MEMBRANE DISTILLATION FOR TEXTILE WASTEWATER TREATMENT USING POLYVINYLIDENE FLUORIDE CLOISITE 15A HOLLOW FIBER COMPOSITE MEMBRANES

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Dedicated to my beloved parents
(Mohd Mokhtar bin Mansor and Che Jamaliah binti Hasshim)
my siblings
(Rusmaizah, Mohd Hasbullah, Mohd Ali and Mohd Khaidir)
my in-laws
(Mohd Aizat, Noorul Hijjah, Nursaidatullah and Farah Izwani)
my nephew and nieces
(Qhaliff, Qhalisya, Qhairina, Amni, Hana and Khayla)
and friends for their support, understanding and encouragement
throughout the success of my study
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ABSTRACT

To date, membrane distillation (MD) has been regarded as a potential candidate in treating textile effluents as this thermally-driven membrane process has unique advantages over pressure-driven membrane processes. However, the main challenge for the MD process to be practically used in textile industry is the difficulty of getting a membrane with desirable characteristics. In this work, polyvinylidene fluoride incorporated Cloisite 15A hollow fiber composite membranes were developed for textile wastewater treatment using direct contact membrane distillation (DCMD) system. The effects of polymer concentrations, types of additives and Cloisite 15A clay loadings on the membrane properties and its DCMD performance were investigated. Membrane made of 12 wt% PVDF was found to be the best performing membrane based on its overall separation performance in comparison to the membranes prepared with higher PVDF concentration. In terms of additive, ethylene glycol (EG) was found to be better pore former agent as compared to polyvinylpyrrolidone (PVP). The 12 wt% PVDF membrane with EG as additive was further modified by Cloisite 15A at different loadings. Results showed that the PVDF membrane incorporated with 3 wt% Cloisite 15A (PVDF-3% C15A) was the best composite membrane in terms of permeate flux (10.13 ± 0.18 kg m⁻² h⁻¹) and dye rejection (>99%). Its membrane contact angle, wetting pressure, mean pore size and surface roughness was reported to improve upon addition of 3 wt% Cloisite 15A. Besides, this membrane also exhibited the highest thermal stability, mechanical strength and overall porosity compared to other composite membranes. In view of this, PVDF-3% C15A membrane was selected for further studied using synthetic dyeing solutions containing dyes and salts. With respect to separation performance, higher rejections were able to achieve in all experimental tests, regardless of operating conditions, which indicate the potential of PVDF-3% C15A membrane in producing purified water from synthetic dyeing solutions. The membrane was further subjected to another experiment using real textile wastewater collected from a textile factory located in Kulai, Johor. The treated water was analyzed with respect to biological oxygen demand (BOD₅), chemical oxygen demand (COD), total dissolved solid (TDS), color, turbidity and conductivity. Higher permeate flux (36.82 ± 1.96 kg m⁻² h⁻¹) with excellent removal efficiency (>90%) was recorded for each measured analytical parameter during textile wastewater treatment. The stability of the membrane was also assessed for up to 40-h. Results showed that a significant flux decline was observed during the long-term operation, owing to fouling resulted from cake layer formed at the outer surface of the membrane. Nevertheless, the quality of permeate could be practically maintained at not less than 72% removal for both COD and color. As a conclusion, it can be said that the in-house made PVDF-Cloisite 15A composite membrane can facilitate the development of textile wastewater treatment if several issues such as membrane fouling and pore wetting can be further addressed.
Sehingga kini, penyulingan bermembran (MD) telah dilihat sebagai calon yang berpotensi dalam merawat air sisa tekstil kerana proses membran terpacu haba ini mempunyai kelebihan yang unik berbanding proses membran terpacu tekanan. Walau bagaimanapun, cabaran utama untuk proses MD digunakan dalam industri tekstil ialah kesukaran untuk mendapatkan membran dengan ciri-ciri yang dikenal pasti. Dalam kajian ini, membran komposit gentian geronggang polivinilidin florida (PVDF) Cloisite 15A telah dibungkungkan untuk rawatan air sisa tekstil menggunakan sistem penyulingan bermembran secara langsung (DCMD). Pengaruh berat kepekatan polimer, jenis bahan tambah dan berat muatan tanah liat Cloisite 15A kepada sifat-sifat membran dan prestasi DCMD telah dikaji. Membran yang diperbuat daripada 12% berat kepekatan PVDF telah dikenal pasti sebagai membran unggul berdasarkan prestasi pemisahan keseluruhan mereka berbanding dengan membran yang dihasilkan dengan berat kepekatan PVDF yang lebih tinggi. Dari segi bahan tambah pula, etilena glikol (EG) didapati sebagai ejen pembentuk liang yang terbaik bagi membran PVDF berbanding polivinil piroidon (PVP). Seterusnya, membran PVDF yang mempunyai berat kepekatan 12% beserta bahan tambah EG telah diubahsuai