate to be applicable in a wide variety of applications such as membrane gas absorption, wastewater treatment as well as for oil/water separation process (Mazzei et al., 2004; Qi & Cussler, 1985). Moreover, as PVDF contains relatively low levels of extractable (Liu et al., 2011b), it could be classified as a pure polymer (Pezeshk et al., 2012), a characteristic which is suitable for membrane material in biomedical and bio-separation purposes. Figure 2.1 depicts the structure of PVDF.

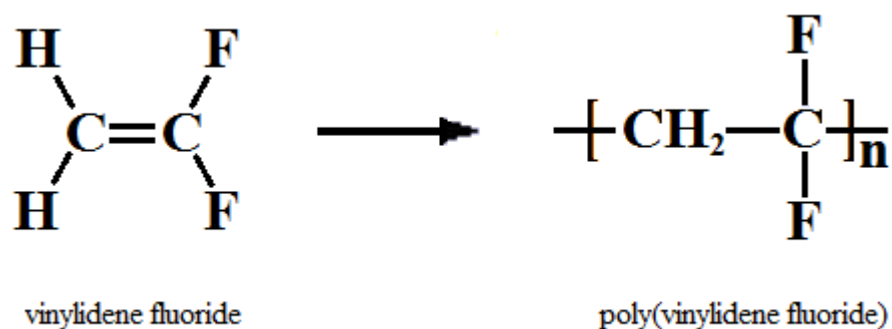


Figure 2.1: Chemical structure of PVDF.

2.2 Application of PVDF membrane

Since 1980's, a number of works have documented the information about fabrication, progress and applications of PVDF membranes (Kang & Cao, 2014; Liu et al., 2011b; Munari et al., 1983; Uragami et al., 1981; Vigo et al., 1981). Polyvinylidene fluoride (PVDF) membrane is used in different type of applications due to its high mechanical and thermal stability, strong resistance towards various chemicals and high hydrophobicity (Kang & Cao, 2014). To date, PVDF membranes have been commonly used in microfiltration and ultrafiltration for general separation purposes, and are now being investigated as a potential candidate in the applications of membrane contactor system (e.g. Membrane gas absorption and membrane distillation).

2.2.1 Microfiltration (MF) /Ultrafiltration (UF)

The excellent mechanical strength and high chemical resistance make PVDF membrane suitable for different filtration operations (Liu et al., 2011a; Zhao et al., 2008). Nevertheless, pure PVDF exhibits high hydrophobicity which makes it easily fouled during the filtration process (Du et al., 2009). For that reason, it is often practiced to do modification on PVDF to turn it into hydrophilic properties. This could be achieved through material blending during membrane fabrication, coating and surface grafting (Du et al., 2009; Hashim et al., 2009; Hester et al., 1999).

Today, hydrophilic PVDF membranes are used in a variety of filtration applications. It was shown that the removal of oil from water could be done using modified PVDF membrane. For instance, Yi et al used a modified PVDF UF membrane with the incorporation of nano-sized $\text{TiO}_2/\text{Al}_2\text{O}_3$ to remove oil emulsion (Yi et al., 2011). Due to high hydrophilicity of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ particles, the modified membrane fouled slightly and presented a good rejection of oil emulsion. PVDF membrane prepared with $\text{LiCl}\cdot\text{H}_2\text{O}$ and TiO_2 as additives is also effective in the refinery wastewater treatment (Yuliwati & Ismail, 2011; Yuliwati et al., 2011). On the other

hand, Pezeshk and Narbaitz prepared a PVDF based membrane, with the addition of L2MM (a type of hydrophilic polyurethane additive) during fabrication and tested using Ottawa River water (ORW) (Pezeshk & Narbaitz, 2012). PVDF membrane with a greater amount of L2MM additives was observed to exhibit the least fouling. The modified membrane was more resistant to fouling compared to the commercial membrane. In addition, the heat treatment was done on the PVDF membrane to improve its morphology and performance prior to milk filtration process (Rahimpour et al., 2009). It was found that the best performance and antifouling properties was achieved when the membrane was treated for 20 minutes with air and water at 100 °C and 95 °C, respectively.

2.2.2 Membrane contactor

Membrane contactor is considered as an excellent development in separation system (Klaassen et al., 2005; Mansourizadeh & Ismail, 2009). A membrane which is typically made from hydrophobic material acts as a well-defined interface area that allows the mass transfer between the phases without mixing or dispersion among them. Membrane contactors have a number of advantages such as no flooding at high flow rates, no unloading at low flow rates, absence of emulsions, no density difference between fluids required and more interfacial area in non-dispersive contact across a membrane. PVDF is currently used as a membrane material for membrane contactor application because it is hydrophobic and stable while attacked by most of the corrosive chemicals and organic compounds (Hashim et al., 2011b). The two most regular membrane contactor processes are membrane gas absorption (gas-liquid contactor) and membrane distillation (liquid-liquid contactor).

Non-dispersive absorption via a gas-liquid contactor is one of the potential applications of PVDF membranes that received increasing attention for the removal of greenhouse gases. It appeared as an alternative to the conventional gas separation

processes such as scrubber and absorption towers. Membrane gas absorption combines the advantages of both membrane technology and absorption processes. The membrane acts as a barrier between the two different phases while the liquid absorbent performs the selectivity of the system. A number of studies showed that PVDF membrane is suitable to be applied for capturing greenhouse gases, including carbon dioxide (CO₂), nitrogen dioxide (NO₂), sulphur dioxide (SO₂) and hydrogen sulphide (H₂S). Figure 2.2 represents a schematic diagram of membrane gas absorption system. During the removal process, the anticipated gas to be eliminated will diffuse through the membrane and be absorbed by the absorption liquid on the other side of the membrane.

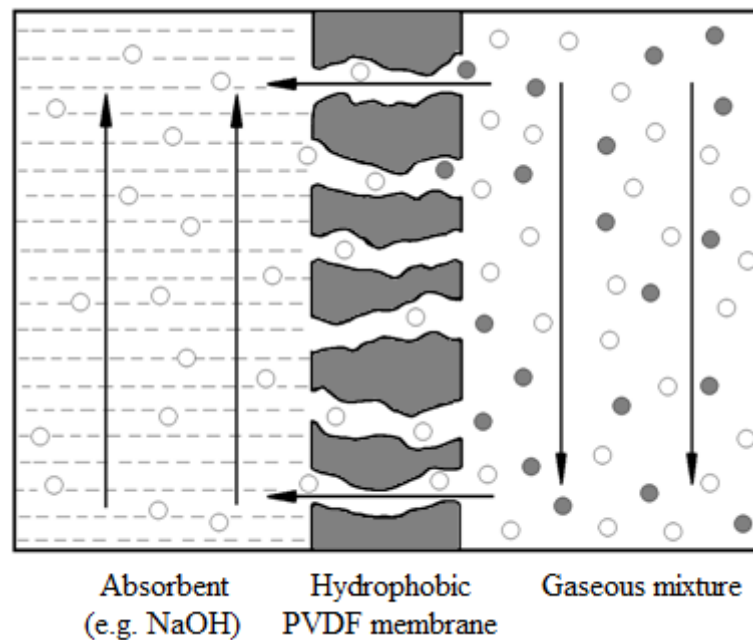


Figure 2.2: Schematic diagram of membrane gas absorption process.

To ensure the high separation performance, the employed membrane should not be wetted by the liquid absorbent. Given by the hydrophobic nature of the PVDF material, membrane wetting could be avoided. In general, the PVDF membrane was found to be very efficient in the separation of toxic gases where the removal of CO₂ from a gas mixture is frequently studied (Atchariyawut et al., 2007; Rajabzadeh et al., 2009). For instance, a CO₂ removal study using commercial PVDF flat sheet membrane

of different pore size was performed with 2-amino-2-methyl-1-propanol (AMP) solution as absorbent (Ahmad et al., 2010). They recommended the use of membrane with smaller pore size to achieve better stability and higher mass transfer of the modules. Lin et al. (2008) used PVDF membrane contactor to capture CO₂ using piperazine (PZ) and AMP. Overall, the systems were shown to be an effective technology for absorbing CO₂ with the use of a mixture of AMP and PZ as promoter resulted in an enhanced CO₂ absorption rate.

Currently, the use of membrane distillation (MD) could offer an innovative desalination process to help in resolving the fresh water shortage (Alkudhiri et al., 2012; Fan & Peng, 2012). The properties of membrane material and its structure are important to guarantee a successful MD operation (Bonyadi & Chung, 2009). Several ideal criteria for membrane selection are hydrophobic, highly porous, exhibit good thermal stability and chemical resistance to feed solution (El-Bourawi et al., 2006). These requirements could be fulfilled by the membranes prepared from PVDF (Hou et al., 2009; Tomaszewska, 1996). Up to now, PVDF membrane has been used in a number of membrane distillation studies. For instance, the performance of the vacuum membrane distillation (VMD) and direct contact membrane distillation (DCMD) process was compared using flat sheet PVDF membrane (Fan & Peng, 2012). There was hardly any wetting during 6 hours of desalination test. The removal of benzene/toluene using PVDF hollow fibre membrane in vacuum membrane distillation (VMD) showed a high efficiency (Wu et al., 2005). In addition, the performance of PVDF hollow fibre membranes was used for the removal of 1,1,1-trichloroethane, benzene and toluene from water. Under optimum operating conditions, the removal efficiency up to 97% was achievable (Wu et al., 2006).

The performance of PVDF membrane in the MD process could be further improved by post treatment or surface coating. Tan et al. (2006) used PVDF hollow fibre membranes treated with ethanol for ammonia removal from water. Both the hydrophobicity and the effective surface porosity of the resulting PVDF hollow fibre membranes were enhanced by post-treatment contributing to a better ammonia removal. The PVDF membranes coated with TiO_2 and 1H,1H,2H,2H-perfluorododecyl-trichlorosilane (FTCS) to create superhydrophobic surfaces were used in the MD process (Meng et al., 2014). All modified membranes showed a notable improvement in salt rejection, signifying a significant reduction in pore wetting.

2.2.3 Other applications

In the biomedical sciences, PVDF is used in immunoblotting as an artificial membrane (Halim et al., 2005). Immunoblotting is a technique for analysing or identifying proteins in a mixture. The commonly applied membranes are those with 0.22 or 0.45 micrometer pore sizes (life technologies), on which proteins are transferred using electricity. PVDF is resistant to solvents and hence this membrane can be simply stripped and reused to observe other proteins. This makes the use of PVDF to be economical. PVDF also found its usage as a ferroelectric layer in semiconductor technology (Han et al., 2009; Ploss et al., 2000).

2.3 Stability of PVDF

2.3.1 Chemical stability of PVDF

Chemical stability of a membrane is vital in ensuring its long lifespan and high performance. Any reaction between membrane material and the employed chemicals will lead to the destruction of the membrane surface layer which then causes the membrane to become weak and fragile. The contact between membrane surfaces with chemicals regularly takes place in membrane system such as membrane distillation,

membrane gas absorption and during the cleaning process. This interaction could cause damage to the surface layer and more severe destruction occurs once the membrane material is incompatible with the employed chemicals. At present, polytetrafluoroethylene (PTFE), a completely fluorinated polymer is highly preferred as a membrane material and it has broad applications in the industrial sector. PTFE is known as one of the most stable membrane materials in terms of chemical stability and mechanical strength. However, because of its pricey cost, there is a high demand to search for a substitute that could offer comparable performance and high stability. In recent years, PVDF has been identified as the best alternative to PTFE, not only due to its economic value, but also supported by its intriguing chemical and mechanical properties (Zhang et al., 2006). Although PVDF has good chemical resistance, it is not compatible with strong alkali, esters and ketones (Hashim et al., 2011b). As reported by earlier works, PVDF experienced declining properties after being exposed to strong alkaline solution (Ross et al., 2000; Zhang et al., 2006). In actual application, the interaction between PVDF membrane and alkaline solution are inevitable because in a gas absorption system or membrane cleaning process, sodium hydroxide solution is often used as absorbent and cleaning agent respectively.

Several studies of PVDF susceptibility towards strong alkalis had been done; though their main objective is to study the degradation mechanism (Ross et al., 2000; Ross et al., 2001; Zhao et al., 2011). Only a few works directed at investigating the effects of alkaline environment towards PVDF stability have been successfully completed. A comprehensive review on PVDF polymer structural damage was documented, but, in regards to PVDF degradation concomitant to alkaline treatment, only a little information had been gathered (Nguyen, 1985). Earlier works have demonstrated the discolouration of PVDF after immersion in alkaline solution for several hours (Komaki, 1979; Shinohara, 1979). The colour changes from white to

brown and finally to black depending on the degree of dehydrofluorination process of the sample. Shinohara (1979) explained that the changes in colour of oxyfluorinated PVDF film from white to dark brown upon hot alkaline treatment indicated the formation of carbon-carbon double bond caused by the loss of HF units from the polymer chain. Furthermore, the shrinkage of PVDF film was detected when it was immersed in NaOH-ethanol solution and the film was found to turn into dark colour and became brittle as well (Komaki & Otsu, 1981).

Hoang and Ouellette (1983) confirmed that PVDF structure was degraded when exposed to NaOH. The intensity of attacks on PVDF is found to be accelerated by introducing load and once sufficient strain is imposed, fracture of the specimen could be observed. The deterioration on PVDF was due to chemical attack of hydroxide ions in α -conformation. Upon immersion in NaOH solution, the colour change of PVDF was observed. Kise and Ogata (1983) performed a research to study the effects of adding phase transfer catalyst into alkaline solution. They studied the reaction of PVDF powder exposed to a NaOH solution with the presence and absence of a phase transfer catalyst. Change in visual appearance of PVDF was observed subsequent to immersion in hot alkaline solution for several hours and the colour changes became more distinct once tetrabutylammonium bromide (TBAB) was added. The chemical reaction between NaOH and PVDF was associated with the dehydrofluorination process which is proven by the emergence of characteristic bands which corresponds to carbon-carbon double and triple bonds. Similar results were observed in a work which examine the outcome of dissolving PVDF granulate in a mixture of dimethylsulfoxide (DMSO) and acetone with NaOH as a catalyst (Wegener et al., 2006). The degradation of fluoropolymer caused by the HF loss from the polymer chain was confirmed by UV-vis spectroscopy and FTIR analyses.

Although various studies concerning PVDF destabilisation with alkaline were successfully documented, only three articles systematically assessed the stability of PVDF membrane in NaOH solution. The earliest work was based on a long term investigation intended to evaluate membrane performance after being subjected to different types of storing solutions (Benzinger et al., 1980). The PVDF membranes were immersed in two different treatment conditions; 1 wt % NaOH solution for two years and 10 wt % NaOH solution for a month. The membranes treated in either condition experienced no major difference in water flux measurement and retention of polyethylene glycol. The effect of membrane immersion in 10 wt % NaOH was significantly detected only after three months of storage period.

In addition, an assessment with regards to the modification in chemical stability of PVDF membrane (sulfonated hydrophilic ultrafiltration) stored in different types of solution up to one year period was performed (Vigo et al., 1984). The treated membranes undergo consistent inspection on permeate flux performance from time to time. In comparison to the membrane immersed in tap water, the one stored in diluted NaOH was observed to experience less ageing effect based on membrane water flux measurement. Membrane stored in tap water exhibit more flux reduction compared to those stored in a 0.1 N NaOH solution. Generally, no specific effect was observed when the PVDF membrane was exposed to different types of medium. Only concentrated NaOH and NaOCl was observed to cause notable effects on PVDF membrane characteristics. The increment in permeate flux is linked to the destruction of membrane structure which was dominated by chemical attack of hydroxide ions on a PVDF polymer chain. Additionally, by bursting pressure measurement, the mechanical integrity of the membrane was detected to experience destabilisation after being exposed to high concentration of sodium hydroxide and sodium hypochlorite solution.

Findings from both studies by Benzinger et al. (1980) and Vigo et al. (1984) were derived from the investigation of long-term exposure of PVDF membrane to NaOH. On the other hand, a systematic study on the effects of short term treatment with alkaline solution towards PVDF has been successfully documented (Hashim et al., 2011b). The membranes were made-up using various kinds of PVDF raw materials and later were immersed in NaOH solution at different conditions. The results demonstrate that the PVDF hollow fibres were instantly attacked by hydroxide ions. The melting temperature and melting enthalpy of alkaline treated membrane was reduced, which can be linked to the decline in crystallinity. Decrement in membrane crystallization can be concomitant with the changes in mechanical characteristics, although the fluctuation in mechanical stability might not only originate from the crystalline phase, but it could be contributed by the amorphous phase as well.

Other than NaOH, researchers have also conducted PVDF membrane stability studies with different chemicals such as potassium hydroxide (KOH) and sodium hypochlorite (NaOCl). The investigation of the changes in the structure of PVDF membranes treated with KOH-alcohol using electron spin resonance (ESR) analysis (Zhang et al., 2006). They observed that the exposure of PVDF membrane to alkaline environment had caused membrane structural modification. FTIR and FT-Raman spectroscopy confirmed the formation of carbon-carbon double bond, while the formation of a radical, $-\text{CF}_2-\text{C}\cdot\text{H}-\text{CF}_2-$ was detected using ESR. The radical was produced following the chemical attack of hydroxide (OH^-) ions on the CH_2 group and deprotonisation takes place. Radical formation was accelerated at an alkaline concentration below 6 g L^{-1} for a treatment period of less than 100 minutes. However, the formed radicals were not as many as formed via electron irradiation method and they could barely be present within two hours exposure to the surrounding.

The effect of using NaOCl on the ageing of PVDF flat sheet membrane was studied (Puspitasari et al., 2010). Membrane cleaning with NaOCl demonstrated a high efficiency in removing irreversible foulant on the membrane surface layer. Even so, the exposure to hypochlorite leads to a declined state of membrane properties. It is found that the degradation of PVDF membrane to be derived from two major steps: firstly, the alteration of its surface properties, followed by the increment in hydrophilic characteristics. Meanwhile, Wang et al. (2010) studied the effects of repeated cleaning with a high dosage of NaOCl on a pilot scale membrane bioreactor (MBR) operating for 63 days. The alterations in membrane contact angle, mechanical and surface properties of PVDF membrane subsequent to hypochlorite cleaning have been reported. The results indicated a declined ultimate tensile strength and the increment in ultimate elongation of the membrane. These features display a worrying signal that the membranes became weaker and more flexible after being exposed to hypochlorite. The FTIR analysis showed that the cleaning process did not impose significant damage to the chemical structure of the PVDF membrane, except for the changes in its surface properties.

The effects of different chemicals for post-fabrication treatment of PVDF hollow fibre membrane with SiO₂ as an additive was also studied (Hashim et al., 2011a). The membranes were treated with either 20 wt % NaOH at 70 °C or 47 to 51 wt % hydrofluoric acid at room temperature. The chemical treatment was intended to remove SiO₂ particle from the membrane precursor after membrane fabrication. Considerable improvement in pure water flux was observed for membranes washed using either solution. Hydrofluoric acid treatment presented higher efficiency in removing SiO₂ as it requires a shorter treatment time as compared to NaOH. The NaOH treated membrane showed a reduction in mechanical strength. Overall, it is concluded that hydrofluoric acid is favourable as it does not alter the membrane properties appreciably.

2.3.2 Thermal stability of PVDF

The thermal stability of a material represents its ability to resist changes in physical shape or size as temperature changes. Thermal stability of the membrane becomes a subject of concern mostly in the industrial sector that involves high temperature condition where membrane material potentially endures thermal destruction or decomposition. In general, the alteration in material properties largely relies on the glass transition temperature (T_g) for amorphous polymers and melting temperature (T_m) for crystalline polymers. Glass transition temperature (T_g) is a temperature below which material becomes hard and brittle or relatively easy to break and above this critical temperature, material possess more flexibility and elasticity. The change in phase from solid to liquid occurs at a specific temperature known as melting temperature (T_m). Both melting and glass transition temperatures have an important part in describing the phase changes of material. Beyond these critical temperatures, the properties of polymers will be affected.

Table 2.1: Glass transition temperature (T_g) and melting temperature (T_m) of commonly applied polymer.

Polymer	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
Polyethylene (PE)	-120	118 – 146
Polyvinylidene fluoride (PVDF)	-40	140 – 170
Polypropylene (PP)	-15	130 – 170
Polytetrafluoroethylene (PTFE)	126	310 – 385
Polyether sulfone (PES)	230	340 – 390

Polymer transition temperature is mainly determined by the chemical structure, which is comprised of chain flexibility and chain interactions. Table 2.1 lists the glass

transition temperature, T_g and melting temperature (T_m) value for common polymer membrane. PTFE, a fully fluorinated polymer contains four fluorine atoms strongly attached to its flexible polyene chain limiting its flexibility. Thus, PTFE exhibit higher T_g in comparison to other famous membrane material and these features contribute to higher stability of PTFE.

PVDF basically acts as inert as fully fluorinated polymer (PTFE), but yet has an added advantage of being easily fabricated via standard paths used for thermoplastic formation along with its good compatibility with common organic solvents (Liu et al., 2011b). PVDF is a semicrystalline fluoropolymer that consists of crystalline and amorphous phases. It is a tough polymer which could withstand a wide temperature range between -40 to 160 °C. The excellent thermal stability of PVDF is attributable to its crystalline phase, along with its flexibility due to the amorphous region of the polymer. In order to evidently notice the changes in chemical structure of PVDF, the temperature must exceed its melting point or lower than its glass transition temperature. In addition, PVDF exhibits thermal decomposition temperature of above 316 °C.

Typically, any factors that could contribute to the changes in T_g and/or T_m as well as the crystallisation process could be associated to membrane chemical and thermal stabilities. In industrial application, a right selection of membrane material having an appropriate T_g is critical to ensure a long life span of the applied membrane. For example, an offshore membrane system for CO_2 removal from natural gas requires membrane with medium T_g since the separation process could be carried out at ambient temperature. Whereas, for the removal of CO_2 from flue gas necessitates membrane material to have moderate T_g value and high melting temperature due to the high temperature of released flue gas, probably more than 100 °C (Li & Chen, 2005). Fluorinated polymers such as PTFE and PDVF are more thermally stable than hydrocarbon polymers thus, are more suitable for high temperature operation. The

chemical bonding between fluorine and carbon (C–F bond) is considered as "the strongest bond in organic chemistry" attributable to fluorine having the highest electronegativity (O'Hagan, 2008). Besides, the C–F bond is also recognized to have the largest bond dissociation energy among other halogen-carbon bonding (Dargaville et al., 2003).

Several works have been done to study the thermal stability of PVDF. For instance, the effect of employing moderate and high temperature in a vacuum on the thermal degradation of PVDF was studied (Madorsky, 1964). The result from the thermochemical decomposition at an elevated temperature in the absence of oxygen (the process known as pyrolysis) indicated that the thermal degradation system of PVDF is caused by the dehydrofluorination reaction. Following the withdrawn of hydrogen fluoride (HF) molecules, the creation carbon-carbon double bonds or cross-linking between different polymer chains are believed to take place. The dehydrofluorination degradation mechanism is shown in Figure 2.3.

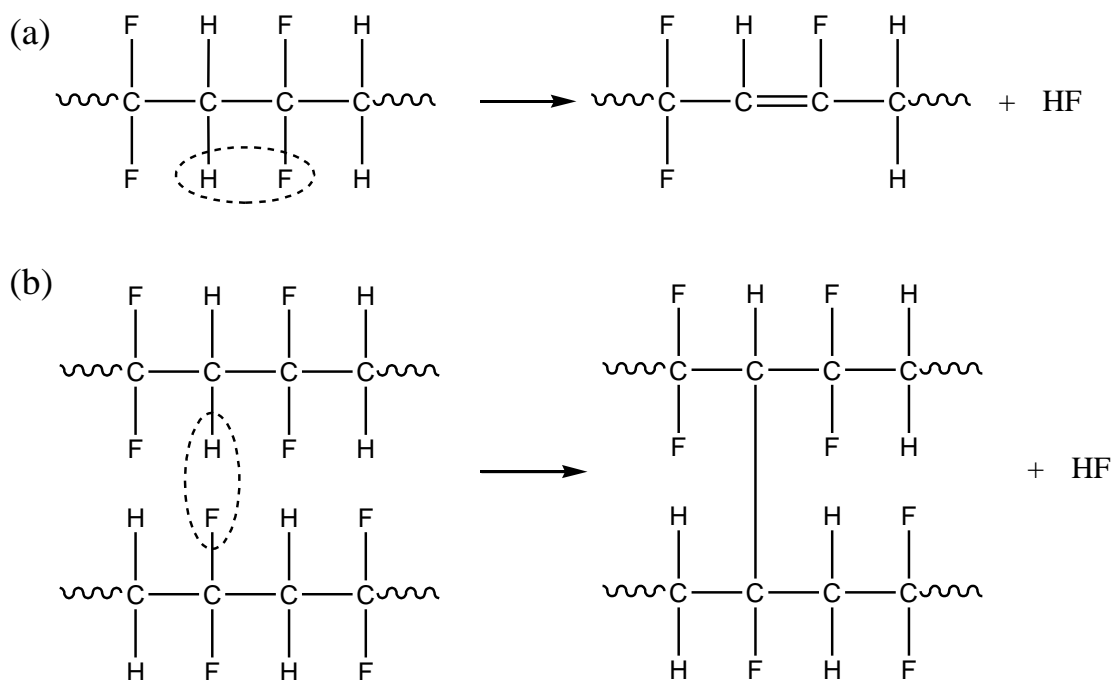


Figure 2.3: Dehydrofluorination reaction in PVDF by means of a) Double bonds formation and b) Crosslinking of the polymer.

A comprehensive review on PVDF polymer thermal stability has been compiled based on the works involving PVDF deterioration process carried out in earlier stages (Nguyen, 1985). The universal discussions on PVDF upon thermal degradation were derived from the dehydrofluorination reaction that leads to the formation of carbon-carbon double bonds. Meanwhile, at elevated temperature (approximately at 160 °C), an inhomogeneous thermal degradation of PVDF polymer, which has been crystallised was detected (Lovinger & Freed, 1980). They found that different spherulitic forms in PVDF degraded in different ways; causing inhomogeneous discoloration of the samples. The degradation process was observed to be a rare phenomenon where the destruction occurs mostly in its crystalline phase. Furthermore, the major part in PVDF degradation mechanism is due to the removal of HF units of the polymer chain which led to chain scission or cross-linking. Sequence and conformational changes in the molecular chain by heat treatment has been detected with the occurrence of many additional absorption bands in the infrared spectrum as a result of the process of crystallising at a prolonged period of time.