pula pada berat muatan Cloisite 15A yang berlainan. Keputusan kajian menunjukkan bahawa membran PVDF yang ditambah dengan 3% berat Cloisite 15A (PVDF-3% C15A) adalah membran komposit yang terbaik dari segi flus resapan (10.13 ± 0.18 kg m⁻² h⁻¹) dan penyingkiran pewarna (> 99%). Membran PVDF yang diubahsuai itu dilaporkan telah meningkatkan nilai sudut sesentuh membran, tekanan kebasahan, purata saiz liang dan kekasaran permukaan selepas ditambah dengan 3% berat Cloisite 15A. Selain itu, membran tersebut juga menunjukkan kestabilan haba, kekuatan mekanikal dan keliangan keseluruhan yang tinggi berbanding dengan membran komposit yang lain. Oleh yang demikian, membran PVDF-3% C15A telah dipilih untuk kajian seterusnya menggunakan larutan pencelupan sintetik yang mengandungi pewarna dan garam. Berkenaan dengan prestasi pemisahan, penyingkiran yang tinggi telah dicapai dalam setiap uji kaji yang dijalankan tanpa mengira keadaan operasi dimana menunjukkan keupayaan membran tersebut dalam menghasilkan air yang bersih daripada larutan pencelupan sintetik. Membran tersebut seterusnya digunakan untuk merawat air sisa tekstil yang diambil dari sebuah kilang tekstil di Kulai, Johor. Air yang telah dirawat kemudiannya dianalisis berdasarkan keperluan oksigen biokimia (BOD₅), keperluan oksigen kimia (COD), jumlah pepejal terlarut (TDS), warna, kekeruhan dan konduktiviti. Kadar flux (36.82 ± 1.96 kg m⁻² h⁻¹) yang tinggi serta kecekapan penyingkiran yang sangat baik (>90%) telah dicatat bagi setiap parameter kualiti air yang dianalisis semasa rawatan air sisa tekstil. Kestabilan membran juga telah dinilai sehingga 40 jam dan hasil keputusan menunjukkan bahawa penurunan flus yang ketara telah diperhatikan semasa operasi jangka panjang tersebut. Hal ini berlaku disebabkan oleh kekoran yang terhasil daripada pembentukan lapisan kotoran di permukaan luar membran. Walau bagaimanapun, kualiti air yang dirawat masih memberangangkan iaitu sekitar 72% keatas bagi penyingkiran COD dan warna. Kesimpulannya, boleh dikatakan bahawa membran komposit PVDF-Cloisite 15A yang dihasilkan ini dapat membantu dalam pembangunan rawatan air sisa tekstil sekiranya beberapa isu seperti masalah membran tersumbat disebabkan kotoran serta kebasahan liang dapat diatasi sepenuhnya.
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<tr>
<td>ADMI</td>
<td>American dye manufactures institute</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>AGMD</td>
<td>Air gap membrane distillation</td>
</tr>
<tr>
<td>AMAL</td>
<td>Maleic anhydride</td>
</tr>
<tr>
<td>AR1</td>
<td>Acid red 1</td>
</tr>
<tr>
<td>ATR-IR</td>
<td>Attenuated total reflection infrared spectroscopy</td>
</tr>
<tr>
<td>AOX</td>
<td>Adsorbable organic halogens</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological oxygen demand</td>
</tr>
<tr>
<td>CA</td>
<td>Contact angle</td>
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<tr>
<td>C15A</td>
<td>Cloisite 15A</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>CR</td>
<td>Congo red</td>
</tr>
<tr>
<td>CMC</td>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>DCMD</td>
<td>Direct contact membrane distillation</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DMAc</td>
<td>N,N-imethylacetamide</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DS</td>
<td>Dissolved solids</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
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<tr>
<td>EE</td>
<td>Thermal efficiency</td>
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<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
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<tr>
<td>FTIR</td>
<td>Fourier-transform infrared</td>
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<tr>
<td>FO</td>
<td>Forward osmosis</td>
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<td>KCl</td>
<td>Potassium chloride</td>
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**LEP** - Liquid entry pressure  
**LiBr** - Lithium bromide  
**LiCl** - Lithium chloride  
**MC** - Membrane contactor  
**MD** - Membrane distillation  
**MF** - Microfiltration  
**MR** - Membrane reactor  
**MW** - Molecular weight  
**MWCO** - Molecular weight cut-off  
**NaCl** - Sodium chloride  
**NaClO** - Sodium hypochlorite  
**NaOH** - Sodium hydroxide  
**NF** - Nanofiltration  
**NMP** - N-methyl-2-pyrrolidone  
**NTU** - Nephelometer turbidity unit  
**PA** - Polyamide  
**PEG** - Polyethylene glycol  
**PES** - Polysulfone  
**PSf** - Polysulfone  
**PP** - Polypropylene  
**PTFE** - Polytetrafluoroethylene  
**PVA** - Polyvinyl alcohol  
**PVDF** - Polyvinylidene fluoride  
**PVP** - Polyvinylpyrrolidone  
**RO** - Reverse osmosis  
**SEM** - Scanning electron microscopy  
**SGMD** - Sweeping gas membrane distillation  
**SS** - Suspended solid  
**TOC** - Total organic carbon  
**TGA** - Thermogravimetric analyzer  
**UF** - Ultrafiltration  
**VLE** - Vapor-liquid equilibrium  
**VMD** - Vacuum membrane distillation  
**XRD** - X-ray diffraction
# LIST OF SYMBOLS