On the other hand, Furusho et al. (1974) used a Torsional Braid Analysis (TBA) to study the thermal dependence of structural changes in PVDF instead of using other common methods such as DSC and TGA. Several types of halogen-containing polymers which include PVDF were inspected and compared. Among all tested polymer samples, PVDF was figured out to be the most thermally stable. Moreover, the thermal stability of ultrafiltration (UF) membrane fabricated from Kynar raw material by employing circular-wound module at an elevated temperature was assessed (Benzinger et al., 1980). There was no indication of destruction on the PVDF membrane when it undergoes a nonstop process at a temperature of 85.6 °C, while maintaining a steady pressure for seven months testing period.

2.3.3 Mechanical stability of PVDF

The mechanical strength of a membrane is associated with its degree of crystallinity and the membrane morphology. Deterioration of mechanical properties is often considered as one of the reasons of early life failures, mainly for thin membranes. The declination in mechanical strength could be due to cracks, tears, punctures or pinhole blisters stress (Collier et al., 2006). A regular mechanical problem in membrane is the reduction of the membrane's strength caused by the chain breaking of polymer materials by chemicals. The chemical attacks on the polymer backbone contribute to a high potential of degradation and destabilisation of membrane mechanical properties. Fundamentally, the mechanical stability of membranes must be a matter of concern, even during its fabrication stage. Throughout the membrane preparation, great caution should be taken as unknown particles (contaminants) which originated from the fabrication process could lead to perforation. Moreover, the damage could also occur at reactant inlets, seals or edges: any areas where the membrane is subjected to increased stress (Collier et al., 2006).

A relative estimation of membrane life span could be done based on the measurements of mechanical strength (Arkhangelsky et al., 2007a). Examination of macroscopic parameters such as tensile strength and elongation could act as a simple, non-invasive test for a periodic assessment of the destruction on membranes. The polymer properties such as its structure, morphology and crystallinity have a huge influence on membrane mechanical stability. The mechanical aspect of a particular membrane system largely depends on the tensile strength of the membrane itself. If the material is subjected to a very high pressure or high strain deformation, its structure will permanently collapse as it endures plastic deformation and thus will experience ultimate failure. For instance, once the membrane rupture occurs, the separation process could not be carried out without a proper barrier between different phases or two different

fluids to be separated. Accordingly, the proper selection of membrane material is crucial to ensure the suitability of fabricated membranes with its proposed application. Considerably flexible membranes are preferred in the membrane system given that the flexibility of the membranes represents the extent of its mechanical strength. For that reason, flexibility has become one of the criteria of a good membrane material since broken fibres will be the main reason of membrane system failure.

A series of experiments have been conducted to investigate the changes in mechanical properties of PVDF hollow fibre membranes upon immersion in alkaline solutions at different conditions (Hashim et al., 2011b). Any changes in PVDF membrane's mechanical properties were studied by the measurement of its tensile strength, Young's modulus and elongation at break. In general, the exposure to NaOH solutions results in a declining membrane elongation and crystallinity. Treatment with 1 and 4 wt% NaOH resulted in a moderate reduction of membrane elongation while using 10 wt% NaOH, a drastic decline in the elongation was observed. The PVDF membrane could hardly endure hot NaOH solutions, even at a lower concentration of the solution. Once the membranes were exposed to NaOH for more than 8 hours at high temperature, treated membranes became very fragile to allow for tensile testing to be performed. The degree of membrane degradation was found to be intensified with the increment in concentration and/or temperature of NaOH solution. Under harsh treatment conditions, PVDF hollow fibre membrane experience a total loss in mechanical integrity in a very short treatment period.

2.4 PVDF membrane in alkaline environments

It is anticipated that the used membrane will not perform or possess the similar properties as a virgin membrane (Shi et al., 2014). This is due to the ageing process which occurs once the membrane is in contact with the chemicals for a certain period of time. In actual applications, there are several cases where PVDF is in contact with

alkaline environments. The following sections discuss the two most common cases of interaction between PVDF and alkaline solution: membrane gas absorption and during membrane cleaning process.

2.4.1 Membrane gas absorption

A typical application of membrane gas absorption aims to reduce poisonous gases up to an acceptable level in accordance to current stringent environmental regulations. Environmental concerns on the substantial emission of toxic industrial gas such as hydrogen sulphide (H_2S), carbon dioxide (CO_2), sulphur dioxide (SO_2), nitrogen oxide (NO) and nitrogen dioxide (NO_2) can be extensively reduced by the employment of this device (Atchariyawut et al., 2007; Li et al., 1999; Luis et al., 2012; Park et al., 2008; Park et al., 2009). During the removal process, the gas intended to be eliminated will diffuse through the membrane and be absorbed by liquid absorbent on the other side of the membrane. The outstanding properties of PVDF such as thermally stable, high mechanical strength and robustness to different types of chemicals has made it eminently to be applied as a gas-liquid membrane contactor for capturing greenhouse gases (Ahmad et al., 2010; Feng et al., 2013; Wang et al., 2004).

Up till now, numerous studies on membrane gas absorption process have been conducted with PVDF membranes (Atchariyawut et al., 2007; Mansourizadeh et al., 2010; Park et al., 2008; Wang et al., 2002). Porous PVDF hollow fibre membranes were used to separate CO_2 from a gas mixture containing methane (CH_4) using NaOH, monoethanolamine (MEA) solution and pure water as liquid absorbent (Atchariyawut et al., 2007). The CO_2 flux was measured to be six times higher when using 1 M NaOH aqueous solution compared to pure water. Temperature elevation has resulted in an increase of the CO_2 flux driven by the enhanced mass transfer coefficient in the liquid phase. Overall, NaOH was found to offer the highest separation, as well as keeping a constant CO_2 flux throughout the experiment.

The application of PVDF hollow fibre membrane for CO₂ removal with NaOH as absorbents was reported (Mansourizadeh et al., 2010). Using 0.2 M NaOH, the gradual flux reduction was observed after a long term operation of 80 hours. The partial wetting has been observed for membrane in contact with NaOH as a result of pore enlargement. In other research, the efficiency of PVDF hollow fibre membrane in gas-liquid contactor for absorption of sulphur dioxide (SO₂) and nitrogen dioxide (NO₂) is studied by Park and co-workers with different absorbents such as sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃) and NaOH (Park et al., 2008; Park et al., 2009). The removal efficiency of NO₂ was measured to be approximately 42 % with 0.2 M NaOH. In the study of SO₂ absorption, the increase in NaOH concentration has resulted in the enhancement of the separation performance. Up to 70 % removal efficiency was achieved when using either 0.2 M or 2 M NaOH at various liquid flow rates.

The above mentioned works had shown the prevalence of PVDF membrane application in the gas absorption process conducted in caustic environments. In general, the application of PVDF membrane in membrane gas absorption shows a high separation efficiency and has a huge potential in large scale application. It is to be noted that the application of alkaline solutions in the membrane contactor could be detrimental to PVDF membranes. Earlier studies indicated that once the alkaline solution is in contact with a PVDF membrane, it will exert impacts on its surface characteristics particularly in harsh conditions (i.e. relatively high alkaline concentration at prolonged term of operations and/or high temperature operation) (Ross et al., 2000; Zhao et al., 2011). For that reason, the suitable ranges of alkaline concentration need to be inspected between PVDF membrane and alkaline absorbent before operating the membrane system.

2.4.2 Membrane cleaning

Apart from the great achievement in membrane separation technology, there are several undesired downsides which limit its effectiveness. One regular setback in the membrane filtration process is the fouling phenomenon. Basically, membrane lifetime and permeated fluxes are influenced by the concentration polarization and the accumulation of undesired materials on the membrane surface (Zularisam et al., 2006). Fouling occurs when certain impurities or constituents are deposited on the membrane surface and plugs into the pores, thus causing a decrement in membrane flux and permeability. It will then lead to a poor separation performance (Puspitasari et al., 2010). The decline in membrane flux can be recovered with membrane cleaning process. Membrane cleaning is regarded as an essential process of the operation of membrane filtration systems. It is common that the cleaning procedure is executed on a routine basis in membrane separation process, even when very well design along with sufficient pre-treatment processes have been integrated into the filtration system.

Fouled membrane can be cleaned via different approaches. In general, there are three cleaning options which are physical, chemical and biological, each depending on the types of foulant. The flux recovering process via physical cleaning is suitable for the removal of the deposited material (also known as cake layer) on the membrane surface, whereas cleaning with chemical works effectively on eliminating minerals, inorganic and organic substances and microorganisms. Biological cleaning on the other hand is used to remove the foulants on the surface or inside the membrane pore by means of biocides, for example microorganisms and enzymes. Physical cleaning via backwashing or flushing could potentially eliminate the cake layer that has been deposited on the surface layer. However, this method is ineffective in a case where the foulants were already absorbed into the membrane layer or pore plugging by means of chemical reaction occurs between the foulants and membrane material. Accordingly, chemical

cleaning is the ideal approach to remove irreversible foulant for optimum restoration of the flux (Kimura et al., 2004).

Prior to cleaning protocols, one should focus on the appropriate selection of reagent, reagent concentration along with proper cleaning cycle and interval. It is important to consider the chemical compatibility of membrane, the nature of foulant and the extent of fouling occurrence. The chemical selected mostly depends on types of foulant and the tolerance of the membrane towards the reagent itself. Membrane chemical cleaning could be done with various types of cleaning agents such as alkaline, acids, oxidants, chelating agents, surfactants and so forth (Simon et al., 2013; Wang et al., 2010). Table 2.2 lists several types of the common cleaning agents used in membrane cleaning procedure (Porcelli & Judd, 2010; Regula et al., 2014).

Table 2.2: Common chemical agents for membrane cleaning

Types	Functions	Typical Reagent
Caustic	Hydrolysis and solubilisation, saponification	NaOH
Acids	Solubilisation	HCl, HNO ₃ , Citric acid
Oxidants/disinfectants	Oxidation and disinfection	H ₂ O ₂ , NaOCl
Chelating agents	Chelation	EDTA
Surfactants	Emulsifying, dispersion and surface conditioning	Sodium dodecyl sulfate (SDS), Tween 20

Description on fouling during the filtration process have been widely recorded in the literature, but there are fewer publications that have been dedicated to presenting a comprehensive overview of membrane cleaning (Levitsky et al., 2011a; Stengaard, 1988). Deliberately to clean the membrane fouled with humic acid (HA) during a PVDF

membrane distillation process, Srisurichan et al. (2005) employed 0.1 M NaOH solution as a cleaning solution. Alkaline cleaner was found to be 100 % efficient in restoring membrane flux attributable to the high dissociation of HA at high pH. Alkaline cleaning was also performed by utilising water/NaOH (1 wt %) in a submerged rotating membrane bioreactor system that was severely fouled (Zuo et al., 2010). Distinct membrane pores were attained after cleaning, since the NaOH solution eliminates the organic contaminants of protein, together with the microorganisms lying inside and on the surface of the membrane.

Until now, the chemical cleaning process, particularly in the polymeric membrane system is still not completely understood. The exposure towards chemicals could potentially affect the properties of the membrane. Therefore, it is important to ascertain the optimum concentration of applied chemical such as alkaline solution or oxidant. Employing extreme concentrations of hydroxide and hypochlorite are found to be unfavourable in terms of operating expenses and a decline in membrane properties (Arkhangelsky et al., 2007b; Ross et al., 2000; Zhao et al., 2011). From previous work, at hypochlorite concentrations over 150 mg L^{-1} and low pH values, chlorination of the carbon-sulphur (C-S) bonds in PES has been observed (Arkhangelsky et al., 2007b). It has been reported that the pH tolerance of PVDF membranes is limited to a value below 11 (Ross et al., 2000). Particularly for PVDF membrane, several works on cleaning study is listed in Table 2.3.

Table 2.3: Studies of cleaning on PVDF membranes

No.	Membrane	Cleaning condition	Remarks	References
1)	PVDF flat sheet membrane with a nominal pore size of 0.22 μm (Millipore)	Cleaning agent: 0-5 % NaOCl. After filtration, rinsing was performed for 2 min using MilliQ water with the same flow rate as the feed. The membrane was then cleaned for 10 min using 1% of NaOCl.	<ul style="list-style-type: none"> • Higher NaOCl concentration improved the cleaning efficiency. For a given NaOCl concentration, lower cleaning efficiency was recorded for cyclical cleaning. • Reduction in hydrophilicity proven with the loss of the carbonyl peak. • Virgin membrane has an average pore of 0.187 μm (lower than the pore size value given by the supplier). Pore size was increased to 0.211 μm for 1-week-aged membrane, and the value decreased to 0.162 μm after 2 weeks of ageing. • NaOCl caused membrane ageing after prolonged exposure and changes in membrane chemical groups, hydraulic performances, mechanical properties and physical structures were observed. 	(Puspitasari et al., 2010)

No.	Membrane	Cleaning condition	Remarks	References
2)	PVDF membranes with 30 kDa (Sterlitech Corporation)	Cleaning agent: 0.15 g L ⁻¹ free chlorine (Unilever), 0.25 g L ⁻¹ Tween 20 (Fluka Chemie), 4.0 g L ⁻¹ NaOH and a NaOCl/Tween 20 composite. Fouled membrane cleaned by consecutive soaking in alkali, surfactant and oxidant.	<ul style="list-style-type: none"> • Tween 20 offers the highest cleaning efficiency followed by NaOCl and NaOH. • Following cleaning, increased membrane permeability and hydrophilicity was observed. • Formulated cleaning offer shorter cleaning time achieved by a multi-stage cleaning mechanism. 	(Levitsky et al., 2012)
3)	PVDF-30 membrane (Sterlitech Corporation)	Cleaning agent: NaOCl (Unilever, 30% free chlorine). Cleaning dose varies from 5 g h L ⁻¹ up to 120 g h L ⁻¹ . Membrane soaked in 50 ml cleaning solution and was fixed on a vibration table for various times.	<ul style="list-style-type: none"> • NaOCl cleaning significantly decreased contact angle values. • Pore enlargement was observed. • Cleaned membrane offers better protein rejection. • The BSA retention mechanism is adsorption governed by membrane hydrophilicity. 	(Levitsky et al., 2011a)

No.	Membrane	Cleaning condition	Remarks	References
4)	PVDF flat sheet membrane (Millipore)	Cleaning agent: 0.1 M NaOH. Cleaning by recirculation of pure water for 2 h, and followed by 20 min of recirculation of the NaOH solution.	<ul style="list-style-type: none"> The permeation flux recovery was 87.5% of the initial flux after water rinsing. Given by good dissociation and dissolution of HA at high pH, a complete flux recovery was attained after recirculation of the alkaline solution. 	(Srisurichan et al., 2005)
5)	PVDF flat sheet membrane with 0.2 μm (supplied by the Institute of Polymer Science, Zhejiang University)	Cleaning agent: Water, 1 wt % NaOH and 0.5 wt % HCl. Water scouring was done prior to chemical cleaning. Alkaline cleaning with NaOH was done for 5 h. The combined cleaning was done consecutively with NaOH and HCl for 5 h each. Membrane was rinsed with water after chemical cleaning.	<ul style="list-style-type: none"> Flushing the membrane surface with water, water/NaOH and water/NaOH/HCl recovered permeate flux to 48.4%, 83.5% and 90.2% of the initial operation, respectively. Organic contaminants nourished on the surface and inside of the membrane were effectively removed by NaOH whereas HCl eliminate inorganic mineral materials and salts on the membrane surface. Membrane pores were observed to be more distinct subsequent to chemical cleaning. 	(Zuo et al., 2010)

No.	Membrane	Cleaning condition	Remarks	References
6)	Hydrophilic PVDF membrane with nominal pore size of 0.04 μm (Siemens)	Cleaning agent: 20,000 ppm NaOCl solutions. Cleaning was done for 17 min per cycle.	<ul style="list-style-type: none"> • Membrane contact angle was observed to slightly decrease. • Decrease in TOC rejection can be explained by the potential increase in pore size or in surface hydrophilicity. • The tensile properties of the PVDF membranes were observed to be more severely compromised following contact with chemicals. 	(Hajibabania et al., 2012)

Other than observing the effect of cleaning on flux recovery, the changes in polymeric membrane stability have also been considered. The hypochlorite cleaned membrane experienced a decline in tensile strength, elongation at break as well as its elasticity (Arkhangelsky et al., 2007a). It was observed that the degree of degradation was influenced by the dosage of oxidant (the product of the concentration (C) and the contact time (t) with a unit of g h/L). The main concern was that the reduction in membrane mechanical strength was detected even at hypochlorite dosage of 250 g h L^{-1} that is considered as safe for membrane cleaning.

All these works have shown that chemical cleaning to be relatively satisfactory for recovering membrane water flux. Nevertheless, it is insufficient to characterize the membrane properties solely by flux recovery since it does not disclose the chemical, thermal and mechanical properties of the membrane in details. The suitability of cleaning agent and the membrane material is necessary in extending the membrane lifetime. Any incompatibility issue will result in potential damage on membrane structural characteristics. Previous studies have shown the significant impact of cleaning process towards the stability of the membrane (Arkhangelsky et al., 2007a; Levitsky et al., 2011a; Levitsky et al., 2012; Regula et al., 2013; Zhang & Ma, 2009); therefore it is suggested that membrane chemical should be minimized to a low frequency. In reality, PVDF is at risk of hydroxide ions attacking when exposed to caustic environment, yet many researchers had overlooked this matter. Indeed, it is inappropriate to use alkaline solutions without setting its limit in membrane cleaning as it tends to damage the PVDF unintentionally.

2.5 BSA protein retention/fouling mechanism

Protein fouling of polymeric membranes is still an area of active research. One of the most commonly employed proteins for research purposes is bovine serum albumin (BSA). BSA is often used to prepare model solutions for membrane fouling experiments due to its stability and lack of interference within biological reactions. A number of protein fouling studies have explained the declination of flux through classic blocking filtration models (Bowen et al., 1995; Hlavacek & Bouchet, 1993; Jonsson et al., 1996). In the case of BSA fouling, general agreement was made based on the literatures concerning the fouling mechanism that occurred in two steps. Earlier work described a two step mechanism for BSA fouling in which the initial flux decline was due to the deposition of large BSA aggregates on the membrane surface, and these aggregates subsequently serves as an attachment (or nucleation) sites for the continual deposition of bulk (native) protein (Kelly & Zydney, 1995).

Several studies have explained that the fouling of membranes occurred as the adsorption of protein aggregates on the membrane surface and subsequent pore blockage (Ho & Zydney, 1999, 2000). At extended filtration times, the behaviour of BSA fouling was governed by a cake filtration mechanism. During filtration, membrane fouling is largely depends on the protein–membrane and protein–protein interactions. The protein–membrane interactions affect irreversible adsorption onto the membrane surface as well as within membrane pores while the protein–protein interactions influence the structure of the cake layer that forms on the membrane surface (Huisman et al., 2000).

Currently, the hydrophilic PVDF membrane has attracted substantial interest in the membrane filtration process largely due to its excellent mechanical properties. A number of works using BSA as a model protein solution for membrane fouling and

cleaning studies with PVDF membrane as the filtration medium have been documented (Levitsky et al., 2011a; Levitsky et al., 2012). Experiments with BSA filtration were performed to evaluate the membrane separation performance as well as the fouling phenomena. It was proposed that the main BSA retention mechanism using PVDF membrane is adsorption governed by membrane hydrophilicity. The membrane pore size does not govern the BSA retention, in which the observed BSA retention trend was opposite to the changes in the membrane pore size (i.e. protein retention, increased even the pore size enlarged). Cleaned membranes with larger pore but having higher degree of hydrophilicity resulted in a better performance than virgin membrane of smaller pore size (Levitsky et al., 2011a).

The protein adsorption is a very complex process which is influenced by various factors. Hydrophobicity and surface charge are two physicochemical properties that are identified to have considerable impact on adsorptive fouling. Xiao et al. (2011) investigated the combined effect of membrane and foulant hydrophobicity and surface charge on adsorptive fouling during microfiltration experimentally and theoretically. It was observed that the adsorptive fouling between different membrane-protein pairs show that the hydrophobicity and/or surface charge of the fouling participants has a significant effect on adsorptive fouling. The hydrophobic interaction as compared to electrostatic interaction is the major mechanism affecting adsorptive fouling. These findings were, however based on semi-empirical investigation, thus the description of protein fouling mechanism is still open for further study.

CHAPTER 3: MATERIALS AND METHODS

This section summarises the experimental procedure for the research work, which includes materials, methods, sample treatment and analysis for respective experiments. The research instruments employed in this work are presented in the next section and followed by the elaboration on analytical testing performed to study the membrane characteristics. Following that, the details on the method used to measure bovine serum albumin (BSA) retention were discussed thoroughly. Prior to experimental work, a comprehensive literature review was conducted to gain as much understanding of the proposed research study and to find research gaps that later became the research questions required to be answered. It is focused on to gain the fundamental knowledge of PVDF membrane characteristics and the properties of the alkaline solutions used for membrane treatment. Major references will be from journals, articles and books. In this project, there were two parts of the experimental work. The first part is focused on the investigation of the effects of alkaline solution towards PVDF membrane via an immersion process, while the second part is highlighted on studying the impacts of chemical cleaning towards fouled PVDF membrane. The design of the proposed experimental plan was expected to be able to characterise the impact of chemical exposure on PVDF membrane properties and performance.

3.1 Materials

In the first part of this study, the hydrophobic PVDF membrane used is in a microfiltration (MF) range with an average pore size of 0.45 μm . The commercial flat sheet MF PVDF membrane was obtained from Sinoma Group (China). The membrane was prepared from pure PVDF without the incorporation of additives (information given by the manufacturer). Sodium hydroxide and potassium hydroxide (both in pellet form) were purchased from R&M Chemicals (Malaysia). Throughout the experiment, ultrapure water (Milli-Q with resistivity of 18.2 M Ω .cm at 25 °C) was used for chemical solution preparation and membrane rinsing.

In the second part of this research work, the commercial ultrafiltration (UF) hydrophilic (modified) PVDF membrane with the 100K molecular weight cut off (MWCO) was purchased from Sterlitech Corporation (USA) was used. Prior to filtration experiment, the membrane was rinsed using ultrapure water to remove any preservative on its surface and soaked in ultrapure water for a day. NaOCl with 4.99% available chlorine was obtained from Fisher Scientific (Malaysia). Bovine serum albumin (BSA) was obtained from Sigma Aldrich (Malaysia) and its characteristics are shown in Table 3.1. The protein solution was prepared by dissolving in ultrapure water.

Table 3.1: BSA characteristics.

Criteria	Specification
Form	Powder
Colour (Solid)	White to Light Tan
Colour (Solution – water)	Clear to slightly hazy
pH	6.5 – 7.5

3.2 Experimental flow chart

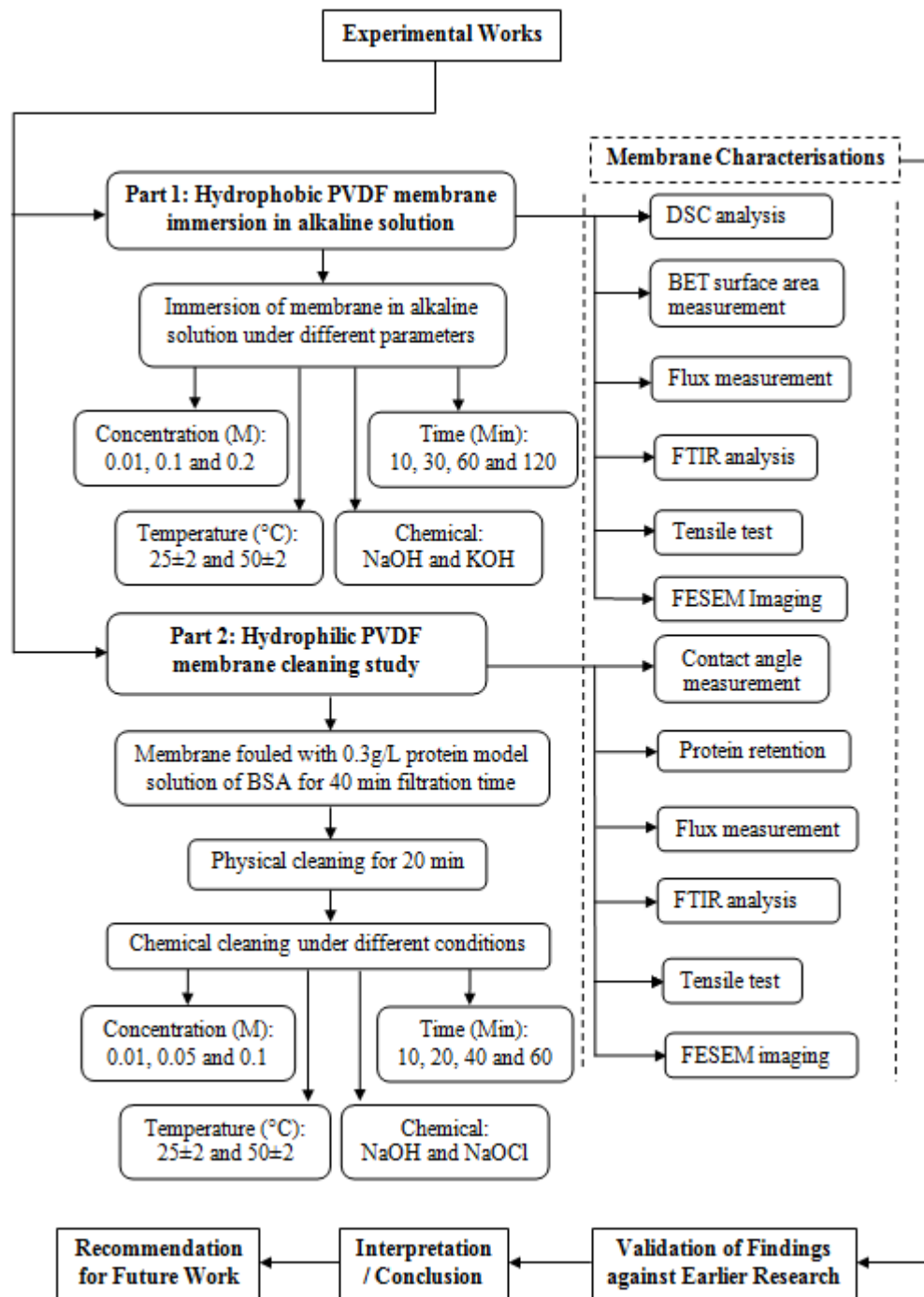


Figure 3.1: Experimental flow chart

3.3 Experimental work

3.3.1 PVDF membrane immersion in alkaline

In the first part of this work, the main purpose was to mimic the condition in a membrane contacting system where the PVDF membrane was exposed to alkaline absorbent. From literatures, the MF PVDF membrane was commonly used in membrane contactor, thus flat sheet membrane with pore size 0.45 μm was chosen for this study. Generally, this work intended to investigate the effects of alkaline environments at mild conditions on the stability of PVDF membranes (hydrophobic and hydrophilic). The term "mild" represents a relatively low concentration, lower temperature and shorter exposure time that was used in this work as compared to previous studies on PVDF membrane stability. The range of parameters was selected based on the literature in which most current studies on membrane gas absorption were conducted at ambient temperature (from 20 to 25 $^{\circ}\text{C}$) with absorbent concentration is typically in a range of 0.01 to 2 M.