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<tr>
<td>$A$</td>
<td>Effective membrane area ($m^2$)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Average specific heat of water (J/kg.K)</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Permeate concentration (mg/L)</td>
</tr>
<tr>
<td>$C_f$</td>
<td>Feed concentration (mg/L)</td>
</tr>
<tr>
<td>$d$</td>
<td>Spacing between layers in the clay structure (Å)</td>
</tr>
<tr>
<td>$d_o$</td>
<td>Outer diameter of hollow fiber (m)</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Pore size diameter (μm)</td>
</tr>
<tr>
<td>$D_{AB}$</td>
<td>Diffusion coefficient ($m^2/s$)</td>
</tr>
<tr>
<td>$E$</td>
<td>Young’s modulus (MPa)</td>
</tr>
<tr>
<td>$h_m$</td>
<td>Heat transfer coefficient of membrane (W/m$^2$.K)</td>
</tr>
<tr>
<td>$J_g$</td>
<td>Gas permeance (mol/m$^2$.s.Pa)</td>
</tr>
<tr>
<td>$J_v$</td>
<td>Permeate flux (kg/m$^2$.h)</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann coefficient (J/K)</td>
</tr>
<tr>
<td>$L$</td>
<td>Effective fiber length (m)</td>
</tr>
<tr>
<td>$L_p$</td>
<td>Effective pore length (m$^{-1}$)</td>
</tr>
<tr>
<td>$n$</td>
<td>Integer (dimensionless)</td>
</tr>
<tr>
<td>$M_B$</td>
<td>Molecular weight of solvent B (g/mol)</td>
</tr>
<tr>
<td>$P$</td>
<td>External pressure (Pa)</td>
</tr>
<tr>
<td>$\bar{P}$</td>
<td>Mean pressure (Pa)</td>
</tr>
<tr>
<td>$r_p$</td>
<td>Pore radius (μm)</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant (J/mol.K)</td>
</tr>
<tr>
<td>$R$</td>
<td>Rejection (%)</td>
</tr>
<tr>
<td>$R_a$</td>
<td>Surface roughness (nm)</td>
</tr>
<tr>
<td>$t_{fm}$</td>
<td>Membrane surface temperature for shell-side (K)</td>
</tr>
<tr>
<td>$t_{pm}$</td>
<td>Membrane surface temperature for lumen-side (K)</td>
</tr>
<tr>
<td>$t_{f,0}$</td>
<td>Feed inlet temperature (°C)</td>
</tr>
</tbody>
</table>
\( t_{p,0} \) - Permeate inlet temperature (°C)
\( t_{p,1} \) - Permeate outlet temperature (°C)
\( T \) - Gas temperature (K)
\( T_f \) - Feed temperature (°C)
\( T_g \) - Glass transition temperature (°C)
\( V_A \) - Solute molar volume (m\(^3\)/kg.mol)
\( \varepsilon \) - Void fraction or surface porosity (%)
\( \mu \) - Gas viscosity (kg/m.s)
\( \mu_B \) - Viscosity of solvent B (Pa.s)
\( \sigma \) - Tensile strength (MPa)
\( \theta \) - Angle of XRD (°)
\( \Phi \) - Association parameter of the solvent (dimensionless)
\( \phi \) - Contact angle of liquid (°)
\( \lambda \) - Wavelength of X-ray (nm)
\( \gamma \) - Surface tension of liquid (dyn/cm)
\( \rho_m \) - Membrane density (g/cm\(^3\))
\( \rho_p \) - Polymer density (g/cm\(^3\))
\( \rho_{wat} \) - Water density (g/cm\(^3\))
\( \Delta W \) - Weight of permeate (kg)
\( \Delta t \) - Predetermined time (h)
\( \Delta H_v \) - Latent heat of vaporization (J/kg)
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CHAPTER 1