The treatment with different types of strong alkaline solutions (NaOH and KOH) on PVDF membranes was carried out using various chemical concentrations at different time and temperature. The effect of different treatment duration on PVDF membrane was conducted for 10, 30, 60 and 120 minutes with various alkaline concentrations of 0.01, 0.1 and 0.2 M. The treatment was performed by membrane immersion in the chemical solutions for designated conditions. The effect of immersion temperature was investigated by immersing PVDF membranes into each set of solution under different temperature of 25 ± 2 and 50 ± 2 $^{\circ}\text{C}$ respectively.

Subsequent to treatment, the membrane samples were rinsed using ultrapure water, then stored in ultrapure water (Milli-Q) for approximately one hour to quench the chemical reaction and remove any residual chemicals that remain on the membrane

surface. The samples were next allowed to dry in room conditions. All of the treated membrane samples were preceded for characterization analysis and performance evaluation.

3.3.2 Membrane cleaning study

In the second part of the study, the major focus was to investigate the short-term effects of chemical exposure on fouled hydrophilic PVDF membrane surface, analogous to a chemical cleaning process in membrane systems. The measurement of membrane water flux was conducted using cross-flow filtration. In this study, the filtration module was fabricated by Solteq (Membrane Bench Filtration Model TR 32). Figure 3.2 represents the flow diagram of the cross-flow filtration. In cross-flow filtration mode, the fluid feed stream travels tangential to the membrane, creating a pressure differential across the membrane. This causes water to pass through while some of the particles deposited onto the membrane. Remaining particles keep on flowing across the membrane and "cleaning it". In comparison to the dead-end filtration module, the use of a tangential flow will prevent thicker particles from building up a filter cake. The cross-flow filtration mode is however also subjected to fouling. In this work, UF flat sheet PVDF membranes were fouled with BSA solution, a commonly used protein concentration standard. The protein was initially in a solid form and the organic solution was prepared by mixing the BSA solid in ultrapure water. For membrane cleaning process, NaOCl and NaOH have been selected as chemical agent since both are regularly used in the industry and commercially available.

Similar to the first part of the study, the parameters in membrane cleaning procedure were selected in accordance with the most commonly employed conditions for the cleaning process (i.e. cleaning agent concentration, cleaning period and temperature) documented in earlier works. Three different concentrations were tested (0.01, 0.05 and 0.1 M) and the cleaning period were 10, 20, 40 and 60 minutes. The

effect of different temperature on cleaning performance was investigated by cleaning the membrane at room condition (25 ± 2 °C) and 50 ± 2 °C. NaOCl and NaOH which are both frequently used in membrane cleaning studies have been selected as cleaning agent for comparison. It is to be noted that the cleaning process was performed in-situ (without removing the membrane from the filtration module), at which cleaning fluid is allowed to flow along the filtration system.

Prior to filtration experiments, the membranes were soaked in ultrapure water for approximately a day. Firstly, the water flux permeation of virgin membrane was measured for at least 40 minutes of filtration process using Milli-Q water. Cross-flow filtration was carried out at a transmembrane pressure of 0.1 MPa. Following that, the membrane was subjected to foul with 0.3 g L^{-1} BSA solution for a filtration period of 40 minutes. This time was designated to be sufficient in order for the fouling to occur. Fouled membrane was subsequently undergone two types of cleaning method, which were physical cleaning using water for 20 minutes and chemical cleaning using a chemical agent for the specific conditions. Subsequent to the cleaning procedure, the filtration system was rinsed for approximately 15 minutes using Milli-Q water. The cleaned membrane was preceded for another fouling experiment, followed by another cycle of cleaning. In general, a sequence of membrane cleaning experiments was carried out as follows:

1. Virgin hydrophilic PVDF membrane water flux measurement for 40 min.
2. Fouling with 0.3 g L^{-1} BSA solution for 40 min.
3. Physical cleaning with ultrapure water for 20 min, followed by chemical cleaning at different parameters.
4. Cleaned membrane water flux measurement for 40 min.
5. Cleaning procedure (as in Step 3) is repeated.
6. Second time cleaned membrane water flux measurement for 40 min.

Subsequent to oxidative cleaning, a little amount of sodium sulphite (0.01M) was added during system rinsing with Milli-Q water to remove traces of NaOCl prior to another cycle of BSA filtration. To evaluate the flux recovery, the ratio of the specific flux ($\text{L h}^{-1} \text{m}^{-2} \text{bar}^{-1}$) of permeate flux for first time cleaned membrane, J_{p1} , to the initial flux of virgin membrane, J_v , was calculated and described as cleaning efficiency (C_{e1}) while the ratio of permeate flux for second time cleaned membrane, J_{p2} , to the initial flux of virgin membrane, J_v , was represented as cleaning efficiency (C_{e2}). The cleaning efficiencies represented using the following equations:

$$\text{First time cleaning efficiency } (C_{e1}) = \left(\frac{J_{p1}}{J_v} \right)_{\text{Ultrapure water}} \quad \text{Equation 1}$$

and

$$\text{Second time cleaning efficiency } (C_{e2}) = \left(\frac{J_{p2}}{J_v} \right)_{\text{Ultrapure water}} \quad \text{Equation 2}$$

It is worth to mention that in this study, the reported value of cleaning efficiency, C_e was the percentage ratio of permeate flux of second time cleaned membrane, J_{p2} to the initial flux of virgin membrane, J_v .

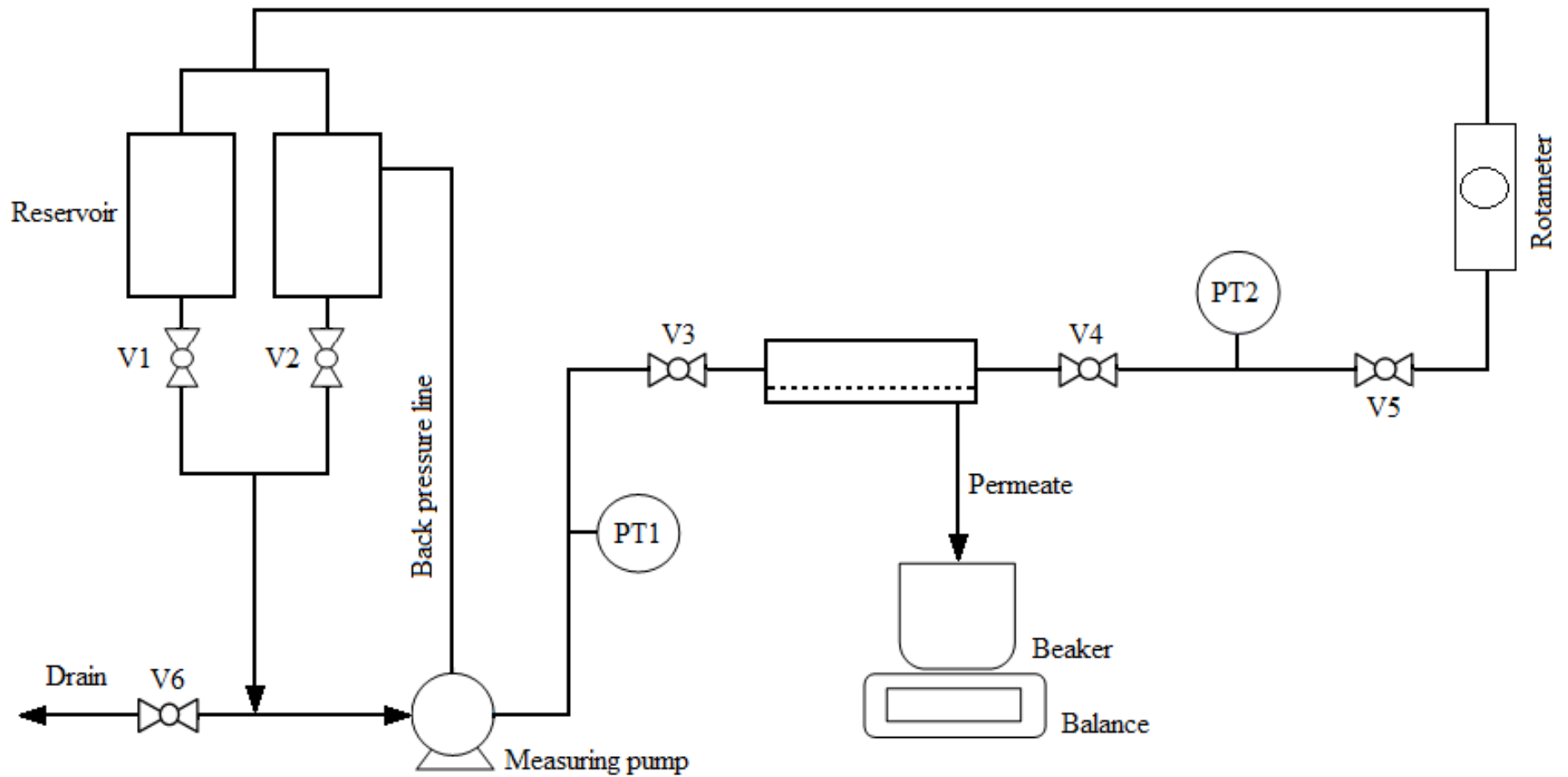


Figure 3.2: Schematic diagram for cross-flow filtration module

3.4 Membrane characterisation

Characterisations of virgin membrane and treated membranes was performed using Field Emission Scanning Electron Microscope (FESEM), BET surface area analysis, Differential Scanning Calorimetry (DSC), Fourier Transform Infra-red (FTIR) spectroscopy, water flux measurement and mechanical strength measurement. Table 3.2 summarises the scope of analysis for this research work.

Table 3.2: Analysis of membrane properties.

Membrane characteristic	Scope of analysis
Morphology	FESEM images provide the visual information of the membrane surface
Surface area	Measurement of specific surface area via BET theory
Mechanical strength	Tensile strength and elongation at break
Chemical composition	Diffraction peaks and characteristic bands via FTIR analysis
Thermal properties	Melting point measurement using DSC analysis
Hydrophobicity/ Hydrophilicity	Contact angle measurement via sessile method

The relationship between the degree of PVDF membrane degradation caused by different chemical solutions with the membrane morphology, properties and performance will be investigated. Afterwards conclusion will be drawn on the recommended chemicals used for the absorption of soluble gaseous in the membrane contacting system and membrane cleaning.

3.4.1 Membrane surface morphology analysis

The morphology of the surface of the PVDF membranes was inspected by the Field Emission Scanning Electron Microscope, FESEM (Carl Zeiss Microscopy, USA). Prior to imaging, it is necessary that the membrane to be coated. The dried, cleaned membrane samples were placed on stubs with conductive paste, and then sputter coated with a thin layer of gold for 30 seconds. The images of the surface of the virgin and treated membranes were taken at different magnifications.

3.4.2 Mechanical strength analysis

Instron 5569 machine (Instron, USA) was used to measure tensile strength and elongation at break of the membranes. Tensile testing of PVDF flat membrane was performed in accordance with ASTM D882. Prior to testing, all specimens were cut into a similar rectangular shape of 1 cm width and 12 cm length. Vertical alignment of the specimen is an important aspect in order to avoid side loading and/or bending moments created in the specimen. The specimen was first mounted in the upper grip assembly then allowed to hang freely. This was practical in helping to maintain a correct alignment prior to testing. Once both ends of the sample were securely clamped, the sample was next pulled at a steady elongation velocity of 50 mm min⁻¹. The initial gauge length was set at 8 cm for all samples. At least five measurements were done for each specimen and the standard deviation determined to be less than 5%. All measurements were conducted at room temperature.

3.4.3 BET surface area analysis

In order to determine any changes in surface area, membranes were tested with the surface area and porosity analyzer, ASAP 2020 (Micromeritics, UK). The specific surface area of membrane was determined by Brunauer, Emmet and Teller (BET) adsorption method. Prior to analysis, the membrane was cut into small pieces and dried

in a lab dryer (Protech). Oven drying is not preferable due to its high temperature that may cause structural changes to the membrane. The sample will next place in the sample tube and the tube was next secured to its position. The sample was first degassed at 120 °C for 3 hours, followed by analysis using mesopore method.

3.4.4 Chemical composition analysis

The structure of virgin PVDF membranes and PVDF membranes exposed to chemical solution were analysed by using FTIR spectrometer. Membranes are tested using FTIR to analyze the surface chemical composition changes. The chemical functional group of membrane is determined in attenuated total reflectance (ATR) mode. All surface infrared spectra were obtained in the wavelength range of 650 to 4000 cm^{-1} using a Nicolet iS-10 spectrometer (Thermo Scientific, USA) by signal averaging 32 scans set at 4 cm^{-1} resolution. It is worth to mention that the selected wavelength range is from 1500 to 2100 cm^{-1} , a range in which peaks representing the carbon-carbon double (1595 to 1650 cm^{-1}) and triple bond (2100 cm^{-1}) could be detected.

3.4.5 Thermal analysis

Differential scanning calorimetry (DSC) was used to measure the rate of heat flow, and compares the differences between the heat flow rate of the test sample and known reference materials. Thermal analysis in this study was based on the determination of melting point of the membranes using Differential Scanning Calorimetry (DSC) 1 machine (Mettler Toledo, Switzerland). For sample preparation, approximately 5 mg of sample (that has been cut into small pieces) was placed into the aluminium (Al) crucible and the crucible with the cap was pressed. A little hole was made on the cap. Subsequently, the data analysis was recorded using STARE software

starting at operating temperature of 0 °C to a maximum of 250 °C with a heating rate of 10 °C min⁻¹.

3.4.6 Membrane water flux measurement

A series of analysis on the membrane water flux of PVDF membranes were evaluated using the cross-flow filtration module (Solteq Membrane Bench Filtration, Model TR 32) with an effective working area of 40.1 cm². Ultrapure water (Milli-Q) was used throughout this study. The filtration experiment using ultrapure water was conducted at trans-membrane pressure of 0.1 MPa. The filtration process was allowed to operate for at least 40 minutes with the readings recorded by RsKey software.

3.4.7 Contact angle measurement

Measurement of the membrane contact angle was made using DataPhysics OCA-15 plus (DataPhysics, USA). To determine the degree of membrane hydrophobicity/hydrophilicity, contact angle measurement was performed using the sessile drop method. This involves direct measurement of contact angle (θ) on a liquid drop deposited on a surface, where the θ is determined by constructing a tangent to the profile at the point of contact of the drop with the surface. The contact angle of virgin and cleaned membranes was measured to determine any changes on PVDF membrane's surface hydrophilicity after cleaning process. In this test, a 20 μ l drop of distilled water was positioned onto the surface of the dried membrane using a microsyringe, and the air-water-surface contact angle was measured within 10 s. At least five measurements of contact angle were taken using separate pieces of membrane with a standard deviation of less than 5%. Hydrophilic membrane exhibit a contact angle value less than 90° while membrane with any value higher than that is considered as hydrophobic.

3.5 Protein retention study

The calculation of BSA retention was conducted in accordance with Bradford assay (Bradford, 1976). The Bradford assay offers several advantages as it involves fewer mixing steps, does not require heating, and provides a more stable colorimetric response. The response is protein dependent and differs with the amount of the protein. Thus making protein standard solutions are necessary. Bradford assay is based on the use of a dye, Coomassie Brilliant Blue G-250, to which protein binds, altering the light absorbance properties of the dye.

Bradford reagent was prepared by dissolving 100 mg Coomassie Blue G-250 in 50 ml 95% ethanol, adding 100 ml of 85% (w/v) phosphoric acid to this solution and the mixture is diluted to one litre with ultrapure water. When the dye is prepared as an acidic solution, it maximally absorbs light with a wavelength of 465 nm. The addition of protein results in a shift of the dye's absorption maximum to 595 nm. As the protein concentration increases, the absorbance of light at 595 nm increases linearly. The increase in absorbance can be measured using Ultraviolet–visible (UV-VIS) spectroscopy.

3.5.1 Preparation of BSA protein assay standard

According to literature, the absorbance of Coomassie blue dye at 595 nm is identified to be proportional to the amount of protein bound. In order to measure the amounts of BSA protein in permeate, it is necessary to establish the assay standard, which is a correspondence between absorbance values and known amounts of protein. Thus, a series of protein standards were prepared. The linear range of the assay for BSA was documented to be from 0.2 to 0.9 mg ml⁻¹. For each standard, the measured absorbance at 595 nm was recorded and a plot of 595 nm absorbance as a function of the identified protein content of each standard was constructed.

0.1 ml of each standard was pipetted into a clean and dry test tube and 5.0 ml of the protein reagent is added to each tube. The absorbance at 595 nm was measured after approximately 5 minutes of incubation time at room temperature. The sample should be incubated for no more than an hour since absorbance will increase over time. It is common that the protein solutions are assayed in duplicate or triplicate. In this study, at least three measurements of protein standard were made to reduce experimental error. From the obtained results, the graph of absorbance at 595 nm against BSA protein concentration was plotted and a linear line was constructed. The best fit of the data to a straight line in the form of the equation "y = m.x" was constructed in which y is the absorbance at 595 nm, x represents the protein concentration and m represent the gradient of the liner line. The BSA standard curve used in this study is shown in Appendix A.

3.5.2 Protein retention measurement

The measurement of BSA available in the filtration permeate was made by referring to the corresponding value of x-axis (concentration of BSA) of the standard curve to the absorbance at 595 nm (y-axis). All measurements were done by at least four replicates. The monitoring of adsorption peak at 595 nm was done with a UV-vis Spectrometer. The calculation protein rejection was done using the following equation:

$$\text{Protein Retention (\%)} = \frac{C_F - C_P}{C_F} \times 100\%$$

Where C_F is the concentration of BSA in feed solution and C_P is the concentration of BSA in the permeate.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 PVDF immersion in alkaline solution

The virgin and treated membranes were characterised via mechanical, chemical and thermal analysis.

4.1.1 Tensile testing

The mechanical stability aspects of PVDF membranes were evaluated by determination of Young's modulus and elongation at break. The significance of studying mechanical stability of membrane is vital as the estimation of membrane lifetime could be obtained by examining the mechanical properties of membrane after the alkaline treatment (Arkhangelsky et al., 2007a). Young's modulus is the ratio of normal stress to the longitudinal strain within elastic limit that correspond to the measure of elastic material's stiffness.

From Figure 4.1, it is demonstrated that the reduction in Young's modulus became greater as the concentration of alkaline used for treatment is increased. The obtained Young's modulus value had shown that the exposure to alkaline solution can cause the impairment of membrane integrity, causing the reduction in the membrane elasticity limit. Membranes immersed in NaOH and KOH experienced an almost similar reduction in Young's modulus value of 0.01 M and 0.1 M alkaline concentrations. At a higher concentration of 0.2 M, it was observed that NaOH treated membrane exhibits lower Young's modulus particularly for two hour treatment period.

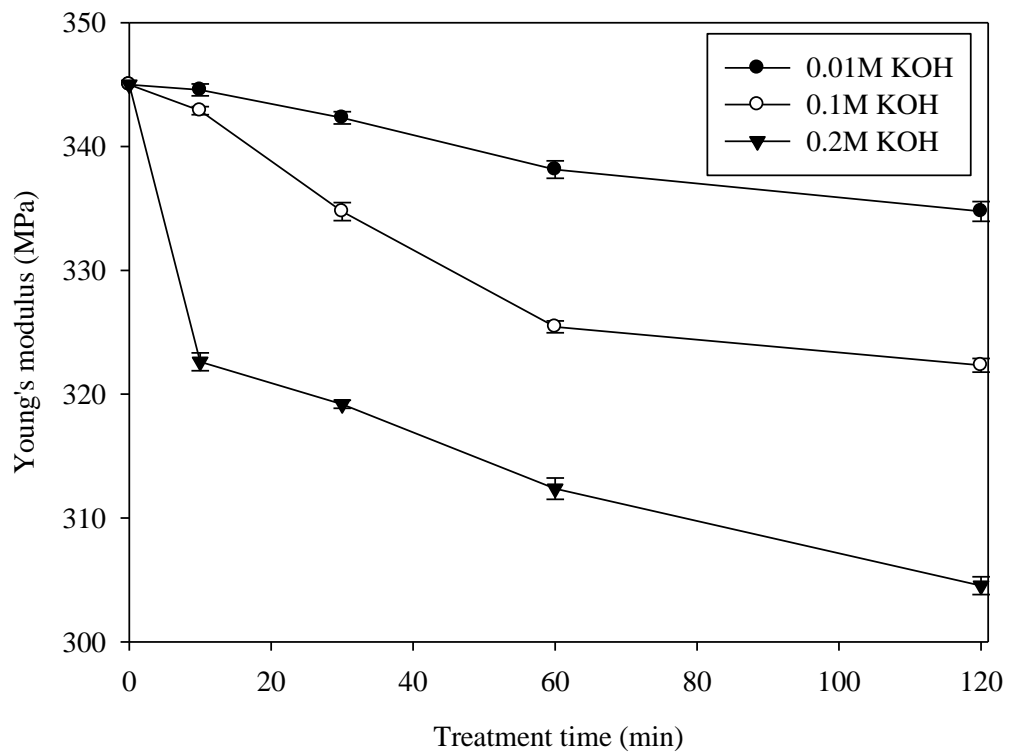
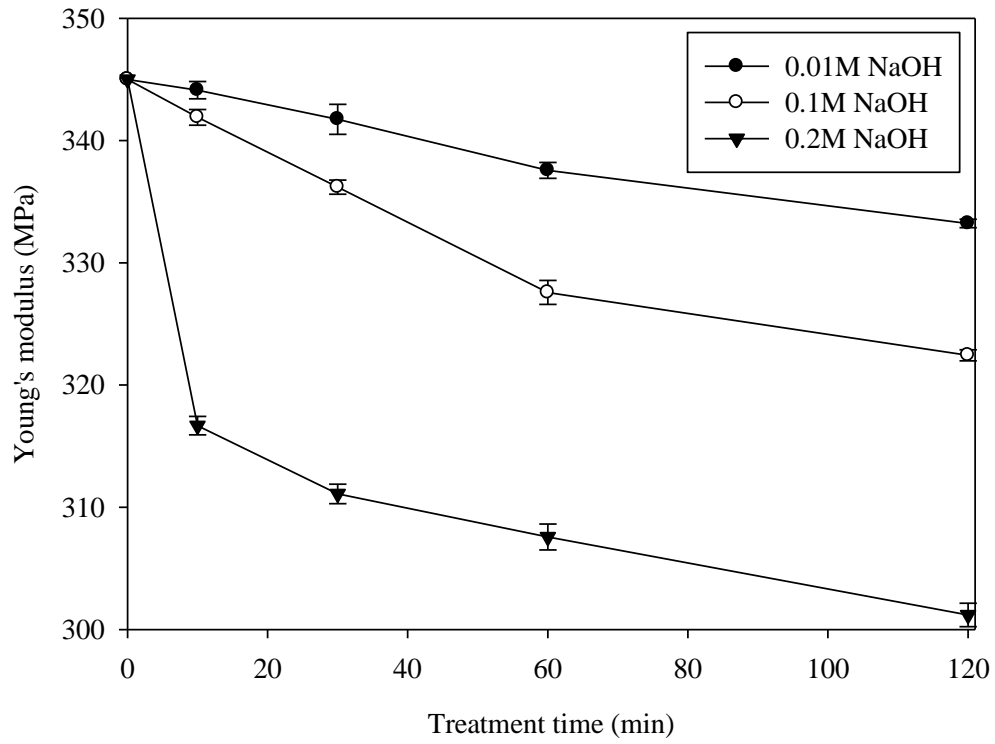


Figure 4.1: Effect of different alkaline treatment; (a) NaOH and (b) KOH on Young's modulus of PVDF membrane at room temperature.

Young's modulus values were found to be further reduced with treatment temperatures, as can be seen in Figure 4.2. At 50 °C, the membranes treated in either NaOH or KOH have shown a significant reduction in their Young's modulus values. The decline in Young's modulus values represents the increase in membrane rigidity and stiffness. The degradation process occurred on the surface layer of the membrane is believed to be the main reason of the reduction in membrane elasticity. This can be further described by FESEM analysis in section 4.1.2. It was shown that membranes could relatively withstand its properties once treated in KOH as the membranes exhibit higher Young's modulus value in comparison to those soaked in NaOH solution.