INTRODUCTION

1.1 Research Background

Over the last decades, membrane processes for water and wastewater treatment are gaining a larger acceptance in the industry, mainly due to its flexibility and cost-competitive in comparison to conventional separation processes (i.e. chemical and biological treatment processes). Since the early 1960s, the membrane separation system has become an alternative way to replace conventional separation process in a wide range of applications such as drinking water production and municipal/industrial wastewater treatment technologies (Baker, 2004). In particular to industrial wastewater treatment, pressure-driven membrane processes have gained more interest in industrial sectors as the technologies are more reliable and sustainable (Gryta et al., 2006). The pressure-driven membrane processes mainly consist of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO).

Advances in pressure-driven membrane technology in recent years have offered many advantages in separating almost all the substances regardless of organic or inorganic compounds (Ramesh Kumar et al., 2013; De Jager et al., 2014; Ong et al., 2014). Compared to the biological treatment plants, membrane separation units can be installed in relatively small-scale facilities and thus lower footprint. Besides, the process is also more environmentally friendly compared with the chemical treatment plants which usually require large amounts of chemicals to treat the wastewater. However, substantial increase in energy consumption resulted from
higher osmotic pressure is the major drawback of the pressure driven membrane processes such as RO and NF (Suksaroj et al., 2005). To deal with that problem, researchers have paid attention into the second generation of membrane processes such as membrane distillation (MD), membrane contactor (MC), membrane reactor (MR) and forward-osmosis (FO) for the industrial applications.

Of these new membrane technologies, MD gains the most remarkable attention, mainly because it is very suitable for feed solution containing water as the major component (Khayet, 2008). MD is seen as a potential candidate in treating industrial effluents as this membrane process has unique advantages over other membrane processes. Unlike NF and RO membrane processes which strongly rely on external osmotic pressure to operate, the existence of vapor pressure difference between the hot solution (wastewater) and cold water across the membrane could act as driving force which potentially minimizes fouling tendency in the long run (Qu et al., 2009). Furthermore, MD in principle has the ability to completely eliminate ions, macromolecules, colloids, cells, and other non-volatile organic compounds from the wastewater (El-Bourawi et al., 2006). Because of this, MD can reduce the process materials requirement and further minimize waste disposal costs by reusing the clean water produced from the membrane process.