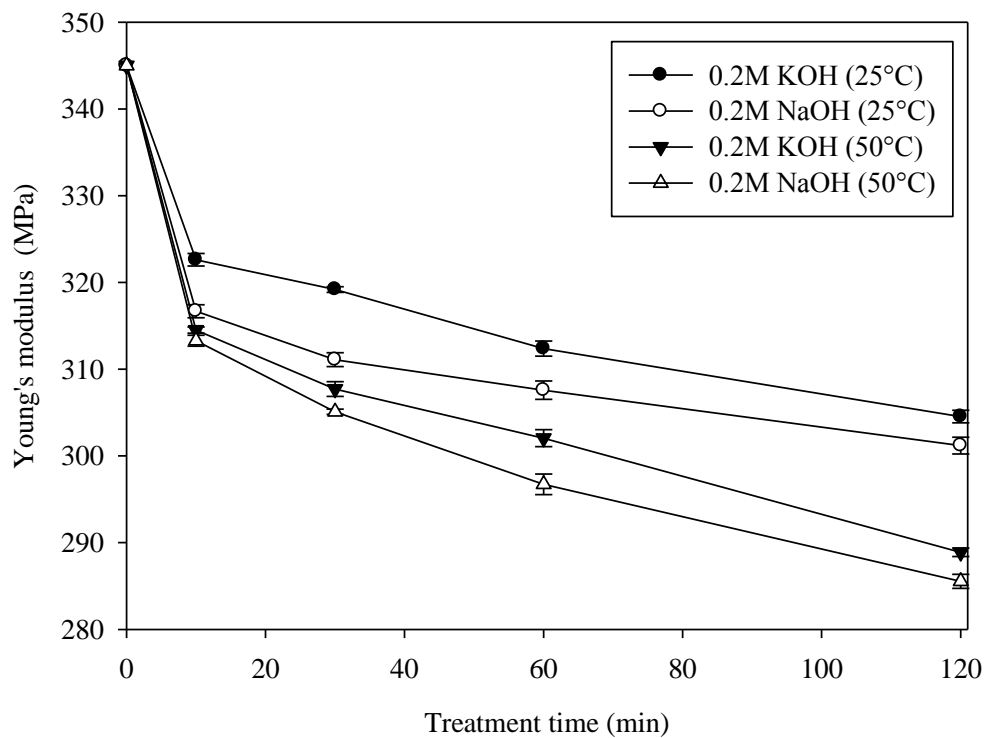


Figure 4.2: Effect of treatment temperature towards Young's modulus of PVDF membrane.

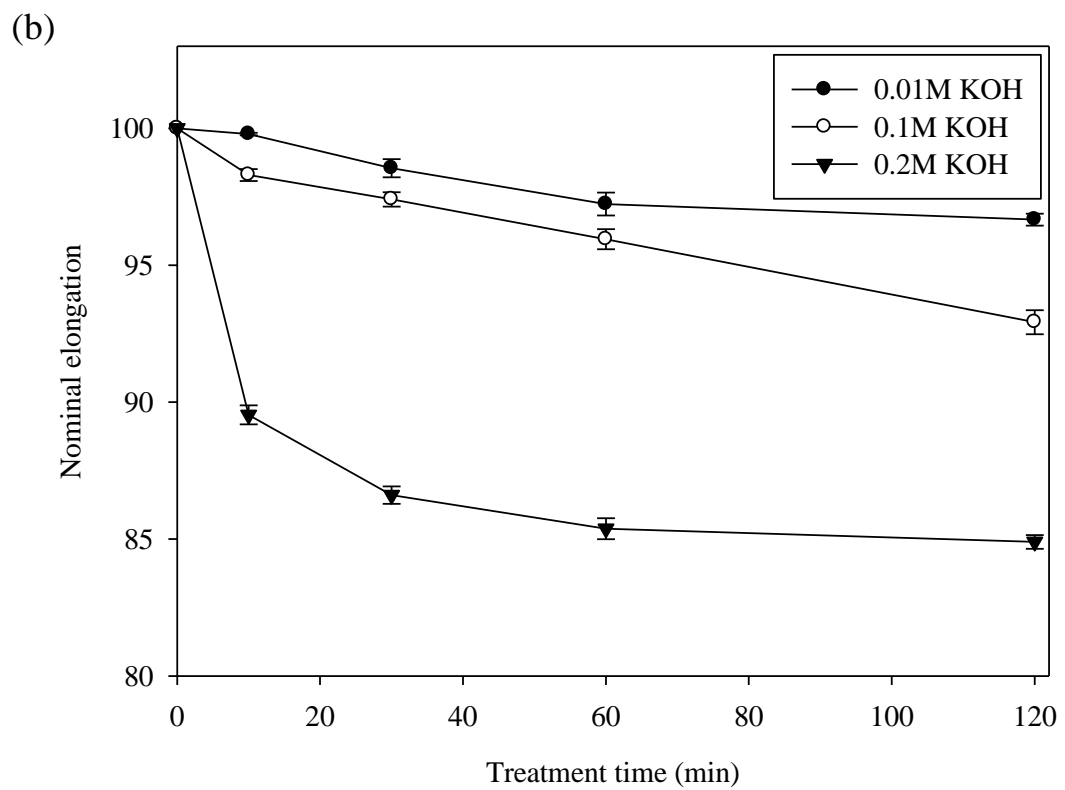
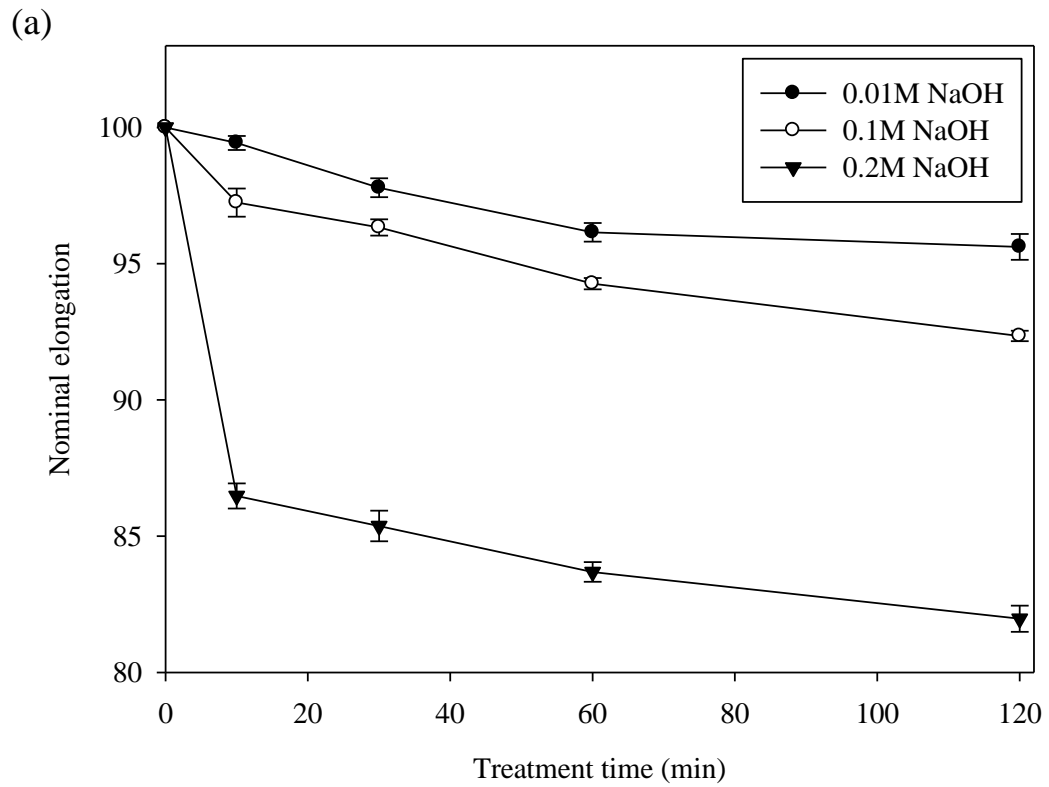


Figure 4.3: Nominal elongation of PVDF membrane treated at room temperature for a different treatment period in (a) NaOH and (b) KOH alkaline solutions.

A similar trend was observed on the membrane elongation after exposure to alkaline, as can be seen in Figure 4.3. In this study, the elongation of treated membrane was normalised and represented as nominal elongation. Nominal elongation was calculated by determining the percentage ratio of the elongation of the treated membrane to the elongation of virgin membrane. Reduction in nominal elongation manifests the decline of membrane's mechanical strength. While the PVDF membranes treated with a 0.01 M solution did not demonstrate major changes (as nominal elongation was maintained in a range of 96 to 99%). The strength of nominal elongation was drastically reduced at higher alkaline concentration. As the concentration increases, PVDF membrane experienced drastic decline in nominal elongation. The decline in nominal elongation became more significant with prolonged treatment time. NaOH treated membrane exhibits lower nominal elongation which corresponds to a higher level of membrane degradation compared to those treated with KOH. At room temperature, nominal elongation was reduced to 85% and 81% for membrane treated in 0.2 M KOH and NaOH solution respectively.

According to Lovinger, the decline of the nominal elongation is ascribed to the chain breaking of membrane materials treated with alkaline treatment (Lovinger, 1982). Chain breaking on membrane polymer influences the continuing deterioration of the membrane layer and subsequently, the interaction between polymer molecules is weakened and become easier to crack (Lovinger, 1982). Besides, the decrease in nominal elongation signifies that the treated membrane becomes brittle as it could easily break when subjected to stress without any significant strain.

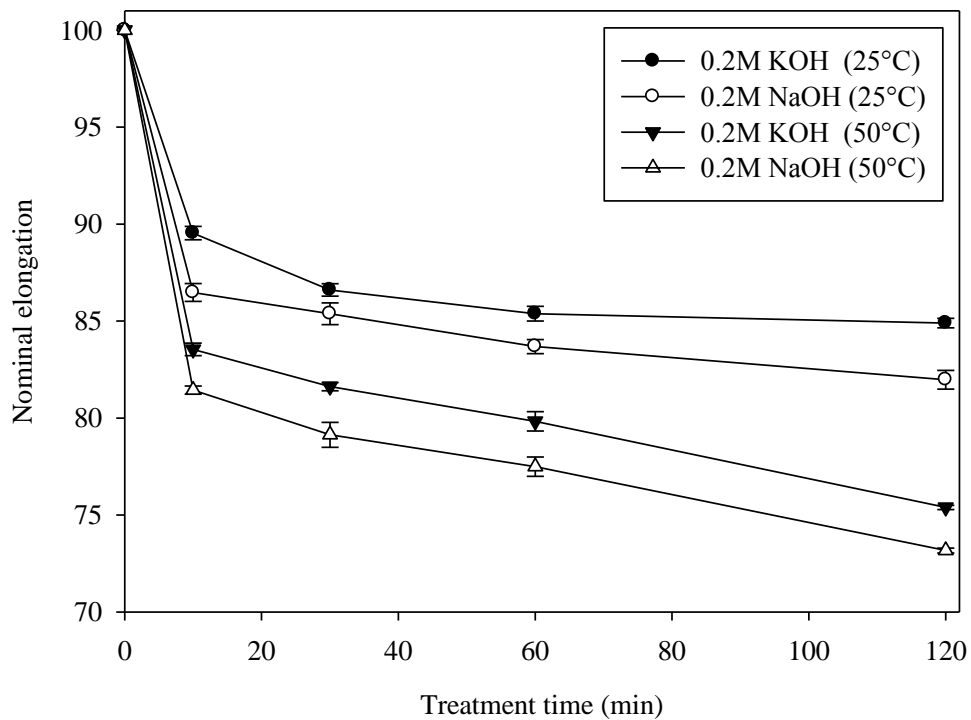


Figure 4.4: Nominal elongation of PVDF membrane treated at different temperature.

The effect of treatment temperature on membrane elongation is represented in Figure 4.4. For 120 minute treatment at 50 °C, the nominal elongation values decreased to 75% and 73% for membrane immersed in 0.2 M KOH and NaOH respectively. The deterioration of membrane's mechanical properties is detrimental for industrial process primarily when the membrane should be sufficiently tough to resist pressure driven operation (Hashim et al., 2011b). Overall, the elongation of PVDF membranes was detected to be reduced by the immersion in alkaline solution with the declining trend turned out to be more significant at higher temperature. In comparison, NaOH exhibits more destruction on PVDF membrane integrity compared to KOH solution.

4.1.2 Morphology of PVDF flat membrane

The study of morphology of PVDF membranes was carried out using FESEM analysis. Figure 4.5 represents the FESEM images of the membrane's outer surface before and after immersion in alkaline solution at 10,000 magnifications. It could be observed that for virgin membrane, depicted by Figure 4.5 (a), the surface of the membrane consists of uniformly distributed pores. FESEM images demonstrated that alkaline treatment of PVDF membranes could change the membrane pore structure in which the pore enlargement was visually observed on the membranes. By comparing Figure 4.5 (b) and (c), it was shown that the membrane treated with NaOH demonstrates relatively larger pore sizes compared to that of KOH treated membrane. It could be estimated from the scale of the FESEM image that the pore sizes of NaOH treated membrane were approximately 0.75 to 1.75 μm , while KOH treated membrane exhibits pore sizes from 0.5 to 1.25 μm .

The image in Figure 4.5 (c) showed that only small changes occurred on the surface layer following KOH treatment. The effect on pore size enlargement was not as apparent as compared to NaOH treated membrane. Therefore, it can be deduced that the chemical attack by hydroxide ions on the PVDF membranes was more intense in NaOH compared to KOH. In addition, from Figure 4.5 (d) and (e), the FESEM images of membrane soaked in an alkaline solution at higher treatment temperature for 120 minutes demonstrated a severe damage on membrane surface layer as the pore became larger. It could be presumed that the detriment of the membrane surface layer was not only affected by the strong alkali, but also influenced by the temperature.

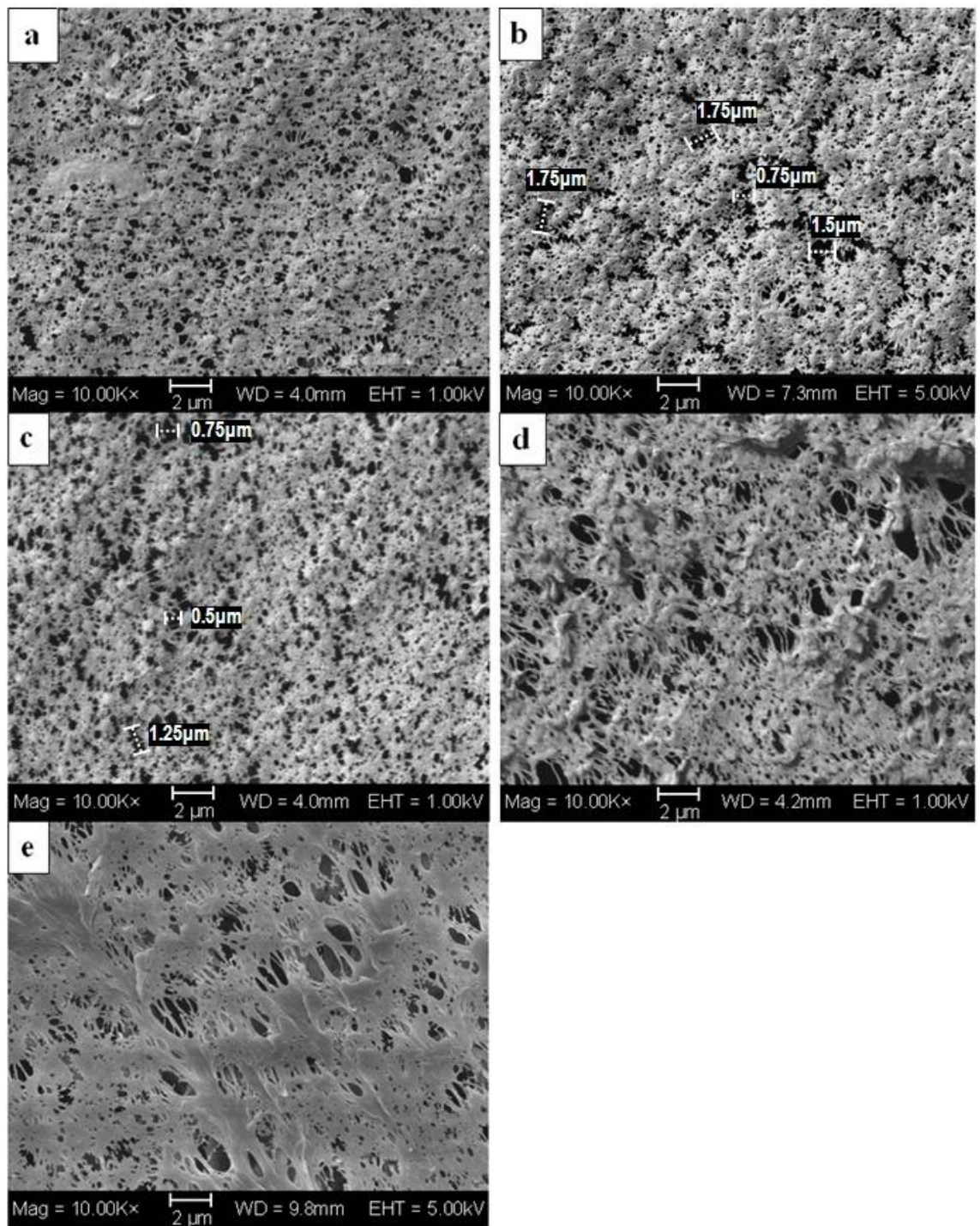


Figure 4.5: FESEM images of the PVDF membrane surface area of (a) virgin; and treated membranes in (b) 0.2 M NaOH at 25 °C (c) 0.2 M KOH at 25 °C (d) 0.2 M NaOH at 50 °C and (e) 0.2 M KOH at 50 °C.

4.1.3 Surface area of PVDF flat membrane

In this work, the surface area of virgin PVDF membrane and treated membranes were measured using BET surface analyser to investigate the relationship between surface area and the stability of PVDF membranes. The BET surface area of virgin PVDF membrane was measured to be $4.09 \text{ m}^2 \text{ g}^{-1}$. As presented in Table 4.1, all treated membranes possess a smaller surface area than the virgin membrane. Moreover, for both chemicals, higher concentration of employed solution results in a further decrease of specific surface area. The specific surface area and mean pore diameter are correlated to each other in which as the pore size increases, the specific surface area decreases. In general, NaOH treated membrane experience more reduction in BET surface area compared to membrane immersed in KOH as disclosed by FESEM images (Figure 4.5). This marked that NaOH causes more damage on membrane surface layer, causing a pore structural modification.

Table 4.1: BET surface area of PVDF membrane after 120 minutes alkaline treatment.

Chemical Solution		BET Surface area ($\text{m}^2 \text{ g}^{-1}$)
KOH	0.01 M	3.84
	0.2 M	3.30
NaOH	0.01 M	2.88
	0.2 M	1.45

One important criterion that makes membrane contactor preferable over traditional separation method is because of its high surface area. It is noted that the chemical reaction usually takes place at the interface of the contacting objects. Besides, the reaction kinetics depend on the specific surface area of the material (Hashim et al., 2011b). Thus, the higher surface area is required for a better membrane contactor performance. Nevertheless, from the obtained result, the treated membranes exhibit

lower surface area indicating that the exposure to caustic environment has altered the properties of the membrane. This phenomenon is undesirable in the membrane contacting system. As lesser surface area is available for separation process, the reduction in its value will result in poor performance. The analysis results show that the unsuitable use of alkali membrane can affect the membrane performance.

4.1.4 FTIR analysis

FTIR was used to qualitatively study the surface chemical composition changes of PVDF membrane prior to and after chemical treatment. The spectrum of virgin PVDF membrane shows the appearance of the characteristic bands at 762, 796, 875, 974, 1070, 1181 cm^{-1} which is similar to PVDF film containing α -phase, whilst some other peaks were detected at 841, 1274 and 1403 cm^{-1} are believed to be attributed by the β -phase (Gregorio, 2006). From earlier works, the occurrence of dehydrofluorination process largely indicated by the presence of the peaks representing carbon-carbon double bond, carbonyl bond and carbon-carbon triple bond. The FTIR peak assignment for PVDF membrane is listed in Table 4.2 (Hashim et al., 2011b; Kise & Ogata, 1983; Zhao et al., 2011).

Table 4.2: FTIR peak assignment for PVDF membrane.

Wavenumbers (cm^{-1})	Functional groups
762, 796, 875, 974, 1070 and 1181	α -phase of PVDF
841, 1274 and 1403	β -phase of PVDF
1590-1650	Carbon-carbon double bond
1700-1800	Carbonyl bond
2100	Carbon-carbon triple bond

As shown in Figure 4.6, it was observed that higher concentration of 0.2 M had caused the destruction on the membrane. The changes in the chemical composition of treated membrane had been noted by a different spectrum pattern. From Figure 4.6 (a), a shoulder at 1650 cm^{-1} could be spotted in the FTIR spectra of membranes treated with NaOH for 30 minutes. This band can be assigned to carbon-carbon double bonds.

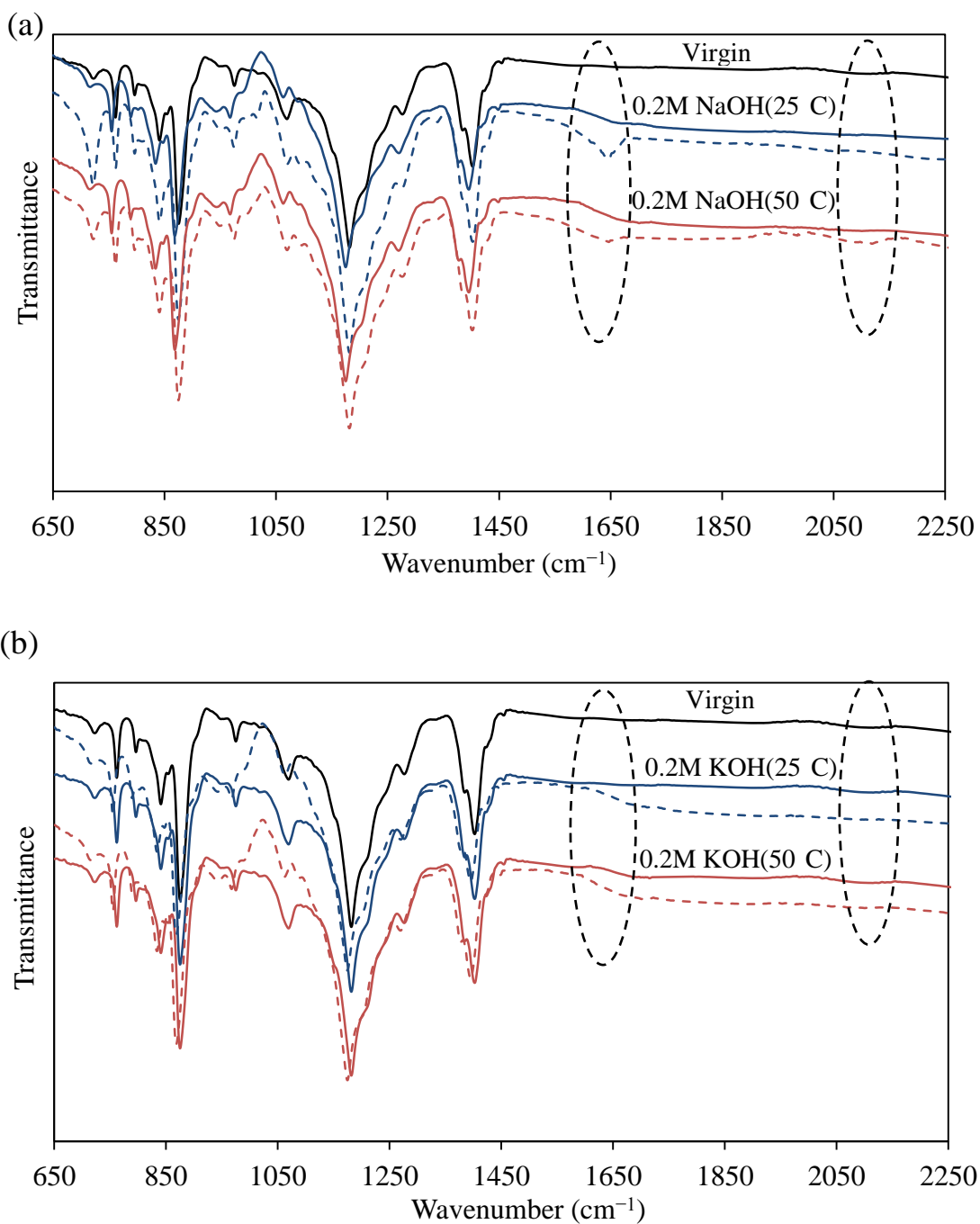


Figure 4.6: FTIR spectra for PVDF membrane treated in (a) NaOH and (b) KOH; solid line for 30 minutes and dashed line for 120 minutes.

The obtained spectra signify the changes in carbon-carbon bonds due to the elimination of HF molecules known as dehydrofluorination. The dehydrofluorination process in polymer chain contributes to the formation of carbon-carbon double bonds. With the increment in treatment temperature, the FTIR results showed the formation of both carbon-carbon double and triple bonds. The formation of carbon-carbon triple bonds was detected in NaOH treated membrane, indicated by the appearance of a new peak at 2100 cm^{-1} . This result is similar to Kise and Ogata findings as in their study; they discovered a new band around 2100 cm^{-1} of the product IR spectra which assigned to the stretching bands of carbon-carbon triple bond. As depicted in Figure 4.6 (b), the absence of carbon-carbon triple bond in the spectra of membrane soaked in KOH solution was justified since there is no significant peak at 2100 cm^{-1} .