1.2 Problem Statements

Current concerns about environmental issues and water shortage have driven scientists and researchers to find effective ways to reduce the amount of contaminants released to the river as well as potential treatment process to reuse process water in industry. The reuse of industrial wastewater is practically applied in developed countries such as United States, Australia, South Africa and Japan as most of the industrial projects having an agricultural vocation, being intended for irrigation (Amar et al., 2009). Statistics revealed that textile factories consume average 0.06–0.40 m$^3$ of fresh water for each 1 kg of finished product and the effluents discharged (Yusuff and Sonibare, 2005; Amar et al., 2009). Furthermore,
textile industries are considered as one of the largest generators of toxic chemical wastewater in the world as they contain more than 2000 types of chemicals and over 7000 types of dyes (Halimoon and Yin, 2010).

Various techniques are used for the conventional treatment of textile wastewater such as coagulation flocculation, biotechnology, electrochemical oxidation and adsorption (Lau and Ismail, 2009; Amar et al., 2009; Amini et al., 2011). Treatment of textile wastewater with biotechnology is most preferred over other technologies because this process is more environmentally friendly and cost-effective (Ahmed et al., 2007; Chen et al., 2007). However, most of the conventional treatment processes are associated with significant drawbacks, i.e. relatively low rejection of salt and insufficient to remove completely color from the textile effluents. Since 1990s, vast research of pressure-driven membrane processes (i.e. UF, MF, NF and RO) in textile wastewater treatment were widely reported in the literature (Marcucci et al., 2001; Fersi et al., 2009; Lau and Ismail, 2009; Amini et al., 2011). It is shown that membrane separation technologies are an attractive alternative to the conventional treatment processes due to their potential to either produce purified water or allow reuse of the auxiliary chemicals used for dyeing process. However, the major problem in these pressure-driven membrane processes is the rapid decline of the permeation flux that arises from membrane fouling during operation (Fersi et al., 2009; Amini et al., 2011).

To tackle this problem, the use of MD in textile wastewater treatment could be the most ideal candidate owing to its low fouling tendency which resulted from relatively low operating pressure (average 1 bar). MD is a promising candidate for textile wastewater treatment as the textile industry originally discharges hot effluent (80–90°C) that can be used directly in the MD process (Criscuoli et al., 2008). By exploiting the hot textile effluent, no/minimum energy is required to maintain the feed (effluent) temperature. A literature search revealed that only commercial membranes made of polypropylene (PP) and polytetrafluoroethylene (PTFE) were used in MD studies of dyeing solution treatment process (Calabro et al., 1991; Banat et al., 2005; Criscuoli et al., 2008; Mozia et al., 2009; Qu et al., 2014). However, the problems associated with these commercial membranes are their high price and
availability. Khayet and Matsuura (2011) stated that some of the commercial membranes were initially developed for MF application and the manufactured data (i.e. rejection and hydraulic permeability) are not relevant to MD application. In view of this, the production of in-house made MD membrane for textile wastewater application is needed.

Currently, special attention is paid to polyvinylidene fluoride (PVDF) development in membrane preparations of MD application. Unlike PP and PTFE, PVDF can be easily dissolved in common organic solvents which make it easier for membrane making process. Besides, PVDF membrane is much cheaper compared to PTFE membrane which makes it more cost-effective (Alklaibi and Lior, 2005). Although PVDF is one of the most commonly used polymers in MD due to its unique advantages such as low melting point, high chemical resistance, good thermal stability, low surface energy, etc. (Bonyadi and Chung, 2007; Kuo et al., 2008; Edwie et al., 2012; Goh et al., 2013), some modification is still needed to improve its structural properties to enhance the MD performance. As reported by Adnan et al. (2012), the key factor in selecting the best MD membrane is not based on the membrane pore size and membrane thickness, instead it is based on membrane porosity.

Conventionally, porous PVDF membranes are produced in various methods, such as polymer nanofibers, thermally induced phase separation and non-solvent induced phase separation (Feng et al., 2008; Kuo et al., 2008; Hou et al., 2009; Prince et al., 2012; Song et al., 2012; Lalia et al., 2013). Of these, many researchers preferred to prepare porous PVDF membrane using a simple blending process by including either organic or inorganic additives (Wang et al., 2008; Wang et al., 2009; Edwie et al., 2012; Tang et al., 2012). As simple blending method is the common technique employed by many researchers to improve MD performances, the effects of ethylene glycol (EG) and polyvinylpyrrolidone (PVP), mainly for membrane porosity enhancement have been explored in this work.