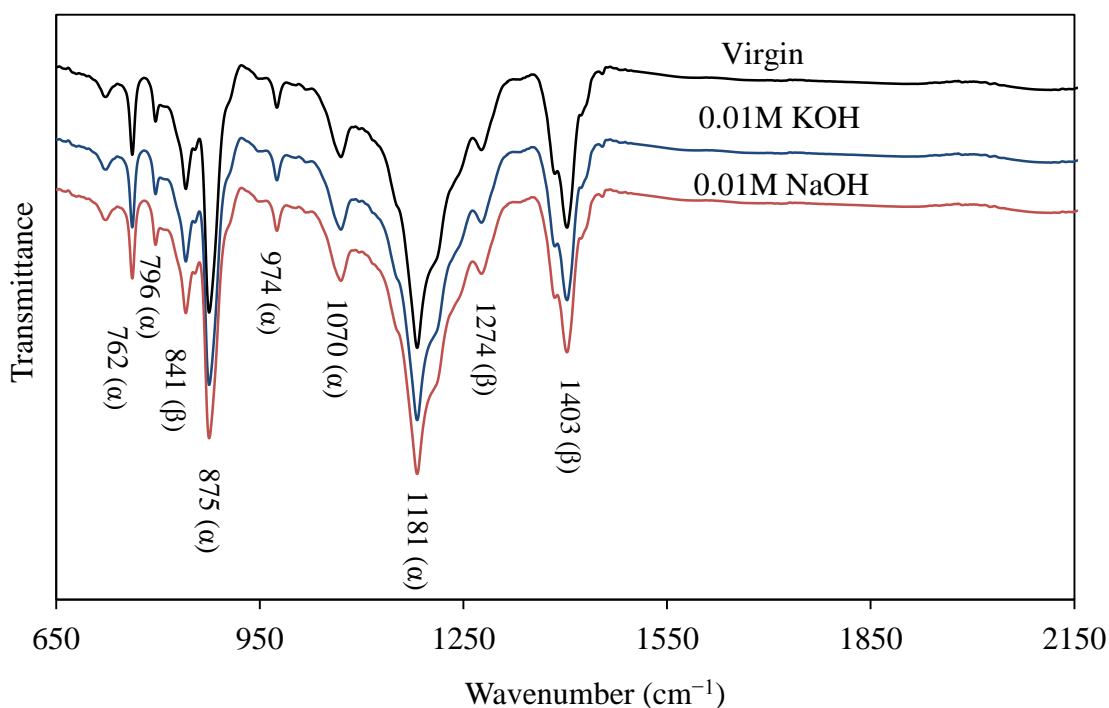


Figure 4.7: FTIR spectra for membrane treated in 0.01 M alkaline solutions at 50 °C for 120 minutes.

On the other hand, as shown in Figure 4.7, the peaks indicating the occurrence of dehydrofluorination could not be seen once the membranes treated in alkaline concentration of 0.01 M. The main reason for no changes had been detected using FTIR analysis was due to the fact that FTIR is mainly used for surface analysis. It could be deduced that FTIR technique was found to be less sensitive in detecting changes occurring on the membrane's surface when it was exposed to a very low alkaline concentration. Besides, it is worth noting that the membrane degradation could not only occur on its surface but also in the inner layer.

It appears that the spectra of KOH treated PVDF membranes do not significantly change with the increase in treatment temperature, since the pattern of the spectra were almost identical. In comparison, the formation of carbon-carbon triple bonds was clearly observed in the FTIR spectra of NaOH treated membranes as a relatively stronger signal was observed. Based on the FTIR analysis, it was demonstrated that NaOH had more damaging effects towards PVDF membrane compared to KOH.

4.1.5 DSC analysis

The effect of alkaline treatment towards membrane's thermal properties was investigated using DSC analysis. DSC was utilized to measure and compare the melting temperature of virgin and treated membranes. The melting point of 164.3 °C for the virgin membrane is represented by the dashed vertical line in the graphs. From Figure 4.8, it can be seen that the melting point did not change remarkably for the membrane treated in either 0.01 M NaOH or KOH. Though, membranes immersed in NaOH solution gave a slightly higher reduction in melting point compared to KOH treated membranes.

Similar to FTIR analysis, the effect of alkaline treatment onto PVDF membrane's melting point became predominant when higher alkaline concentration was

applied. At higher chemical concentrations, the melting temperature has shown to further reduce with treatment time. Changes in melting point of membranes treated in either alkaline solution are indicated by curves shifting to the left, showing a reduction in melting point. This trend was most notably demonstrated by NaOH treated membrane. After 120 minutes of NaOH treatment, the melting temperature has reduced to 160.8 °C while for KOH treated membrane, the melting point has dropped to 161.5 °C.

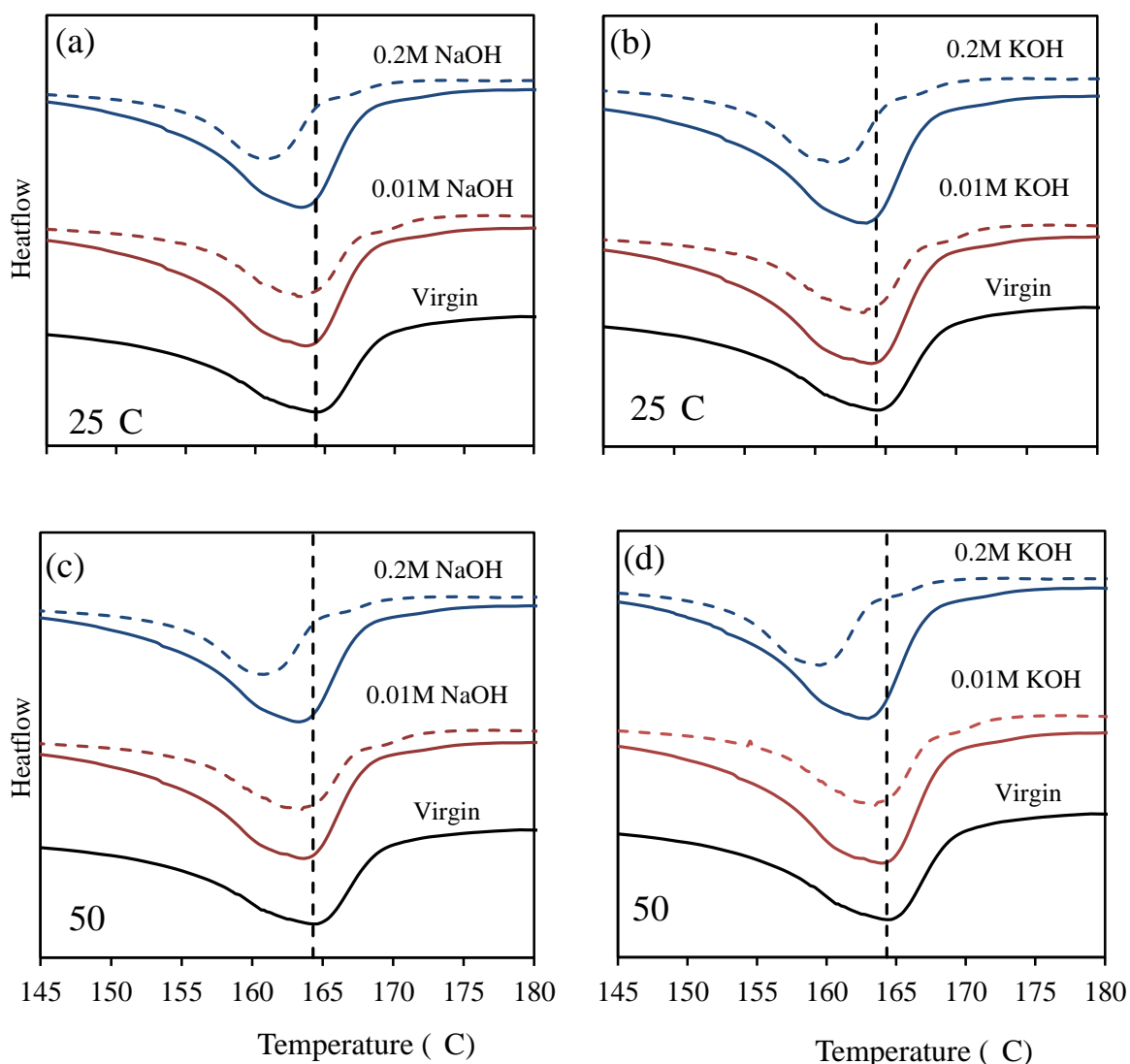


Figure 4.8: DSC thermograms representing the membranes treated with (a) NaOH (25°C), (b) KOH (25°C), (c) NaOH (50°C) and (d) KOH (50°C); solid line for 30 minutes and dashed line for 120 minutes.

The effect of higher treatment temperature on PVDF membrane's melting point was also investigated for a treatment period of 120 minutes and raising the temperature to 50 °C. It occurs that the deviation in melting point becomes more significant as the curve shifted to the left side of the original curve. The melting temperature values dropped further to 159.5 °C and 158.3 °C for membranes treated in 0.2 M KOH and NaOH, respectively. Table 4.3 lists the melting temperature of alkaline treated membranes at different treatment conditions.

Table 4.3: Melting temperature of treated PVDF membranes at different parameter.

	NaOH		KOH	
Treatment time (min)	30	120	30	120
Treatment at 25 °C	(°C)	(°C)	(°C)	(°C)
0.01 M	163.8	163.3	164.2	163.7
0.2 M	163.3	160.8	163.7	161.5
Treatment at 50 °C				
0.01 M	163.7	163.2	164.0	163.3
0.2 M	162.8	158.3	163.0	159.5

Once PVDF membranes were exposed to strong alkaline solution, their structure will be destructed due to the occurrence of the dehydrofluorination process. HF molecules were eliminated and thus, carbon-carbon double bonds formed leading to a reduction in the crystallinity of PVDF membrane (Hashim et al., 2011b). The reduction in the degree of crystallinity results in the decline of melting point. Increasing the treatment time of the PVDF membranes causes more destruction of the membrane structure. At low concentration treatment condition, PVDF melting point does not change considerably neither with the increases in treatment time nor at elevated

temperature. The utmost reduction in melting point was determined when the membrane is immersed in 0.2 M concentration and at higher temperature for a longer time. This suggests that the melting point of PVDF membrane can be significantly affected by harsh alkaline environment.

PVDF excellent thermal stability is attributed to strong carbon-fluorine (C-F) bonding and the high electronegativity of F atoms, leading to the formation of a very stable fluoropolymers compared to hydrocarbon polymers (O'Hagan, 2008). Therefore, high temperature is required to break the bond. It could also be spotted that when treatment time is prolonged, the curve shifted slightly to the left, indicating the small decline in melting point of the membrane. Melting point of material decreases in correspondence to the degradation of its crystalline structure (Hashim et al., 2011b).

The information obtained from various PVDF materials suppliers reported that the melting point of pure PVDF ranging from 140 to 170°. In this work, the virgin hydrophobic PVDF membrane was determined to have a melting point of 164.3°. DSC analysis can show polymer degradation by the lowering of the expected melting point. It is worth mentioning that there is a possibility that a lower and/or wider melting point range could signify that the sample was contaminated with trace amounts of impurities. As the membrane used in this research is made from pure PVDF (without additives), the declined melting point was believed to be solely due to the chemical attack on the membrane structure.

Since membrane contactor studies in a lab-scale typically test at ambient temperature, the thermal stability of the membrane is less considered. Nevertheless, this is essential for industrial operations. In particular, during flue gas treatment, the gas stream is probably exceeding 100 °C, thus a high membrane thermal stability is required (Zhang et al., 2013). The membranes must be chemically and thermally stable once

exposed to the liquid absorbent to maintain high separation performance. Analysis on PVDF membrane thermal stability is crucial as the flue gases often discharge at high temperature and could be detrimental to the membrane material. From the DSC analysis, it can be concluded that the PVDF membranes had been attacked by the alkaline solution under all tested conditions, which led to a reduction in the melting temperature. The attacked on PVDF membrane was intensified at a high temperature or in concentrated alkaline solutions.

4.1.6 Pure water permeability and contact angle measurement

In general, a similar trend was observed on membranes exposed to alkaline solutions whereby the flux increases with increasing chemical concentration. The percentage flux increments for membrane treated at various treatment parameters is listed in Table 4.4. Referring to Table 4.4, merely a small variation on flux increments was detected for membranes treated for 30 minutes. By increasing the duration of immersion to 120 minutes at room condition, the flux percentage increments were increased slightly. This finding is significant as it revealed that PVDF membrane properties were altered even at a low alkaline concentration. For a treatment at room temperature and 120 minutes treatment time, membrane soaked in 0.2 M NaOH exhibits the increase in flux by 21.2%, while membrane treated with 0.2 M KOH contributes to 16.4% in flux increment. It is recognised that hydroxide ions attack PVDF chemically causing intense deterioration of the membrane structure via pore widening thus resulted in higher permeate flux. KOH treated membranes were found to exhibit a comparatively lower flux increment compared to those immersed in NaOH. This finding is analogous with the surface layer inspection using FESEM images (refer to Figure 4.5), where it is visibly seen that pore enlargement of NaOH treated membrane was more extensive. Membrane immersed in KOH is however demonstrated a minor enlargement on its pore sizes.

Table 4.4: Percentage flux increments for membrane treated at various treatment conditions.

		Percentage flux increments (%)			
Concentration (M)	0.01M (25°C)	0.2M (25°C)	0.01 M (50 °C)	0.2 M (50 °C)	
30 min treatment					
KOH	6.63 ± 0.30	10.80 ± 0.28	9.25 ± 0.28	11.58 ± 0.31	
NaOH	7.71 ± 0.28	12.29 ± 0.31	11.32 ± 0.33	14.98 ± 0.32	
120 min treatment					
KOH	8.63 ± 0.27	16.43 ± 0.30	11.34 ± 0.30	25.57 ± 0.29	
NaOH	9.80 ± 0.30	21.25 ± 0.27	13.64 ± 0.28	42.90 ± 0.28	

The effect of higher temperature on membrane water flux was studied with membrane immersed in alkaline solution at 50 °C. Following that, escalating trend of percentage flux increment was detected for membranes treated at higher temperature mostly for the 120 minute treatment period. The membranes treated with either KOH or NaOH solution at 50 °C, showed a larger flux increment as the chemical attack on PVDF was thought to accelerate upon temperature elevation. For high alkaline concentrations used, the water fluxes have increased noticeably with higher treatment temperature while flux increment for membrane treated with a low alkaline solution did not change considerably. A flux increment for membranes treated for 30 minutes using either 0.2 M of alkaline solutions showed almost similar values, yet slightly more than using 0.01 M. Water flux permeability was further enhanced with prolonged immersion time. After two hours immersion, the membranes treated in 0.2 M KOH and NaOH at 50 °C recorded the values up to 25.6 % and 42.9 % of flux increment respectively. In general, minor changes in terms of treated membrane water flux were determined when using low concentration and shorter treatment time. An increase in alkaline

concentration, treatment temperature and immersion time were found to contribute to a larger flux increment. Pure water flux enhancement is linked to the degradation of membrane structure, specifically pore enlargement. In addition, it could be seen that PVDF membrane exhibits a decrease in contact angle values following alkaline treatment indicating an increase in the membrane hydrophilicity.

The contact angle for virgin hydrophobic PVDF membrane was measured to be $100.51 \pm 0.75^\circ$. After 120 minutes of treatment with 0.01 M NaOH and 0.01 M KOH, the contact angle values reduced to $98.22 \pm 0.51^\circ$ and $98.96 \pm 0.61^\circ$ respectively. The membrane's contact angle was further reduced once we applied higher alkaline solution. It was measured that the contact angle values were reduced to $91.15 \pm 0.67^\circ$ and $92.28 \pm 0.61^\circ$ after immersion in 0.2 M NaOH and 0.2 M KOH respectively.

It is worth mentioning that the use of membranes in membrane contactor is different from how membranes are used for water or wastewater filtration. Membrane used in filtration process is typically highly water permeable, while for membrane gas absorption, the membrane should be highly hydrophobic to prevent wetting problem. It is presumed that the increased water permeation rate using the treated membranes as a worrying signal for alteration in membrane surface properties which could compromise membrane separation efficiency.

4.1.7 Assessment of a relatively stronger alkaline

In this work, characterization of virgin and treated membranes was conducted using various analyses. Generally, membranes soaked in NaOH showed a poor performance in terms of mechanical strength, thermal stability and presented higher flux increment compared to KOH treated membrane. Membranes immersed in either alkaline solution showed similar trends in which having a decline in mechanical strength, reduction in melting point, as well as an increase in BET surface area. It is

identified that PVDF is not compatible with the basic solution, especially when dealing with strong alkalis as the membrane is at risk for being attacked chemically by the hydroxide ions.

Table 4.5: pH values of different types of alkaline concentration.

Concentration (M)	pH Values		
	0.01	0.1	0.2
NaOH	11.44	13.05	13.50
KOH	11.41	12.85	13.46

NaOH and KOH are both classified as strong alkali and serve as a source of hydroxide ion (OH^-), a very nucleophilic anion that attacks polar bonds in inorganic and organic materials. Theoretically, strong alkali will be completely ionized in aqueous solution. Among these two, one is indeed relatively stronger alkaline than the other one. Stronger alkali is one that dissociates more hydroxide ions that led to more severe damage to PVDF membranes. The determination of which chemical is the stronger base could be made by referring to its pH values. Table 4.5 lists pH values for different types of alkaline concentration. All values were measured at least five times (included prior to, during and after membrane immersion) with a standard deviation of less than 5%. It was found that NaOH shows higher pH values, suggesting that it is a relatively stronger base. This explains the more severe degradation occurred on NaOH treated membranes compared to those treated with KOH.

In addition to pH measurement, the determination of which could be the stronger alkali has been done via solubility calculations. The data on the chemical material solubility at a temperature of 0 °C and 100 °C was obtained from Perry's Chemical Engineers' Handbook and listed in Table 4.6 (Perry & Green, 1997).

Table 4.6: The solubility of chemical (by parts) in 100 parts of water. Interpolated values were designated with an asterisk symbol (*).

Solubility of chemical (by parts) in 100 parts of water				
Temperature (°C)	0	25	50	100
NaOH	42.00	118.25*	194.50*	347.00
KOH	97.00	117.25*	137.50*	178.00

Throughout this study, the experiments were performed at room temperature (25 °C) and 50 °C. Nevertheless, the solubility of chemical at these temperatures is not provided in the handbook. Fundamentally, linear interpolation is an approach to fill in the “holes” in the table. Hence linear interpolation was used to estimate the values of chemical solubility at both temperatures of 25 °C and 50 °C respectively. In general, the solubility of chemicals increases with temperature elevation. From temperature of 25 °C and onwards, the corresponding interpolated values of NaOH solubility were calculated to be greater than KOH. This strengthens the proposition that NaOH is a stronger alkaline.

Moreover, the overall physicochemical analysis presented that NaOH treated membranes experience more degradation which fits the claim that NaOH is a relatively stronger alkali compared to KOH. At present, NaOH is regularly used as a liquid absorbent in membrane gas absorption. Though, findings from this work indicated that PVDF membrane was in fact susceptible towards alkaline environment. These findings also signify that the use of strong alkali with PVDF membranes must be restricted within the allowable pH limit that is lower than 11. It is thus recommended that other alternatives to caustic liquid absorbent for membrane contactor should be acquired.

4.2 Membrane cleaning study

4.2.1 Membrane water flux measurement

As a preliminary study, the cleaning process was done by means of physical cleaning since some foulants might probably be detached by hydraulic means. Physical cleaning was found to be ineffective to recover water flux since the result was only approximately 33% of the cleaning efficiency as shown in Figure 4.9.

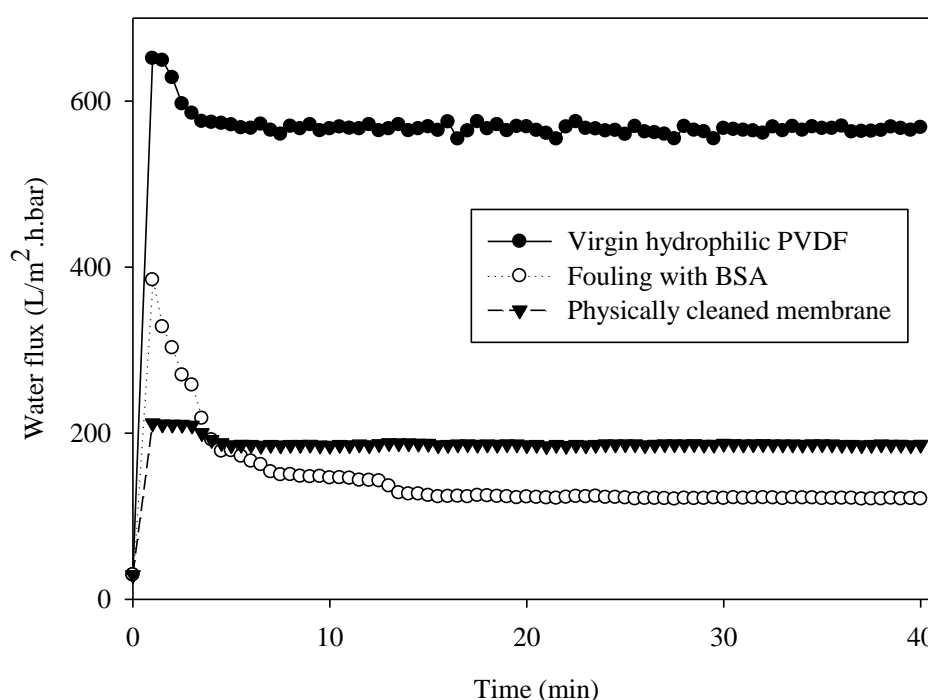


Figure 4.9: Physically cleaned membrane water flux.

This low efficiency is believed to be caused by a strong absorption of BSA particle to the membrane surface, wherein the strong bond could only be broken by means of chemical attack or reaction. Hence, the cleaning with chemical agent is an ideal option for protein removal. Despite the low efficiency of physical cleaning, it was performed with the intention to loosen the interactions of BSA particle deposited on the membrane. The target for cleaning efficiency was set to 1 which means that the flux for cleaned membrane should be comparable to the flux of the virgin membrane. It has been

generally accepted that a higher concentration of chemical agent will contribute to a better cleaning on the fouled membrane. Figure 4.10 depicts the effect of various chemical concentrations towards cleaning efficiency. As found in this study, the cleaning effect of either NaOH or NaOCl increases when their concentration is increased. This trend is similar to the membrane cleaning performance recorded in previous works (Puspitasari et al., 2010; Wang et al., 2013). The lower chemical concentration resulted in a relatively lower cleaning efficiency as compared when cleaning with 0.1 M of the solutions contributed to a flux restoration of approximately 80 % from the initial flux.

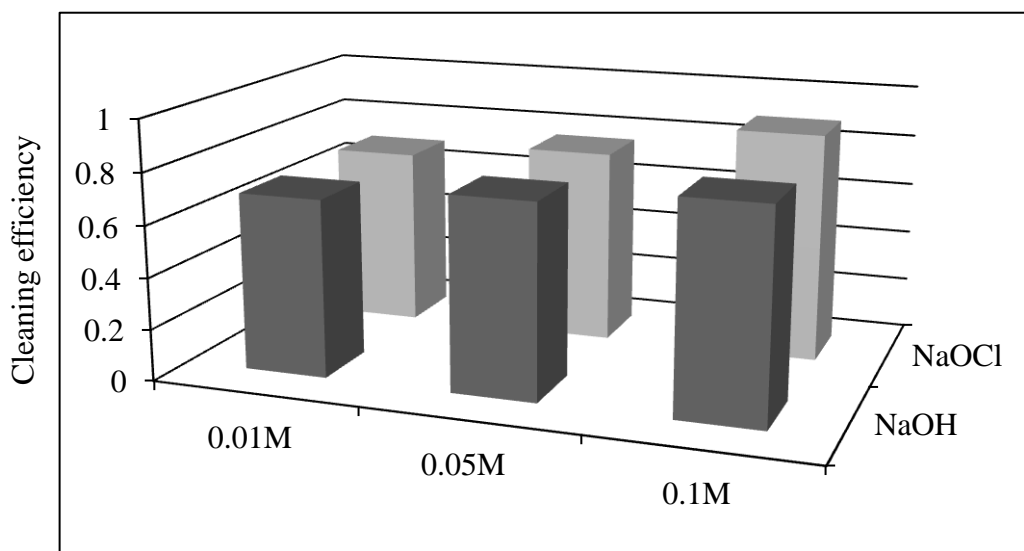


Figure 4.10: Cleaning efficiency of membranes cleaned at different chemical concentration for 60 minutes at room temperature.

As suggested in the technical manual provided by one of the membrane manufacturers (Dow, USA), the temperature of the cleaning solutions must be more than 25 °C for a maximum effectiveness. Elevating the temperature of the cleaning solution will assist in organic removal from the membrane surface. The effect of

temperature on cleaning efficiency is depicted in Figure 4.11 which shows higher temperature improves the merit of cleaning performance.

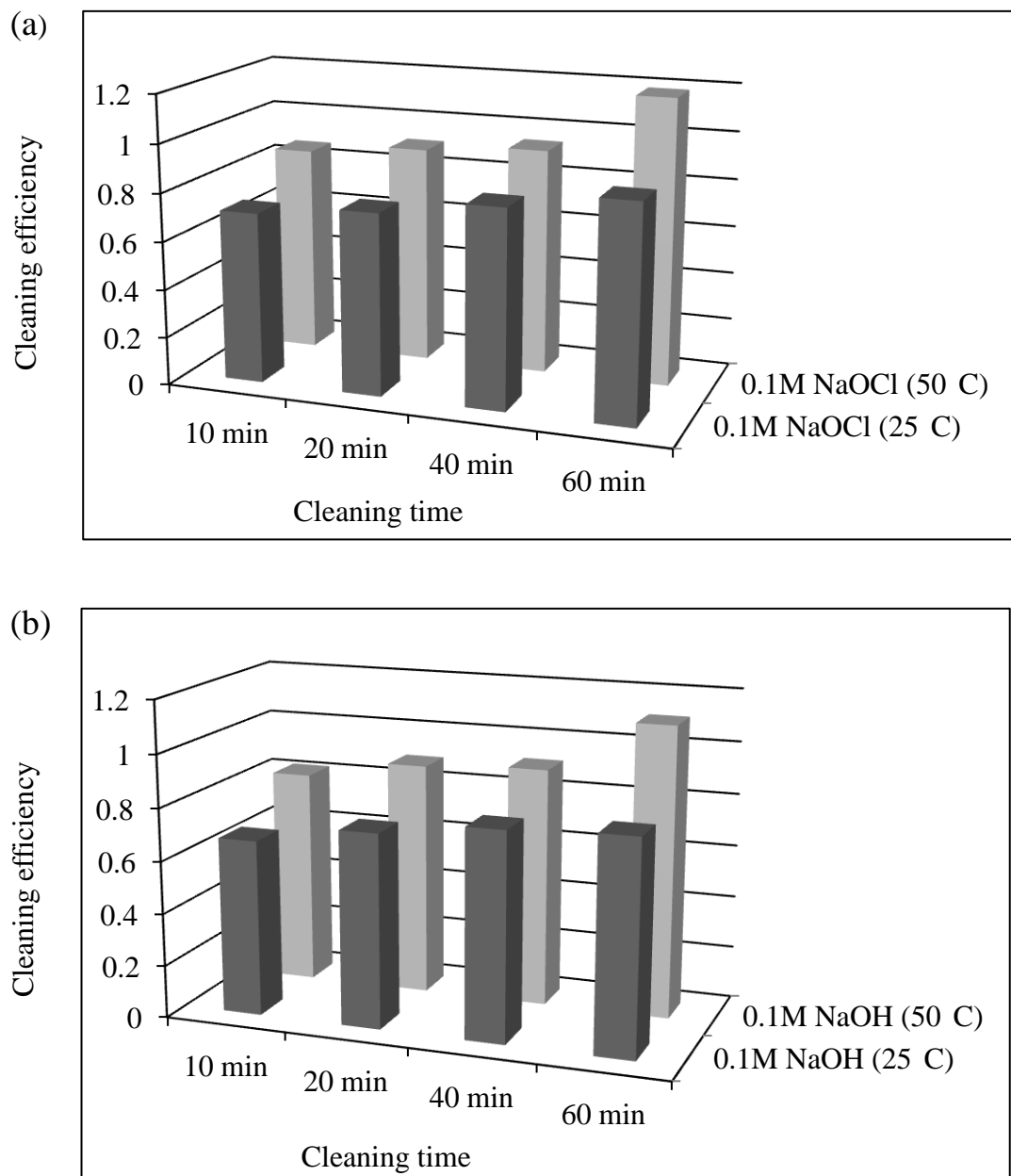


Figure 4.11: Cleaning efficiency for membrane cleaned with (a) NaOCl and (b) NaOH at different temperature.