Over the past several years, EG is reported as the preferable additive for MD membrane preparation due to its ability to induce pore formation and produce a thin
skin layer during phase inversion process (Wang et al., 2008; Bonyadi and Chung, 2009; Teoh and Chung, 2009; Wang et al., 2009; Edwie et al., 2012). Compatibility of EG in the dope solution is not a main concern as EG is highly miscible with dope solution containing both NMP (solvent) and water (non-solvent) (Wang et al., 2009). It has been previously reported that PVDF membrane blended with EG exhibited much better performances than that of neat PVDF membrane in the desalination process, mainly due to its highly porous structure (Wang et al., 2008). On one hand, PVP is scarcely reported in MD process but this type of additive is widely used in other membrane applications to improve the pore size, pore size distribution, degree of hydrophilicity as well as increase water permeability (Yoo et al., 2004; Basri et al., 2011; Xu et al., 2012). Apart of issue in MD process regarding the hydrophilic properties of this additive, relatively few researchers have reported their studies on the utilization of PVP additives in MD membranes (Simone et al., 2010; Drioli et al., 2013; Figoli et al., 2014). Both studies proved that the incorporation of PVP into membrane matrix has improved the membrane porosity and enhanced permeate flux.

Although the highly porous membrane is desirable in MD process, there are also some limitations of the PVDF membrane blended with additives. Usually, the additives affect the membrane hydrophobicity and mechanical strength (Yoo et al., 2004; Simone et al., 2010). In view of this, composite membrane was developed in this study to overcome the limitations. Among various polymers and inorganic composites, PVDF membranes incorporated with clays have attracted considerable attention because clays are highly compatible with polymer and relatively abundant. In MD, various types of Cloisite groups were used as inorganic filler for their inhouse made membranes especially for desalination process. Bonyadi and Chung (2007) utilized both Cloisite Na⁺ and Cloisite 15A to their inner and outer dope solutions to induce different surface tension properties between the two layers of the dual layer hydrophilic-hydrophobic hollow fiber membrane. Meanwhile, Wang et al. (2009) incorporated Cloisite 20A clay particles to their dope solution to reinforce fiber mechanical strength and control the coefficients of thermal expansion and heat insulation by forming a kind of mixed matrix membrane embedded with a dispersed inorganic phase. The Cloisite 20A also showed a good potential in preventing pore wetting problem during MD process (Prince et al., 2012).
In this work, Cloisite 15A was chosen as this type of clay exhibits the highest hydrophobicity compared with other organically modified clays (Jaafar et al., 2009; Daraei et al., 2013). Previous works have shown the importance of Cloisite 15A in improving the properties of PVDF composite which include enhanced melting and crystallization temperatures, membrane toughness and hydrophobicity (Yu et al., 2008; Patro et al., 2008; Hwang et al., 2011). The enhancement in properties can be attributed to the interaction between the cation di-tallow and the PVDF crystalline structure. Hence, this is also the aims of this work to study the effect of the clay loading on the structural properties of PVDF membrane and how the changes in membrane properties (upon clay incorporation) would alter the membrane performances during DCMD process of dyeing solution.

1.3 Objectives of the Study

Based on the research background and the problem statement as written earlier, the main objectives of this study are:

i. To study the effect of polymer weight concentrations and different types of additives on the performances of the PVDF-based hollow fiber membranes for MD application.

ii. To select the best composition of the PVDF Cloisite 15A hollow fiber composite membranes in terms of structural properties and performances.

iii. To evaluate the performances of the selected PVDF Cloisite 15A hollow fiber composite membrane for treatment of synthetic dyeing solutions and industrial textile wastewater using direct contact membrane distillation (DCMD) system.
1.4 Scopes of the Study

In order to achieve the above mentioned objectives, the following scopes of works have been performed;

i. Designing and constructing laboratory-scale DCMD system which the installation consisted of two thermostatic cycles (hot feed and cold permeate) that were connected to a stainless steel membrane module.