The maximum cleaning efficiency was recorded to be approximately 0.80 using either one of the cleaning solution at room temperature whilst a significantly higher flux recovery was observed for a similar cleaning time at 50 °C. At higher cleaning temperature, during 10 to 40 minutes of cleaning process, a comparable cleaning

efficiency was recorded to be in the range of 0.80 and 0.85. The cleaning efficiency was further improved with a cleaning process of 60 minutes, at which the measured water flux was recorded to be higher than the virgin membrane. The flux recovery of more than 100% could be a potential remark of the alteration in membrane characteristic and probable membrane degradation (Hajibabania et al., 2012).

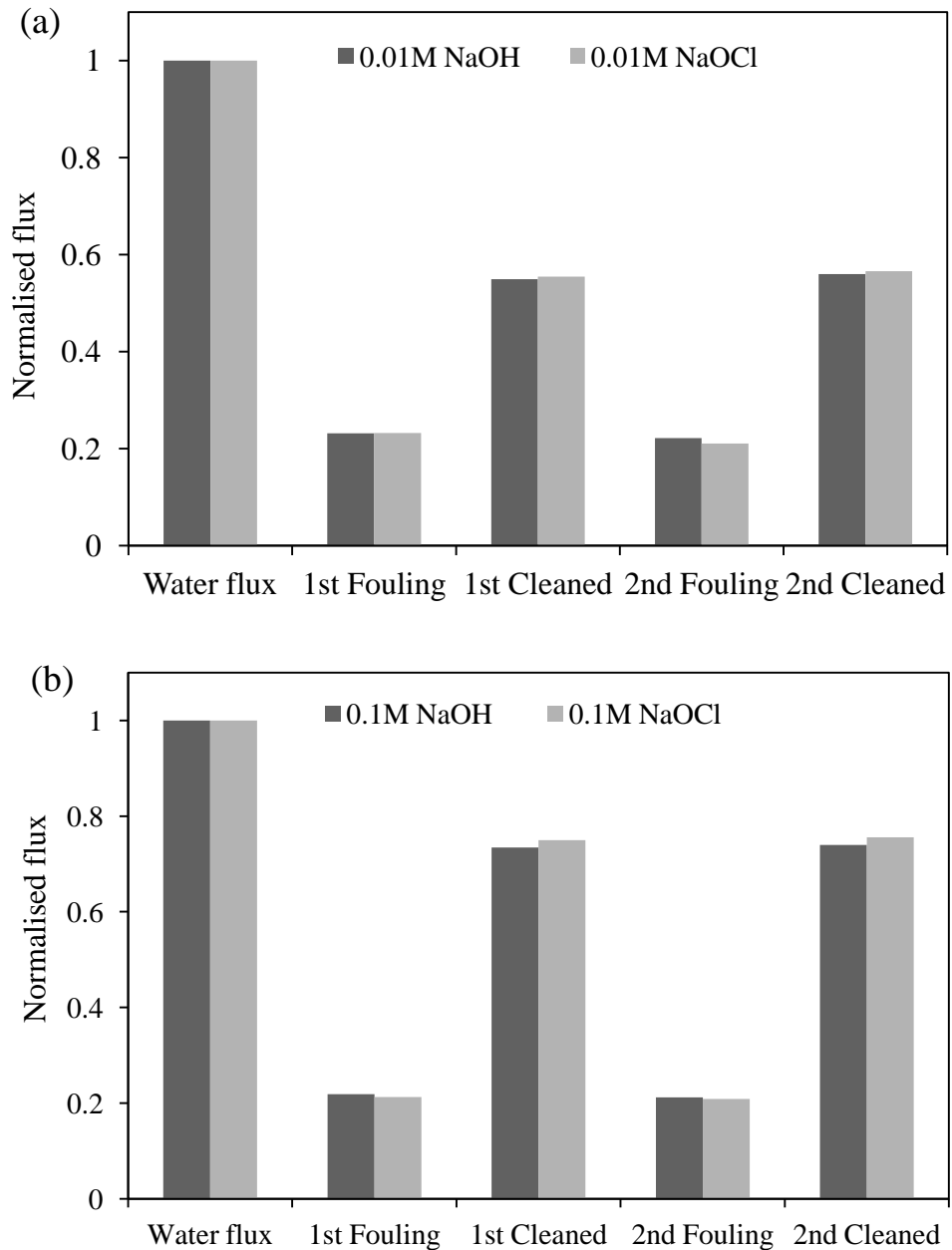


Figure 4.12: Effect of repetitive cleaning on membrane water flux for 20 minutes cleaning time using different chemical concentration of (a) 0.01 M and (b) 0.1 M.

Notwithstanding an increase in cleaning effectiveness, a higher chemical concentration employed was liable for more severe future fouling. The fouling tendency of the membranes was observed from the decline in water flux permeability during ultrafiltration of BSA solution. As presented in Figure 4.12, it was shown that the cleaning agent's concentration is the major contributor in the upcoming fouling. During the second cycle of BSA filtration, the cleaned membrane was observed to experience a further decline in flux as represented by second fouling. The degree of fouling becomes greater once a higher concentrated solution of cleaning agent is being used. Generally, NaOCl cleaned membrane displays a better flux recovery than NaOH cleaned membrane. However, when the cleaned membrane was subjected to another BSA filtration, the membrane which was cleaned by the former experienced a more severe fouling. For instance, during cleaning of the membrane with 0.01 M NaOCl, the normalized flux for first fouling was recorded to be at 0.23 and reduced to 0.21 during the second fouling cycle, whereas when 0.01 M NaOH was used, it showed only a slight reduction from 0.23 to 0.22.

It is previously alleged that chemical cleaning improves the degree of PVDF membrane hydrophilicity (Hajibabania et al., 2012; Levitsky et al., 2011b), thus, giving the higher water flux. Conversely, the contrary outcome was observed in our work as membranes became less hydrophilic (based on contact angle values) after cleaning. Further discussion on contact angle measurement is explained in section 4.2.4. Subsequent to first cleaning process, the membrane was determined to exhibit higher contact angle values. This result could be explained by the instability of the PVDF modified membrane to retain its hydrophilicity. Pure PVDF is indeed hydrophobic by nature. Through surface modification, PVDF could be turned into a hydrophilic membrane. Commercial membrane is usually made with the addition of hydrophilic additive to its casting solution purposely for pore forming and surface modification (Liu

et al., 2011b). The reduced hydrophilicity contributes to the inclination of BSA to foul on the membrane surface as a more severe fouling can be observed during the second cycle of protein filtration. The reason for this event is supported by the fact that hydrophobic membranes (in this particular work, cleaned membrane became less hydrophilic than the virgin membrane) have been recognized to be more susceptible to fouling by organic material. This finding signifies that during cleaning, the cleaning agent attacks the structure of membrane which causes the alteration in hydrophilicity of the membrane.

In general, NaOCl offers a better cleaning performance to restore the membrane flux and permeability than NaOH. The higher cleaning efficiency by the oxidant is contributed by the effective oxidation in the layer of adsorbed organic macromolecules which is close to the membrane surface (Kuzmenko et al., 2005). Taken as a whole, chemical cleaning has demonstrated its capability to eliminate BSA from the membrane surface. However, the exposure of chemical to PVDF membrane during cleaning affects the membrane hydrophilicity which leads to a more severe fouling.

4.2.2 Morphology of PVDF flat membrane

The morphology and structure of the virgin and cleaned membranes were inspected using FESEM analysis and the images are illustrated in Figure 4.13. From Figure 4.13, the membrane which was cleaned with either NaOCl or NaOH showed almost no trace of BSA deposition on the membrane surface. This may generally suggest that the cleaning using chemical is capable to remove foulant from the membrane surface. When 0.01 M of these cleaning agents was used, the cleaned membrane displayed no significant changes in pore sizes as depicted in Figure 4.13 (a) and (b). Noticeable changes in membrane pore structure could be observed after higher chemical concentration was used during the cleaning procedure. As shown in Figure 4.13 (c) and (d), the membranes, which were cleaned with 0.1 M chemical solution

experienced more destruction as indicated by the apparent pore enlargement. The enlargement of membrane pore can be linked to the polymer chain breakage (Rabuni et al., 2013). In the case which involves PVDF material, it undergoes dehydrofluorination reaction once it is exposed to the alkaline environment (Hashim et al., 2011b).

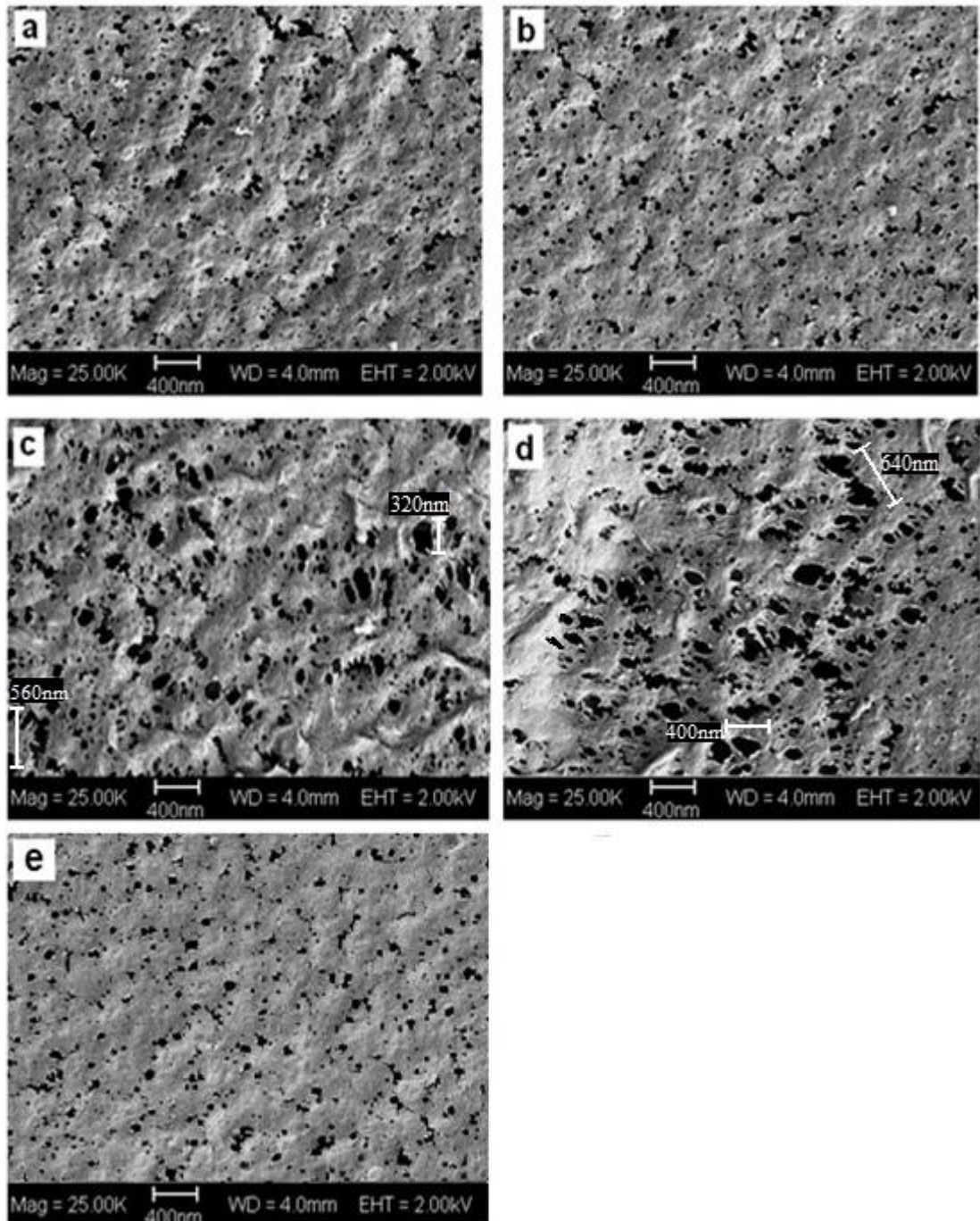


Figure 4.13: FESEM images with 25 000 magnification of membrane surface area cleaned at room temperature by: (a) 0.01 M NaOH, (b) 0.01 M NaOCl, (c) 0.1 M NaOH, (d) 0.1 M NaOCl and (e) Virgin membrane.

4.2.3 FTIR analysis

The typical wavenumber for PVDF membrane and its assignments is listed in Table 4.2. Any changes occurred in PVDF chemical composition could be largely detected by the appearance of carbon-carbon double and triple bond (Hashim et al., 2011b; Kise & Ogata, 1983; Ross et al., 2000).

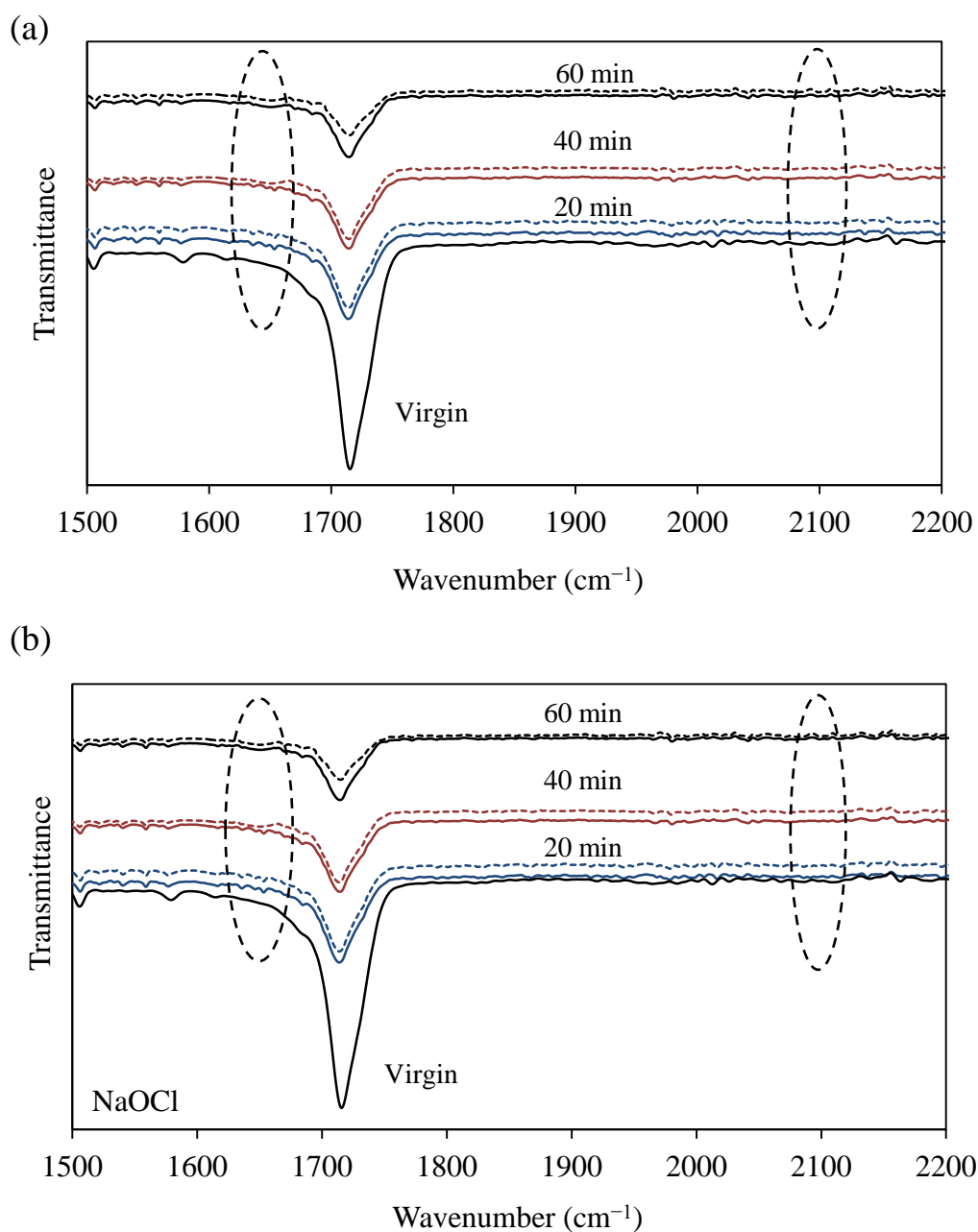


Figure 4.14: Spectra of membrane cleaned at different time with (a) NaOH and (b) NaOCl; solid line represents 0.01 M and dashed line represents 0.1 M alkaline solutions.

The spectra of membranes cleaned at various times are presented in Figure 4.14. For a period of 20 minutes cleaning time, the spectra of all cleaned membranes showed a similar pattern regardless of the chemical concentration used. At a longer cleaning time, the FTIR analysis showed changes which occurred in chemical groups on the membrane surface. Particularly for PVDF membrane, the alteration in chemical composition can be associated with the dehydrofluorination reaction. From previous studies, the occurrence of dehydrofluorination process is mainly indicated by the occurrence of the peaks at a range of 1590 to 1650 cm^{-1} assigned for carbon-carbon double bond and 2100 cm^{-1} for the carbon-carbon triple bond (Hashim et al., 2011b; Kise & Ogata, 1983). It was observed that a small peak at 1650 cm^{-1} (assigned for carbon-carbon double bond) appeared for membranes that were cleaned using 0.1 M of either NaOH or NaOCl for a lapse of 40 and 60 minutes, and membranes that were cleaned with 0.01 M for 60 minutes. The appearance of carbon-carbon double bond denoted the occurrence of dehydrofluorination reaction on the cleaned membrane surface (Zhao et al., 2011). Although the peak signal was relatively low, its appearance signifies that there was an alteration in chemical composition when membranes were cleaned using the chemicals. In all cases, no peak indicating carbon-carbon triple bond was observed.

From Figure 4.14, an apparent change in the relative intensity was observed for a peak at approximately 1710 cm^{-1} (assigned for C=O). The relative intensity for cleaned membrane was reduced significantly as compared to the virgin membrane. We believe that the peak representing carbonyl bond (C=O) is attributed by the additive that is responsible for the hydrophilicity of the PVDF membrane and this assumption is in a good agreement with earlier works (Abdullah & Berube, 2013; Puspitasari et al., 2010). Therefore, the reduction in C=O peak intensity suggested a decline in hydrophilicity.

This finding is in line with the contact angle measurement as the membrane was found to be less hydrophilic upon cleaning process.

Generally, the changes in chemical composition of cleaned and virgin membrane are mainly indicated by the differences in pattern between the recorded spectra. The emergence of small peak which corresponds to carbon-carbon double bonds denotes that cleaning process had in fact, altered the chemistry of the membrane surface as well as a significant change in the relative intensity for the C=O band with prolonged cleaning times. Henceforth, it could be deduced that an appropriate selection of cleaning agent and their compatibility with PVDF material is essential for a longer membrane lifespan.

4.2.4 Contact angle measurement

The contact angle is used to measure the membrane surface hydrophobicity or hydrophilicity in which, when it is below 90° , it is considered as hydrophilic, while for a value more than 90° , it is hydrophobic. In general, the cleaned membranes were determined to experience a decrease in surface hydrophilicity, whereas the contact angle had increased substantially as shown in Table 4.7. The increased contact angle was associated with the membrane surface modification that was caused either by the foulant, chemical agents or may have been by both of them. Furthermore, the enhanced hydrophilicity may also be due to the alteration in the membrane structure or its composition. As previously discussed in section 4.2.1, the modified PVDF which contains additives is affected due to its exposure to strong alkaline solution and oxidant. The instability of these additives towards harsh chemical has altered the membrane hydrophilicity. It was observed that the reduction in hydrophilicity became more significant as the concentration of chemical used increases.

Table 4.7: Contact angle of virgin hydrophilic PVDF membranes and cleaned PVDF membrane at room temperature.

Concentration (M)	Contact angle (°)			
	NaOH		NaOCl	
	20 min	60 min	20 min	60 min
0	66.49 ± 0.43	66.49 ± 0.43	66.49 ± 0.43	66.49 ± 0.43
0.01	71.88 ± 0.19	72.58 ± 0.19	73.91 ± 0.20	74.42 ± 0.36
0.05	73.19 ± 0.21	73.43 ± 0.27	74.33 ± 0.16	75.40 ± 0.29
0.1	74.28 ± 0.33	75.38 ± 0.25	75.25 ± 0.31	76.84 ± 0.22

Our finding is consistent with previous work by Abdullah et al. in which the contact angle had increased upon contact with chemical (Abdullah & Berube, 2013). This is further supported by the FTIR analysis where the spectra denotes that the chemical additive used to enhance the hydrophilic nature of the membrane may have been removed during cleaning. Therefore, the contact angle could be determined to be inversely proportional to the content of hydrophilic additives in the membrane. It is also worth mentioning that the current finding in this work is a contradiction to the study made by Levitsky and co-workers in which the membrane becomes more hydrophilic subsequent to chemical cleaning (Levitsky et al., 2011b).

In addition, the declination in hydrophilicity of PVDF membranes after cleaning may have been caused by the remains of the foulants on the membrane. Through 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 it will decrease otherwise. Given the hydrophobic character of BSA, the deposition of this organic material onto the membrane surface had caused the membrane to be less hydrophilic.

4.2.5 Protein retention

It has always been presumed that the virgin membrane offers a better performance than the used membrane. According to the pore enlargement scenario, the highest protein retention is expected when using a virgin membrane with smaller pore size. Chemical cleaning had caused the pore size to increase, which consequently, produces a membrane with poorer retention performance. This trend is observed in our study where all of the cleaned membrane showed lower protein retention as compared to virgin membrane and the summary is shown in Table 4.8. The analysis shows membrane that was cleaned with a more concentrated solution resulted in a poorer BSA retention. Subsequent to chemical cleaning, increment in membrane pores was observed as disclosed in FESEM images (Figure 4.13). The increase in pore size is believed to contribute to a poorer separation performance as the BSA particles had passed through the membranes easily. For all cases, NaOCl cleaned membrane presented a poorer protein retention performance as compared to membrane cleaned by NaOH.

Table 4.8: BSA retention (%) for membrane cleaned at 25 °C with various chemical.

Concentration (M)	Protein retention (%)			
	NaOH		NaOCl	
	20 min	60 min	20 min	60 min
0	97.90 ± 0.02	97.90 ± 0.02	97.90 ± 0.02	97.90 ± 0.02
0.01	88.48 ± 0.02	84.45 ± 0.01	84.15 ± 0.02	80.20 ± 0.02
0.05	85.26 ± 0.02	81.65 ± 0.03	81.18 ± 0.02	77.16 ± 0.02
0.1	81.40 ± 0.01	76.86 ± 0.01	75.65 ± 0.01	72.24 ± 0.03

Based on the contact angle values, the cleaned membrane exhibits a relatively higher contact angle value than a pristine membrane representing the reduction in

surface hydrophilicity. Observation on the membrane water flux (as discussed in section 4.2.1) had also showed the cleaned membrane is more prone to fouling in comparison to the virgin membrane, suggesting that more protein is probably retained by the cleaned membrane. Nevertheless, there was only a small difference between the normalised flux of cleaned membrane and the virgin membrane during fouling experiment, implying small variation in terms of the amount of protein retained. Figure 4.15 displays the linear relationship between BSA retention and the contact angle of the membrane. It was observed that the increase in contact angle value resulted in a lower protein retention. Earlier study suggested the separation of protein is governed by membrane hydrophilicity (Levitsky et al., 2011b) in which, the higher the hydrophilicity, the better the retention and vice versa. In our work, the rejection performance is presumed to be inversely proportional to the contact angle value. In addition to this reason, we suggested that the reduction in BSA retention can also be associated with the size exclusion mechanism of the membrane. We found that the virgin membrane with a smaller pore showed the highest BSA retention as compared to the cleaned membrane having a larger pore size. The bigger pore sizes of membrane were unable to exclude the protein molecules and allow them to pass through the membrane pores.

It was previously anticipated that the amount of protein retention is dependable on the membrane surface properties, whereas the pore size does not play any significant role (Levitsky et al., 2011b). Nevertheless, in this study, we suggest that the changes in membrane properties such as hydrophilicity/hydrophobicity and pore size can result in compromised membrane hydraulic and rejection performances. Overall, this study has implicated that the exposure to aggressive chemical is successful in removing foulant, but it suffers a reduced protein retention performance by changing the membrane surface properties and pore size.

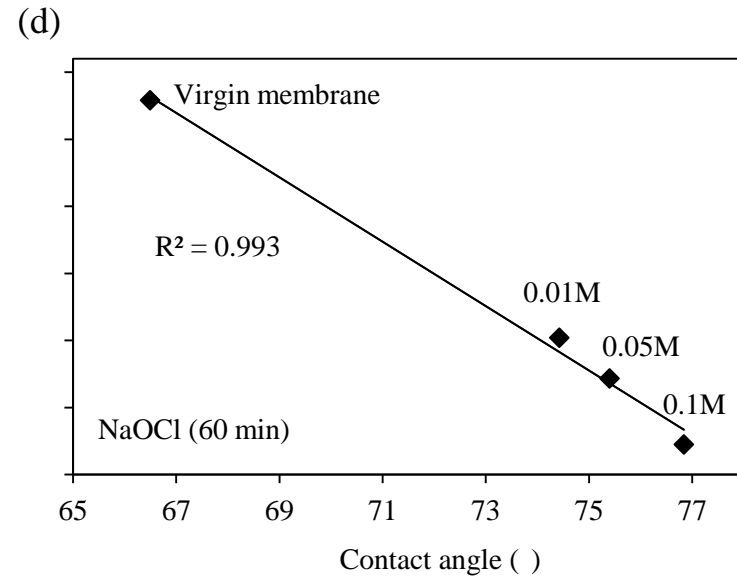
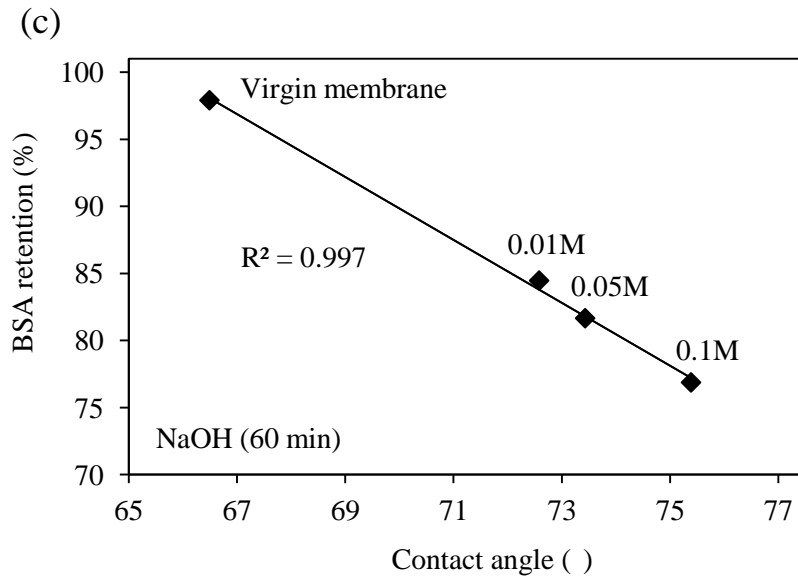
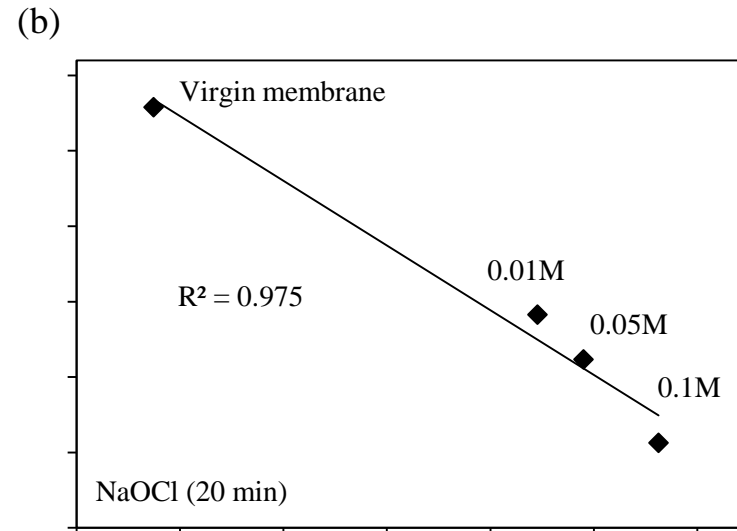
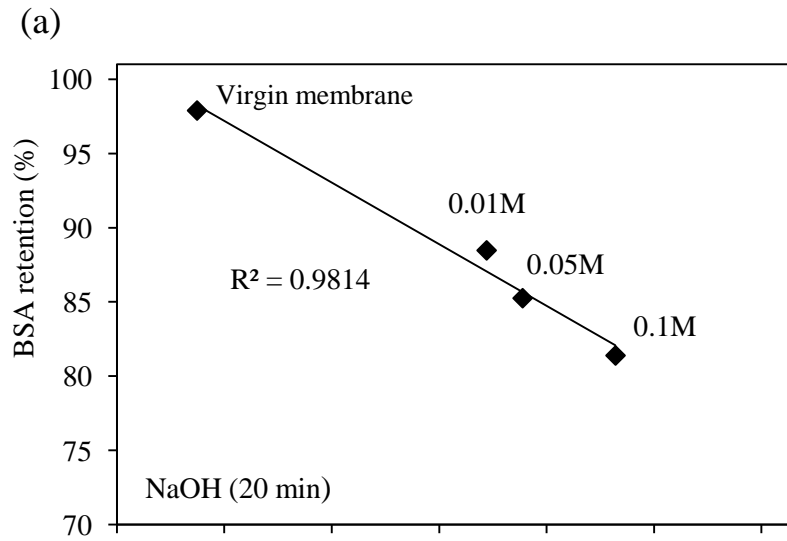


Figure 4.15: BSA retention for membrane cleaned at 25 °C by (a) NaOH (20 min), (b) NaOCl (20 min), (c) NaOH (60 min) and (d) NaOCl (60 min).

4.2.6 Tensile testing

Another aspect such as mechanical testing is also important to identify changes in membrane properties that could affect the operation of membrane processes. The estimation of membrane lifetime could be done by examining the mechanical properties of the membrane after its contact with chemicals (Arkhangelsky et al., 2007a). In this work, nominal elongation is selected as the parameter to study the alteration in the membrane mechanical stability. It is predicted that the nominal elongation will be further reduced when there is an increase in chemical concentration used for cleaning. The effect of chemical concentration and cleaning period towards membrane elongation is presented in Figure 4.16. As expected, the increase in chemical concentration has caused a constant reduction in nominal elongation. The reduction was more evident for the NaOCl cleaned membrane. The nominal elongation of the cleaned membrane further decreases at a more prolonged time in which, the membrane with higher chemical concentration displayed the most evident reduction. PVDF membrane ageing is fundamentally related to the modification of the macromolecular skeleton either by chain scission or cross linking of the PVDF via dehydrofluorination reaction (Hashim et al., 2011b). The breaking of polymeric functional groups upon contact with cleaning chemical induces a gradual deformation of the membrane structure and contributes to the decline in mechanical strength leading to potential membrane embrittlement (Lovinger, 1982).

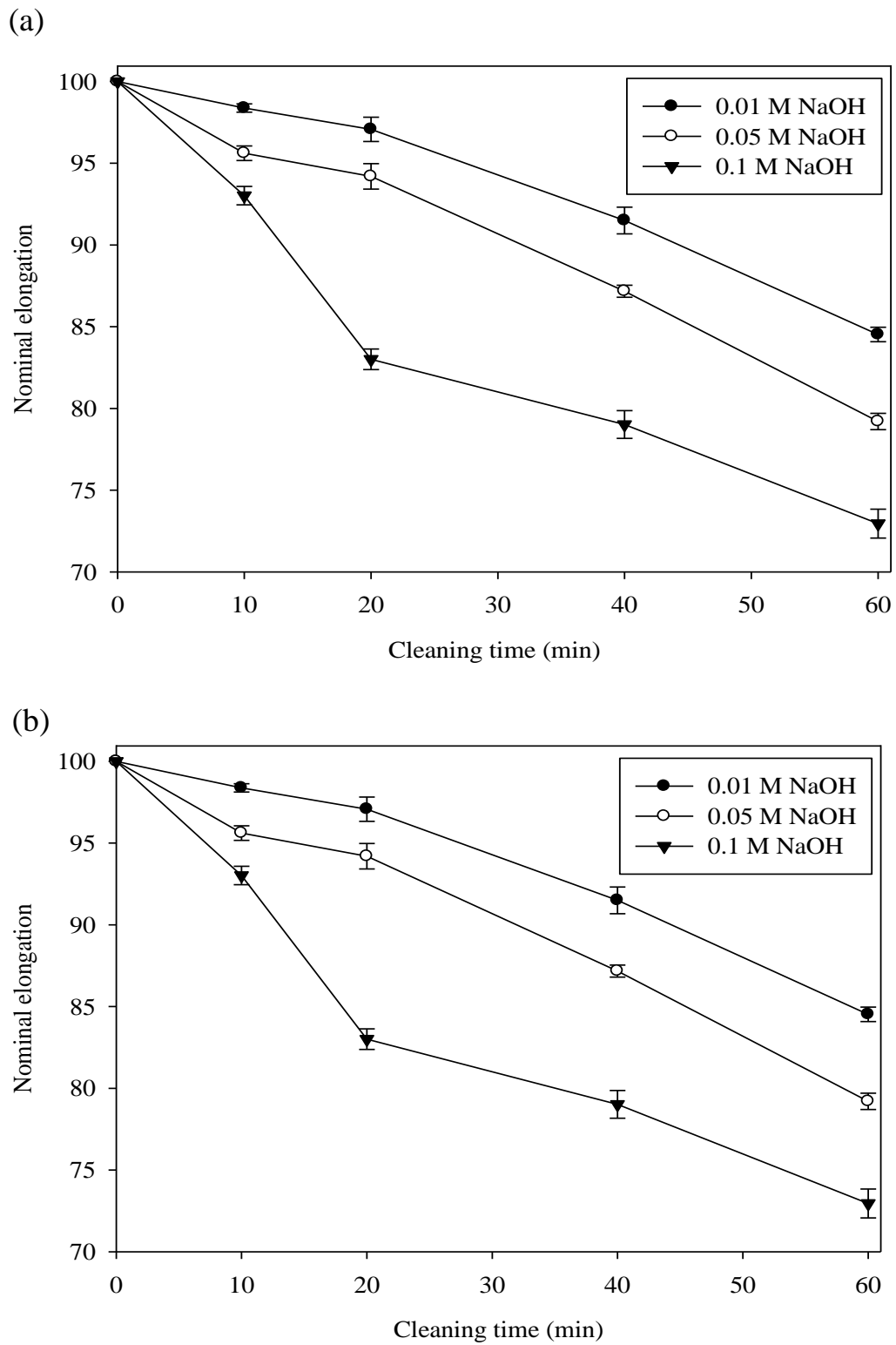


Figure 4.16: Effects of cleaning time towards nominal elongation for membrane cleaned by (a) NaOH and (b) NaOCl.

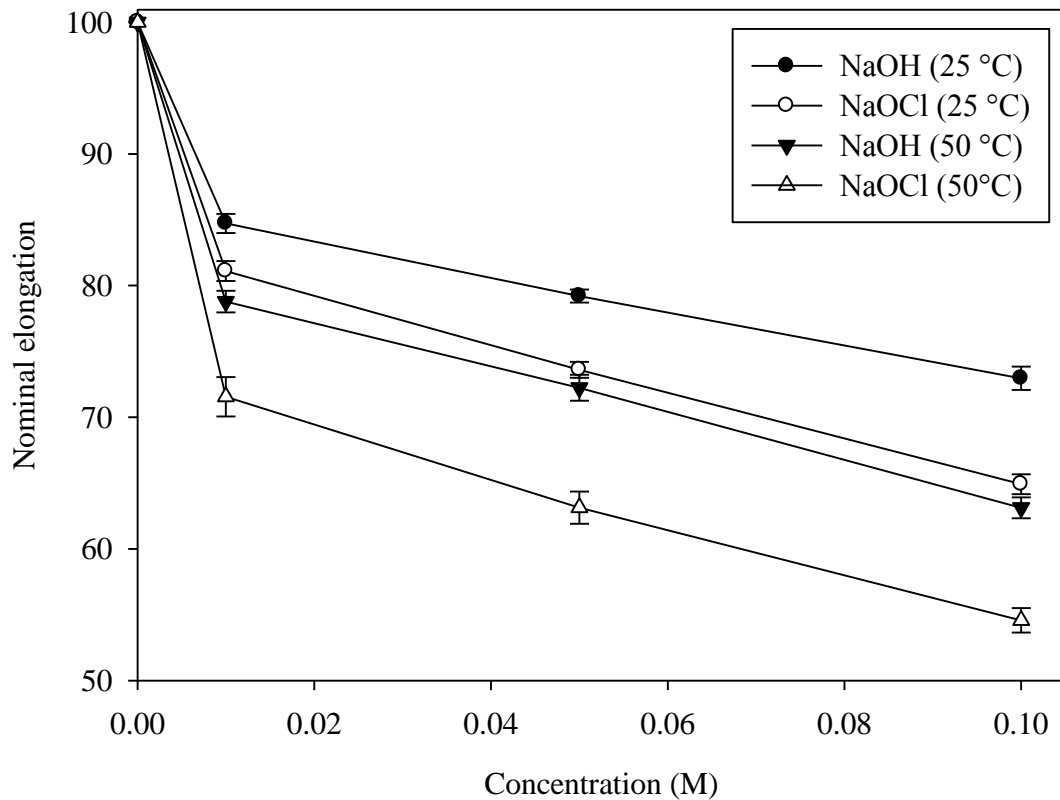


Figure 4.17: Effects of cleaning temperature towards membrane nominal elongation for 60 minutes cleaning time.

Temperature elevation is known to increase the solubility of chemical species. Thus, it is generally accepted to perform the cleaning procedure at an elevated temperature in order to boost the cleaning performance. In this study, temperature elevation was observed to have negative effects towards the membrane mechanical strength. As depicted in Figure 4.17, the cleaned membrane exhibits an even lower elongation than those of which was cleaned at room condition. It should be noted that the fouled membranes, which were exposed to NaOCl cleaning suffers a significant decrease in maximum elongation when compared to those cleaned by NaOH. Although NaOCl is a strong oxidant and found to be effective to remove BSA from the surface of a membrane, it has a major setback where it will cause the highest reduction in tensile

strength. Previous works also reported that mechanical properties of PVDF membrane decreased after chemical cleaning (Hajibabania et al., 2012; Wang et al., 2010)

In general, all cleaned membranes became weaker and brittle following a physical contact with chemicals. PVDF membrane degradation is associated with dehydrofluorination reaction which is responsible for the deterioration in the membrane structure (Hashim et al., 2011b). Exposure to alkaline solution has caused a modification in the membrane texture and thus, membrane structural degradation is demonstrated to be directly related to the declination in the membrane mechanical properties as disclosed in FESEM images (refer to Figure 4.13). The observed reductions in membrane flexibility provided a clear signal that the cleaning process imposes a potential harmful impact on the mechanical properties of the membrane. Despite the success in flux recovery, it should be noted that the exposure to the chemical even at a concentration of 0.01M was found to reduce the membrane mechanical properties. This is hostile as it indicates the membrane's inability to withstand high pressure operation. This is an important remark for the industrial sector to select an appropriate cleaning practice for a better flux recovery without compromising the significant changes in properties of the membrane. Therefore, it is suggested that the alternatives for NaOH and NaOCl should be considered in PVDF membrane cleaning to extend its lifetime.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This research work has highlighted the effects of alkaline solution towards PVDF stability at the typical concentrations used in membrane cleaning and membrane contactor processes such as gas absorption using alkaline solution. In the first part of the study, PVDF membranes treated with two types of strong alkali, NaOH and KOH were analyzed by mechanical, thermal and chemical analysis. The second part involved the study on the effects of chemical cleaning by NaOH and NaOCl towards PVDF membrane characteristics. In general, the obtained results indicate that the reaction between PVDF and alkaline solution was initiated even at low concentration, which is as low as 0.01 M and was accelerated by a prolonged treatment time. One of the main outcomes of these experiments was that NaOH was identified to be relatively stronger alkali and causes more degradation on PVDF membrane compared to KOH.

The higher flux recovery was attributed to the higher concentration of the cleaning agent and the temperature applied, yet the overall cleaning process sees a declination in PVDF membrane stability. When compared to NaOH, NaOCl was found to be more efficient in removing BSA particles, but it has a more significant effect on the membrane properties. All cleaned membranes experience a reduction in mechanical properties and an altered chemical composition. It is found that the modified PVDF membrane is unable to maintain its hydrophilicity, as indicated by the reduction in contact angle value subsequent to cleaning. The efficiency of membrane protein retention was compromised upon chemical cleaning in which the cleaned membrane presented a poorer retention performance. This event is deduced to be inhibited by pore enlargement and membrane hydrophilicity.

5.2 Recommendations

In this work, the commercial PVDF membrane was used in both parts (treatment by immersion and membrane cleaning). The exact composition of the fabricated membrane, particularly the modified PVDF membrane is confidential for the manufacturer. It is recommended in future study; the self fabricated PVDF membrane should be used to improve the merit of the study.

Given that chemicals such as NaOH and NaOCl could be detrimental to PVDF membrane, thus, alternative to these chemicals for membrane cleaning process is essential. Currently, the usage of bio-cleaning products (i.e. enzymatic agent or bio-surfactant) become much more cost effective and could potentially replace the conventional cleaning agent. It is suggested that the use of this type of cleaning agent could be studied in the future to observe their impacts on the characteristics of PVDF membrane.

REFERENCES

- Abdullah, S. Z., & Berube, P. R. (2013). Assessing the effects of sodium hypochlorite exposure on the characteristics of PVDF based membranes. *Water Res*, 47(14), 5392-5399. doi: 10.1016/j.watres.2013.06.018
- Ahmad, A. L., Sunarti, A. R., Lee, K. T., & Fernando, W. J. N. (2010). CO₂ removal using membrane gas absorption. *International Journal of Greenhouse Gas Control*, 4(3), 495-498. doi: DOI 10.1016/j.ijggc.2009.12.003
- Alkhudhiri, A., Darwish, N., & Hilal, N. (2012). Membrane distillation: A comprehensive review. *Desalination*, 287(0), 2-18. doi: DOI 10.1016/j.desal.2011.08.027
- Arkhangelsky, E., Kuzmenko, D., & Gitis, N. V. (2007a). Hypochlorite cleaning causes degradation of polymer membranes. *Tribology Letters*, 28(2), 109-116. doi: DOI 10.1007/s11249-007-9253-6
- Arkhangelsky, E., Kuzmenko, D., & Gitis, V. (2007b). Impact of chemical cleaning on properties and functioning of polyethersulfone membranes. *Journal of Membrane Science*, 305(1-2), 176-184. doi: DOI 10.1016/j.memsci.2007.08.007
- Atchariyawut, S., Jiraratananon, R., & Wang, R. (2007). Separation of CO₂ from CH₄ by using gas-liquid membrane contacting process. *Journal of Membrane Science*, 304(1-2), 163-172. doi: 10.1016/j.memsci.2007.07.030
- Benzinger, W. D., Parekh, B. S., & Eichelberger, J. L. (1980). High Temperature Ultrafiltration With Kynar® Poly(Vinylidene Fluoride) Membranes. *Separation Science and Technology*, 15(4), 1193-1204. doi: 10.1080/01496398008076294
- Bonyadi, S., & Chung, T. S. (2009). Highly porous and macrovoid-free PVDF hollow fiber membranes for membrane distillation by a solvent-dope solution co-extrusion approach. *Journal of Membrane Science*, 331(1-2), 66-74. doi: DOI 10.1016/j.memsci.2009.01.014

- Bowen, W. R., Calvo, J. I., & Hernández, A. (1995). Steps of membrane blocking in flux decline during protein microfiltration. *Journal of Membrane Science*, *101*(1–2), 153-165. doi: [http://dx.doi.org/10.1016/0376-7388\(94\)00295-A](http://dx.doi.org/10.1016/0376-7388(94)00295-A)
- Bradford, M. M. (1976). A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding. *Analytical Biochemistry*, *72*(1–2), 248-254. doi: [http://dx.doi.org/10.1016/0003-2697\(76\)90527-3](http://dx.doi.org/10.1016/0003-2697(76)90527-3)
- Collier, A., Wang, H. J., Yuan, X. Z., Zhang, J. J., & Wilkinson, D. P. (2006). Degradation of polymer electrolyte membranes. *International Journal of Hydrogen Energy*, *31*(13), 1838-1854. doi: DOI 10.1016/j.ijhydene.2006.05.006
- Dargaville, T. R., George, G. A., Hill, D. J. T., & Whittaker, A. K. (2003). High energy radiation grafting of fluoropolymers. *On Progress in Polymer Science*.
- Du, J. R., Peldszus, S., Huck, P. M., & Feng, X. (2009). Modification of poly(vinylidene fluoride) ultrafiltration membranes with poly(vinyl alcohol) for fouling control in drinking water treatment. *Water Res*, *43*(18), 4559-4568. doi: 10.1016/j.watres.2009.08.008
- El-Bourawi, M. S., Ding, Z., Ma, R., & Khayet, M. (2006). A framework for better understanding membrane distillation separation process. *Journal of Membrane Science*, *285*(1-2), 4-29. doi: DOI 10.1016/j.memsci.2006.08.002
- Fan, H. W., & Peng, Y. L. (2012). Application of PVDF membranes in desalination and comparison of the VMD and DCMD processes. *Chemical Engineering Science*, *79*(0), 94-102. doi: DOI 10.1016/j.ces.2012.05.052
- Feng, C. Y., Khulbe, K. C., Matsuura, T., & Ismail, A. F. (2013). Recent progresses in polymeric hollow fiber membrane preparation, characterization and applications. *Separation and Purification Technology*, *111*, 43-71. doi: DOI 10.1016/j.seppur.2013.03.017

- Furusho, N., Komatsu, T., & Nakagawa, T. (1974). A study of thermal degradation of several halogen-containing polymers by torsional braid analysis. *Bulletin of the Chemical Society of Japan*, 47(7), 1573–1577.
- Gregorio, R. (2006). Determination of the α , β , and γ crystalline phases of poly(vinylidene fluoride) films prepared at different conditions. *Journal of Applied Polymer Science*, 100(4), 3272-3279. doi: 10.1002/app.23137
- Hajibabania, S., Antony, A., Leslie, G., & Le-Clech, P. (2012). Relative impact of fouling and cleaning on PVDF membrane hydraulic performances. *Separation and Purification Technology*, 90(0), 204-212. doi: DOI 10.1016/j.seppur.2012.03.001
- Halim, N. D., Joseph, A. W., & Lipska, B. K. (2005). A novel ELISA using PVDF microplates. *Journal of Neuroscience Methods*, 143(2), 163-168. doi: <http://dx.doi.org/10.1016/j.jneumeth.2004.09.025>
- Han, H. S., Jeon, H. S., Lee, G. G., Kim, K. J., & Park, B. E. (2009). Electric Properties of PVDF-TrFE (75/25) thin film with Lanthanum Zirconium Oxide Buffer Layer for FeRAM. *Journal of the Korean Physical Society*, 55(2), 898-901.
- Hashim, N. A., Liu, F., & Li, K. (2009). A simplified method for preparation of hydrophilic PVDF membranes from an amphiphilic graft copolymer. *Journal of Membrane Science*, 345(1-2), 134-141. doi: DOI 10.1016/j.memsci.2009.08.032
- Hashim, N. A., Liu, Y., & Li, K. (2011a). Preparation of PVDF hollow fiber membranes using SiO₂ particles: The effect of acid and alkali treatment on the membrane performances. *Industrial and Engineering Chemistry Research*, 50(5), 3035-3040.

- Hashim, N. A., Liu, Y., & Li, K. (2011b). Stability of PVDF hollow fibre membranes in sodium hydroxide aqueous solution. *Chemical Engineering Science*, 66(8), 1565-1575. doi: <http://dx.doi.org/10.1016/j.ces.2010.12.019>
- Hester, J. F., Banerjee, P., & Mayes, A. M. (1999). Preparation of protein-resistant surfaces on poly(vinylidene fluoride) membranes via surface segregation. *Macromolecules*, 32(5), 1643-1650. doi: Doi 10.1021/Ma980707u
- Hlavacek, M., & Bouchet, F. (1993). Constant flowrate blocking laws and an example of their application to dead-end microfiltration of protein solutions. *Journal of Membrane Science*, 82(3), 285-295. doi: [http://dx.doi.org/10.1016/0376-7388\(93\)85193-Z](http://dx.doi.org/10.1016/0376-7388(93)85193-Z)
- Ho, C.-C., & Zydney, A. L. (1999). Effect of membrane morphology on the initial rate of protein fouling during microfiltration. *Journal of Membrane Science*, 155(2), 261-275. doi: [http://dx.doi.org/10.1016/S0376-7388\(98\)00324-X](http://dx.doi.org/10.1016/S0376-7388(98)00324-X)
- Ho, C.-C., & Zydney, A. L. (2000). A Combined Pore Blockage and Cake Filtration Model for Protein Fouling during Microfiltration. *Journal of Colloid and Interface Science*, 232(2), 389-399. doi: <http://dx.doi.org/10.1006/jcis.2000.7231>
- Hoa, S. V., & Ouellette, P. (1983). Stress-Corrosion Cracking of Poly(Vinylidene Fluoride) in Sodium-Hydroxide. *Polymer Engineering and Science*, 23(4), 202-205. doi: DOI 10.1002/pen.760230407
- Hou, D. Y., Wang, J., Qu, D., Luan, Z. K., & Ren, X. J. (2009). Fabrication and characterization of hydrophobic PVDF hollow fiber membranes for desalination through direct contact membrane distillation. *Separation and Purification Technology*, 69(1), 78-86. doi: DOI 10.1016/j.seppur.2009.06.026
- Huisman, I. H., Prádanos, P., & Hernández, A. (2000). The effect of protein–protein and protein–membrane interactions on membrane fouling in ultrafiltration. *Journal*

of Membrane Science, 179(1–2), 79-90. doi: [http://dx.doi.org/10.1016/S0376-7388\(00\)00501-9](http://dx.doi.org/10.1016/S0376-7388(00)00501-9)

Jonsson, G., Prádanos, P., & Hernández, A. (1996). Fouling phenomena in microporous membranes. Flux decline kinetics and structural modifications. *Journal of Membrane Science*, 112(2), 171-183. doi: [http://dx.doi.org/10.1016/0376-7388\(95\)00286-3](http://dx.doi.org/10.1016/0376-7388(95)00286-3)

Kang, G.-d., & Cao, Y.-m. (2014). Application and modification of poly(vinylidene fluoride) (PVDF) membranes – A review. *Journal of Membrane Science*, 463(0), 145-165. doi: <http://dx.doi.org/10.1016/j.memsci.2014.03.055>

Kelly, S. T., & Zydney, A. L. (1995). Mechanisms for BSA fouling during microfiltration. *Journal of Membrane Science*, 107(1–2), 115-127. doi: [http://dx.doi.org/10.1016/0376-7388\(95\)00108-O](http://dx.doi.org/10.1016/0376-7388(95)00108-O)

Khayet, M., Feng, C. Y., Khulbe, K. C., & Matsuura, T. (2002). Preparation and characterization of polyvinylidene fluoride hollow fiber membranes for ultrafiltration. *Polymer*, 43(14), 3879-3890. doi: [http://dx.doi.org/10.1016/S0032-3861\(02\)00237-9](http://dx.doi.org/10.1016/S0032-3861(02)00237-9)

Kimura, K., Hane, Y., Watanabe, Y., Amy, G., & Ohkuma, N. (2004). Irreversible membrane fouling during ultrafiltration of surface water. *Water Res*, 38(14-15), 3431-3441. doi: [10.1016/j.watres.2004.05.007](http://dx.doi.org/10.1016/j.watres.2004.05.007)

Kise, H., & Ogata, H. (1983). Phase Transfer Catalysis in Dehydrofluorination of Poly(vinylidene fluoride) by Aqueous Sodium Hydroxide Solutions. *Journal of polymer science. Part A-1, Polymer chemistry*, 21(12), 3443-3451.