ii. Fabricating neat PVDF hollow fiber membrane at three different polymer concentrations and preparing modified PVDF hollow fiber membrane blended with different types of additives using dry-jet wet phase inversion method with fixed spinning conditions.

iii. Identifying the ideal control PVDF-based dope solution by selecting the best polymer concentrations, either 12, 15 or 18 wt% and the best type of pore former additive, either ethylene glycol (EG) or polyvinylpyrrolidone (PVP) for DCMD application with respect to permeate flux and dye rejection.

iv. Preparing the PVDF Cloisite 15A hollow fiber composite membranes by varying the clay concentration in the control PVDF-based dope solution at three different concentrations (3, 5 and 10 wt% per total polymer).

v. Characterizing membrane morphology and Cloisite 15A dispersion in the PVDF Cloisite 15A hollow fiber composite membranes using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and energy dispersive X-ray (EDX).

vi. Determining physicochemical properties of the PVDF Cloisite 15A hollow fiber composite membranes in terms of membrane porosity, mean pore size, liquid entry pressure (LEP), contact angle (CA), surface roughness (Ra),
tensile strength, elongation, Young’s modulus, glass transition temperature (T_g) and thermal decomposition behaviors.

vii. Identifying the optimum clay loadings for the PVDF Cloisite 15A hollow fiber composite membranes based on DCMD performances.

viii. Evaluating the selected PVDF Cloisite 15A hollow fiber composite membrane in treating synthetic dyeing solutions under various operating conditions.

ix. Investigating the feasibility of the selected PVDF Cloisite 15A hollow fiber composite membrane for industrial application using the real textile wastewater.

1.5 Rational and Significance of the Study

MD is relatively new in industrial application and has not been extensively studied like other membrane processes. Therefore, this study is an attempt to establish a framework for better understanding the MD process and to provide the starting point for membrane researchers to develop this thermally driven separation process for industrial purpose. Three strategies towards implementation of MD in industrial scale should be optimized in order to fulfill the high performance criteria. These strategies include membrane characteristics, process conditions and module design. This research covers the membrane characteristics and process conditions in terms of fabricating improved membrane materials with desirable structural properties as well as high mechanical and thermal stability for the textile wastewater treatment process.

Composite membrane consisted of inorganic clay and organic polymer was prepared and characterized to meet the MD requirements. The attempt is made to
investigate the potential of the composite membrane in treating industrial textile wastewater. Although PVDF is not a common polymeric membrane used for this application, the significance impacts from that type of material have proved its effectiveness towards wastewater treatment applications. The addition of Cloisite 15A as the inorganic clay into membrane does not increase cost of production owing to the low material cost of Cloisite 15A. From the experiment works, it is proved that the composite membrane is effective in producing clean water (potentially suitable for reuse) and further reducing environmental impacts. It is expected that this study may provide a better understanding for the academicians and industrial scientists, particularly in environmental areas to recognize MD as a new technology in textile wastewater treatment process.

1.6 Organization of the Thesis

This thesis consists of five chapters. Chapter 1 outlines brief information on membrane separation processes in water and wastewater application including MD process. Then, the details of the problem statements, objectives and scopes of this study have also been stated in detail. In Chapter 2, general literature review about the main topics of this thesis is discussed. This chapter covers background information about the current textile wastewater treatment technologies, chronological development and fundamental of MD process and overview of composite membranes used for MD application. Chapter 3 focuses on the experimental works such as materials, characterization methods and DCMD experimental setup that were performed in this study.

Chapter 4 describes in detail the characterizations and performance evaluations of neat PVDF membrane made of different polymer weight concentrations, modified PVDF membrane blended with different types of additives and PVDF Cloisite 15A composite membrane made of different Cloisite 15A clay concentrations. This chapter also evaluates the membrane performances from the best composition of PVDF Cloisite 15A hollow fiber composite membranes in
treating effluents containing dyes and salts under different feed properties and operating conditions. After that, the selected composite membrane was further studied using real textile wastewater to study the potential of the fabricated composite membrane for industrial application. Finally, the general conclusions and some recommendations are given in Chapter 5, outlining the directions for further research and optimization.
REFERENCES