Klaassen, R., Feron, P. H. M., & Jansen, A. E. (2005). Membrane contactors in industrial applications. *Chemical Engineering Research & Design*, 83(A3), 234-246. doi: [Doi 10.1205/Cherd.04196](http://dx.doi.org/10.1205/Cherd.04196)

- Komaki, Y. (1979). Growth of fine holes by the chemical etching of fission tracks in polyvinylidene fluoride. *Nuclear Tracks*, 3(1-2), 33-44.
- Komaki, Y., & Otsu, H. (1981). Observation of Nuclear Track Development in Polyvinylidene Fluoride with Several Etchants. *Journal of Electron Microscopy*, 30(4), 292-297.
- Kuzmenko, D., Arkhangelsky, E., Belfer, S., Freger, V., & Gitis, V. (2005). Chemical cleaning of UF membranes fouled by BSA. *Desalination*, 179(1-3), 323-333. doi: <http://dx.doi.org/10.1016/j.desal.2004.11.078>
- Levitsky, I., Duek, A., Arkhangelsky, E., Pinchev, D., Kadoshian, T., Shetrit, H., . . . Gitis, V. (2011a). Understanding the oxidative cleaning of UF membranes. *Journal of Membrane Science*, 377(1-2), 206-213. doi: DOI 10.1016/j.memsci.2011.04.046
- Levitsky, I., Duek, A., Arkhangelsky, E., Pinchev, D., Kadoshian, T., Shetrit, H., . . . Gitis, V. (2011b). Understanding the oxidative cleaning of UF membranes. *Journal of Membrane Science*, 377(1-2), 206-213. doi: <http://dx.doi.org/10.1016/j.memsci.2011.04.046>
- Levitsky, I., Duek, A., Naim, R., Arkhangelsky, E., & Gitis, V. (2012). Cleaning UF membranes with simple and formulated solutions. *Chemical Engineering Science*, 69(1), 679-683. doi: DOI 10.1016/j.ces.2011.10.060
- Li, J. L., & Chen, B. H. (2005). Review Of CO₂ absorption using chemical solvents in hollow fiber membrane contactors. *Separation and Purification Technology*, 41(2), 109-122. doi: DOI 10.1016/j.seppur.2004.09.008
- Li, K., Kong, J. F., Wang, D. L., & Teo, W. K. (1999). Tailor-made asymmetric PVDF hollow fibers for soluble gas removal. *Aiche Journal*, 45(6), 1211-1219. doi: DOI 10.1002/aic.690450607

- Lin, S.-H., Chiang, P.-C., Hsieh, C.-F., Li, M.-H., & Tung, K.-L. (2008). Absorption of carbon dioxide by the absorbent composed of piperazine and 2-amino-2-methyl-1-propanol in PVDF membrane contactor. *Journal of the Chinese Institute of Chemical Engineers*, 39(1), 13-21. doi: <http://dx.doi.org/10.1016/j.jcice.2007.11.010>
- Liu, F., Abed, M. R. M., & Li, K. (2011a). Hydrophilic modification of P(VDF-co-CTFE) porous membranes. *Chemical Engineering Science*, 66(1), 27-35. doi: DOI 10.1016/j.ces.2010.09.026
- Liu, F., Hashim, N. A., Liu, Y., Abed, M. R. M., & Li, K. (2011b). Progress in the production and modification of PVDF membranes. *Journal of Membrane Science*, 375(1-2), 1-27. doi: 10.1016/j.memsci.2011.03.014
- Lovinger, A. J. (1982). Annealing of poly(vinylidene fluoride) and formation of a fifth phase. *Macromolecules*, 15(1), 40-44.
- Lovinger, A. J., & Freed, D. J. (1980). Inhomogeneous Thermal-Degradation of Poly(Vinylidene Fluoride) Crystallized from the Melt. *Macromolecules*, 13(4), 989-994. doi: Doi 10.1021/Ma60076a044
- Luis, P., Van Gerven, T., & Van der Bruggen, B. (2012). Recent developments in membrane-based technologies for CO₂ capture. *Progress in Energy and Combustion Science*, 38(3), 419-448. doi: DOI 10.1016/j.peccs.2012.01.004
- Madorsky, S. L. (1964). Thermal degradation of organic polymers *Fluorocarbon and chlorocarbon polymers* (pp. 130-172): John Wiley & Sons Inc.
- Mansourizadeh, A., & Ismail, A. F. (2009). Hollow fiber gas-liquid membrane contactors for acid gas capture: a review. *J Hazard Mater*, 171(1-3), 38-53. doi: 10.1016/j.jhazmat.2009.06.026
- Mansourizadeh, A., Ismail, A. F., & Matsuura, T. (2010). Effect of operating conditions on the physical and chemical CO₂ absorption through the PVDF hollow fiber

- membrane contactor. *Journal of Membrane Science*, 353(1–2), 192-200. doi: 10.1016/j.memsci.2010.02.054
- Mazzei, R. O., Bermudez, G. G., Tadey, D., & Rocco, C. (2004). Grafting of poly(vinylidene fluoride) foils induced by swift heavy ions. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 218(0), 313-317. doi: DOI 10.1016/j.nimb.2003.12.010
- Meng, S. W., Mansouri, J., Ye, Y., & Chen, V. (2014). Effect of templating agents on the properties and membrane distillation performance of TiO₂-coated PVDF membranes. *Journal of Membrane Science*, 450(0), 48-59. doi: DOI 10.1016/j.memsci.2013.08.036
- Munari, S., Bottino, A., & Capannelli, G. (1983). Casting and Performance of Polyvinylidene Fluoride Based Membranes. *Journal of Membrane Science*, 16(Dec), 181-193. doi: Doi 10.1016/S0376-7388(00)81309-5
- Nguyen, T. (1985). Degradation of poly(vinyl fluoride) and poly(vinylidene fluoride). *Journal of Macromolecular Science, Part C: Polymer Reviews*, 25(2), 227-275. doi: 10.1080/15583728509412823
- O'Hagan, D. (2008). Understanding organofluorine chemistry. An introduction to the C-F bond. *Chem Soc Rev*, 37(2), 308-319. doi: 10.1039/b711844a
- Park, H., Deshwal, B., Kim, I., & Lee, H. (2008). Absorption of SO₂ from flue gas using PVDF hollow fiber membranes in a gas–liquid contactor. *Journal of Membrane Science*, 319(1-2), 29-37. doi: 10.1016/j.memsci.2008.03.023
- Park, H. H., Deshwal, B. R., Jo, H. D., Choi, W. K., Kim, I. W., & Lee, H. K. (2009). Absorption of nitrogen dioxide by PVDF hollow fiber membranes in a G–L contactor. *Desalination*, 243(1-3), 52-64. doi: 10.1016/j.desal.2008.04.014
- Perry, R. H., & Green, D. W. (1997). Physical Properties of Pure Substances *Perry's Chemical Engineers' Handbook (7th Edition)* (pp. 2-21 -22-24): Mc-Graw Hill

- Pezeshk, N., & Narbaitz, R. M. (2012). More fouling resistant modified PVDF ultrafiltration membranes for water treatment. *Desalination*, 287(0), 247-254. doi: DOI 10.1016/j.desal.2011.11.048
- Pezeshk, N., Rana, D., Narbaitz, R. M., & Matsuura, T. (2012). Novel modified PVDF ultrafiltration flat-sheet membranes. *Journal of Membrane Science*, 389(0), 280-286. doi: DOI 10.1016/j.memsci.2011.10.039
- Ploss, B., Ploss, B., Shin, F. G., Chan, H. L. W., & Choy, C. L. (2000). Pyroelectric activity of ferroelectric PT/PVDF-TRFE. *Ieee Transactions on Dielectrics and Electrical Insulation*, 7(4), 517-522. doi: Doi 10.1109/94.868071
- Porcelli, N., & Judd, S. (2010). Chemical cleaning of potable water membranes: A review. *Separation and Purification Technology*, 71(2), 137-143. doi: DOI 10.1016/j.seppur.2009.12.007
- Puspitasari, V., Granville, A., Le-Clech, P., & Chen, V. (2010). Cleaning and ageing effect of sodium hypochlorite on polyvinylidene fluoride (PVDF) membrane. *Separation and Purification Technology*, 72(3), 301-308. doi: DOI 10.1016/j.seppur.2010.03.001
- Qi, Z., & Cussler, E. L. (1985). Microporous hollow fibers for gas absorption. *Journal of Membrane Science*, 23(3), 321-332. doi: 10.1016/s0376-7388(00)83149-x
- Rabuni, M. F., Nik Sulaiman, N. M., Aroua, M. K., & Hashim, N. A. (2013). Effects of Alkaline Environments at Mild Conditions on the Stability of PVDF Membrane: An Experimental Study. *Industrial & Engineering Chemistry Research*, 52(45), 15874-15882. doi: 10.1021/ie402684b
- Rahimpour, A., Madaeni, S. S., Amirinejad, M., Mansourplanah, Y., & Zeresghi, S. (2009). The effect of heat treatment of PES and PVDF ultrafiltration membranes

on morphology and performance for milk filtration. *Journal of Membrane Science*, 330(1-2), 189-204. doi: DOI 10.1016/j.memsci.2008.12.059

Rajabzadeh, S., Yoshimoto, S., Teramoto, M., Al-Marzouqi, M., & Matsuyama, H. (2009). CO₂ absorption by using PVDF hollow fiber membrane contactors with various membrane structures. *Separation and Purification Technology*, 69(2), 210-220. doi: DOI 10.1016/j.seppur.2009.07.021

Regula, C., Carretier, E., Wyart, Y., Gésan-Guiziou, G., Vincent, A., Boudot, D., & Moulin, P. (2014). Chemical cleaning/disinfection and ageing of organic UF membranes: A review. *Water Research*, 56(0), 325-365. doi: <http://dx.doi.org/10.1016/j.watres.2014.02.050>

Regula, C., Carretier, E., Wyart, Y., Sergent, M., Gésan-Guiziou, G., Ferry, D., . . . Moulin, P. (2013). Ageing of ultrafiltration membranes in contact with sodium hypochlorite and commercial oxidant: Experimental designs as a new ageing protocol. *Separation and Purification Technology*, 103(0), 119-138. doi: 10.1016/j.seppur.2012.10.010

Ross, G. J., Watts, J. F., Hill, M. P., & Morrissey, P. (2000). Surface modification of poly(vinylidene fluoride) by alkaline treatment 1. The degradation mechanism *Polymer* (Vol. 41, pp. 1685-1696).

Ross, G. J., Watts, J. F., Hill, M. P., & Morrissey, P. (2001). Surface modification of poly(vinylidene fluoride) by alkaline treatment Part 2. Process modification by the use of phase transfer catalysts. *Polymer*, 42(2), 403-413. doi: Doi 10.1016/S0032-3861(00)00328-1

Shi, X., Tal, G., Hankins, N. P., & Gitis, V. (2014). Fouling and cleaning of ultrafiltration membranes: A review. *Journal of Water Process Engineering*, 1(0), 121-138. doi: <http://dx.doi.org/10.1016/j.jwpe.2014.04.003>

- Shinohara, H. (1979). Fluorination of polyhydrofluoroethylenes. II. Formation of perfluoroalkyl carboxylic acids on the surface region of poly(vinylidene fluoride) film by oxyfluorination, fluorination, and hydrolysis. *Journal of Polymer Science: Polymer Chemistry Edition*, 17(5), 1543-1556. doi: 10.1002/pol.1979.170170526
- Simon, A., McDonald, J. A., Khan, S. J., Price, W. E., & Nghiem, L. D. (2013). Effects of caustic cleaning on pore size of nanofiltration membranes and their rejection of trace organic chemicals. *Journal of Membrane Science*, 447(0), 153-162. doi: <http://dx.doi.org/10.1016/j.memsci.2013.07.013>
- Srisurichan, S., Jiratananon, R., & Fane, A. G. (2005). Humic acid fouling in the membrane distillation process. *Desalination*, 174(1), 63-72. doi: DOI 10.1016/j.desal.2004.09.003
- Stengaard, F. F. (1988). Preparation of Asymmetric Microfiltration Membranes and Modification of Their Properties by Chemical Treatment. *Journal of Membrane Science*, 36(0), 257-275. doi: Doi 10.1016/0376-7388(88)80022-X
- Tan, X. Y., Tan, S. P., Teo, W. K., & Li, K. (2006). Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water. *Journal of Membrane Science*, 271(1-2), 59-68. doi: DOI 10.1016/j.memsci.2005.06.057
- Tomaszewska, M. (1996). Preparation and properties of flat-sheet membranes from poly(vinylidene fluoride) for membrane distillation. *Desalination*, 104(1-2), 1-11. doi: Doi 10.1016/0011-9164(96)00020-3
- Uragami, T., Naito, Y., & Sugihara, M. (1981). Studies on Synthesis and Permeability of Special Polymer Membranes .39. Permeation Characteristics and Structure of Polymer Blend Membranes from Poly(Vinylidene Fluoride) and Poly(Ethylene Glycol). *Polymer Bulletin*, 4(10), 617-622. doi: 10.1007/bf00256290

- Vigo, F., Capannelli, G., Uliana, C., & Munari, S. (1981). Asymmetric Polyvinylidene fluoride (Pvdf) Radiation Grafted Membranes - Preparation and Performance in Reverse-Osmosis Application. *Desalination*, 36(1), 63-73. doi: Doi 10.1016/S0011-9164(00)88631-2
- Vigo, F., Uliana, C., Cavazza, B., & Salvemini, F. (1984). Mechanical, Chemical and Bacterial-Resistance of Modified Polyvinylidene Fluoride Membranes Suitable for Ultrafiltration of Oily Emulsions. *Journal of Membrane Science*, 21(3), 295-306. doi: Doi 10.1016/S0376-7388(00)80220-3
- Wang, Z. Wang, Z. Wu, Q. Zhou, & D. Yang. (2010). Effect of hypochlorite cleaning on the physiochemical characteristics of polyvinylidene fluoride membranes. *Chemical Engineering Journal*, 162(3), 1050-1056. doi: <http://dx.doi.org/10.1016/j.cej.2010.07.019>
- Wang, D. L., Teo, W. K., & Li, K. (2002). Removal of H₂S to ultra-low concentrations using an asymmetric hollow fibre membrane module. *Separation and Purification Technology*, 27(1), 33-40. doi: Doi 10.1016/S1383-5866(01)00186-1
- Wang, D. L., Teo, W. K., & Li, K. (2004). Selective removal of trace H₂S from gas streams containing CO₂ using hollow fibre membrane modules/contractors. *Separation and Purification Technology*, 35(2), 125-131. doi: Doi 10.1016/S1383-5866(03)00135-7
- Wang, L., Wang, Q., Li, Y., & Lin, H. (2013). Ultrasound-assisted chemical cleaning of polyvinylidene fluoride membrane fouled by lactic acid fermentation broth. *Desalination*, 326(0), 103-108. doi: <http://dx.doi.org/10.1016/j.desal.2013.06.010>

- Wegener, M., Kuenstler, W., & Gerhard-Multhaupt, R. (2006). Poling behavior and optical absorption of partially dehydrofluorinated and uniaxially stretched polyvinylidene fluoride. *Ferroelectrics*, 336(1), 3-8. doi: Doi 10.1080/00150190600694761
- Wu, B., Tan, X. Y., Li, K., & Teo, W. K. (2006). Removal of 1,1,1-trichloroethane from water using a polyvinylidene fluoride hollow fiber membrane module: Vacuum membrane distillation operation. *Separation and Purification Technology*, 52(2), 301-309. doi: DOI 10.1016/j.seppur.2006.05.013
- Wu, B., Tan, X. Y., Teo, W. K., & Li, K. (2005). Removal of benzene/toluene from water by vacuum membrane distillation in a PVDF hollow fiber membrane module. *Separation Science and Technology*, 40(13), 2679-2695. doi: Doi 10.1080/01496390500283456
- Xiao, K., Wang, X., Huang, X., Waite, T. D., & Wen, X. (2011). Combined effect of membrane and foulant hydrophobicity and surface charge on adsorptive fouling during microfiltration. *Journal of Membrane Science*, 373(1-2), 140-151. doi: <http://dx.doi.org/10.1016/j.memsci.2011.02.041>
- Yi, X. S., Yu, S. L., Shi, W. X., Sun, N., Jin, L. M., Wang, S., . . . Sun, L. P. (2011). The influence of important factors on ultrafiltration of oil/water emulsion using PVDF membrane modified by nano-sized TiO₂/Al₂O₃. *Desalination*, 281(0), 179-184. doi: DOI 10.1016/j.desal.2011.07.056
- Yuliwati, E., & Ismail, A. F. (2011). Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced wastewater treatment. *Desalination*, 273(1), 226-234. doi: DOI 10.1016/j.desal.2010.11.023
- Yuliwati, E., Ismail, A. F., Matsuura, T., Kassim, M. A., & Abdullah, M. S. (2011). Effect of modified PVDF hollow fiber submerged ultrafiltration membrane for

- refinery wastewater treatment. *Desalination*, 283(0), 214-220. doi: DOI 10.1016/j.desal.2011.03.049
- Zhang, B., & Ma, S. (2009). Study on Fouling and Cleaning of PVDF Membrane. *Modern Applied Science*, 3(11), 7.
- Zhang, S. C., Shen, J., Qiu, X. P., Weng, D. S., & Zhu, W. T. (2006). ESR and vibrational spectroscopy study on poly(vinylidene fluoride) membranes with alkaline treatment. *Journal of Power Sources*, 153(2), 234-238. doi: DOI 10.1016/j.jpowsour.2005.05.020
- Zhang, Y., Sunarso, J., Liu, S., & Wang, R. (2013). Current status and development of membranes for CO₂/CH₄ separation: A review. *International Journal of Greenhouse Gas Control*, 12(0), 84-107. doi: <http://dx.doi.org/10.1016/j.ijggc.2012.10.009>
- Zhao, X. D., Song, L. Z., Fu, J., Tang, P., & Liu, F. (2011). Experimental and DFT investigation of surface degradation of polyvinylidene fluoride membrane in alkaline solution. *Surface Science*, 605(11-12), 1005-1015. doi: DOI 10.1016/j.susc.2011.02.022
- Zhao, Y. H., Qian, Y. L., Zhu, B. K., & Xu, Y. Y. (2008). Modification of porous poly(vinylidene fluoride) membrane using amphiphilic polymers with different structures in phase inversion process. *Journal of Membrane Science*, 310(1-2), 567-576. doi: DOI 10.1016/j.memsci.2007.11.040
- Zularisam, A. W., Ismail, A. F., & Salim, R. (2006). Behaviours of natural organic matter in membrane filtration for surface water treatment - a review. *Desalination*, 194(1-3), 211-231. doi: DOI 10.1016/j.desal.2005.10.030
- Zuo, D. Y., Li, H. J., Liu, H. T., & Wu, G. P. (2010). A study on submerged rotating MBR for wastewater treatment and membrane cleaning. *Korean Journal of Chemical Engineering*, 27(3), 881-885. doi: DOI 10.1007/s11814-010-0123-9

APPENDIX A

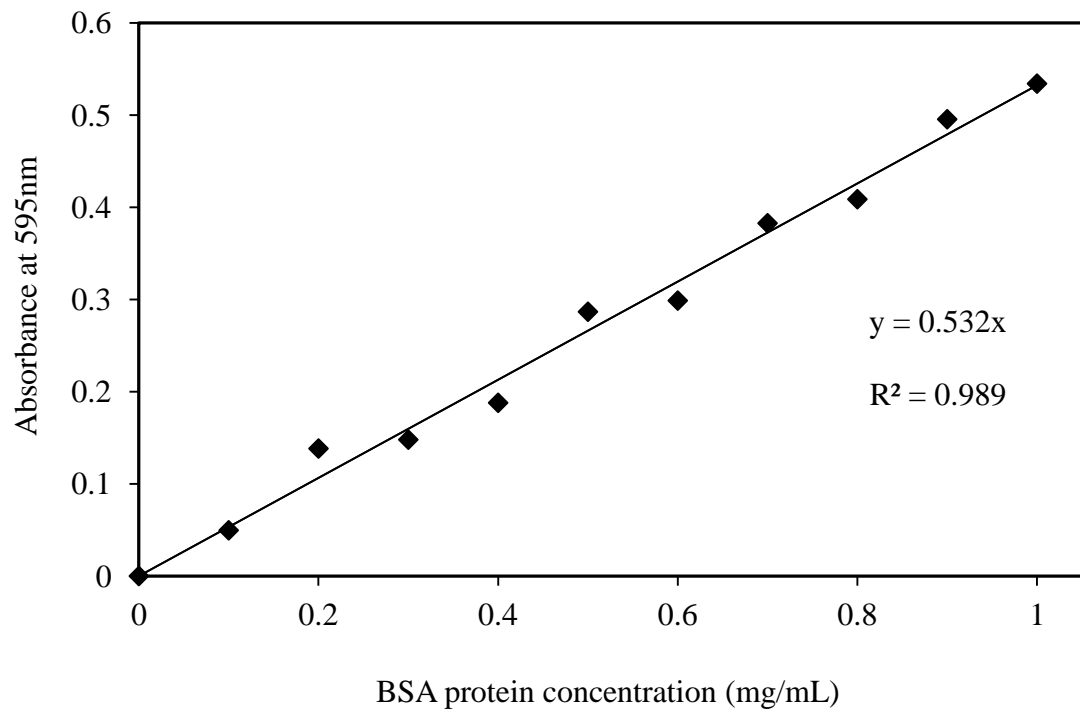


Figure A1: Bovine serum albumin (BSA) standard curve.

APPENDIX B

Table A1: Membrane water flux for virgin and treated hydrophobic PVDF.

(a) 30 minutes treatment

Treatment conditions	Virgin membrane flux (L/m².h.bar)	Treated membrane flux (L/m².h.bar)	% Flux increment
0.01M NaOH(25°C)	40.15	43.24	7.71
0.01M KOH (25°C)	40.08	42.73	6.63
0.01M NaOH (50°C)	40.15	44.69	11.32
0.01M KOH (50°C)	40.08	43.78	9.25
0.2M NaOH(25°C)	40.04	45.15	12.78
0.2M KOH (25°C)	40.14	44.49	10.8
0.2M NaOH (50°C)	40.15	46.16	14.98
0.2M KOH (50°C)	40.15	44.8	11.58

(b) 120 minutes treatment

Treatment conditions	Virgin membrane flux (L/m².h.bar)	Treated membrane flux (L/m².h.bar)	% Flux increment
0.01M NaOH(25°C)	40.15	44.08	9.8
0.01M KOH (25°C)	40.08	43.54	8.63
0.01M NaOH (50°C)	40.15	45.62	13.64
0.01M KOH (50°C)	40.08	44.62	11.34
0.2M NaOH(25°C)	40.15	48.68	21.25
0.2M KOH (25°C)	40.07	46.66	16.43
0.2M NaOH (50°C)	40.08	57.28	42.9
0.2M KOH (50°C)	40.07	50.32	25.57

*All calculated values were rounded to two decimal place.

APPENDIX C

LIST OF PAPERS AND PROCEEDINGS

Article in academic journal

1. Rabuni, M. F., Nik Sulaiman, N. M., Aroua, M. K. and Hashim, N. Awanis. 2013. Effects of Alkaline Environments at Mild Conditions on the Stability of PVDF Membrane: An Experimental Study. *Industrial & Engineering Chemistry Research* 52(45): 15874-15882. (ISI-Cited Publication)
2. Rabuni, M. F., Nik Sulaiman, N. M., Aroua, M. K. and Hashim, N. Awanis. Impact of in situ physical and chemical cleaning on PVDF membrane properties and performance. (Paper under correction after review process by the *Chemical Engineering Science* - 17th September 2014)

Conference and Proceedings

1. Stability of Hydrophobic Polyvinylidene Fluoride (PVDF) Membranes in Alkaline Environment. Oral presentation at the AOTULE Student Conference 2012, University of Malaya, Kuala Lumpur, Malaysia.
2. The Effect of Chemical Cleaning on the Stability of PVDF Membrane. Oral presentation at the AOTULE Student Conference 2013, Chulalongkorn University, Bangkok, Thailand.
3. PVDF Membrane Stability in Alkaline Environment. Poster presented at the International Membrane Science and Technology (IMSTEC) 2013 Conference, Melbourne, Australia.