SYNTHESIS OF CARBON NANOTUBE REINFORCED PES/PSF BLEND MEMBRANES FOR TREATMENT OF PHENOL-CONTAINING PRODUCED WATER

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A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Master of Science in Engineering.

June 2020

DECLARATION

I declare that this research report is my own unaided work under the supervision of Prof M.O Daramola and Dr. O.A Aberefa. It is being submitted for the degree of Master of Science at the University of the Witwatersrand. It has not been submitted before for any degree or examination to any other University.

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Mabusha Sharon Rameetse

.23. Day of ……June…… 2020

ABSTRACT

The existence of the petroleum industry is vital to many industries and accounts for a large percentage of the world's energy supply. However, it also poses a serious threat due to the amount of wastewater produced daily, which needs to be treated to meet the EPA regulatory standards before disposal to the environment. In this study, blended Polysulfone (PSF) and Polyethersulfone (PES) polymeric membranes were synthesized for the treatment of phenol-containing wastewater. The main aim was to enhance the quality and separation performance of the membranes by improving its mechanical strength, morphology, and hydrophilicity. This is because polymeric membranes are commonly brittle and foul easily due to their hydrophobic nature, and this limits their commercial application. Polymer blending is one of the modifying techniques currently being explored to develop materials with unique anticipated properties depending on the type of membrane needed.

The blended membranes were synthesized at different PSF: PES ratio (100%:0%, 0%:100%, 50%:50%, 80%:20%, 20%:80% and 25%:75%) via the phase inversion method using N-Methyl-2-pyrrolidone (NMP) as the solvent. The thermal property, surface roughness, and mechanical strength of the membranes were checked using Thermogravimetric analysis (TGA), Atomic force microscopy (AFM), and nano-tensile measurement, respectively. The performance of the membrane was tested through pure water permeation and separation of phenol and benzene from synthetic wastewater containing 20 ppm of phenol and 20 ppm of benzene using a dead-end filtration cell at a feed pressure of 100 kPa.

AFM images show lower roughness in the pure PSF membrane as compared to the blended membranes. The tensile strength only improved on the 25%:75% membrane while the elasticity increased with an increase in PES concentration in the blended membranes. The flux, % rejection, and porosity as the performance criteria of membranes showed an improvement in the majority of the blended membranes than in pure PES and PSF membranes. The PSF/PES blend of 25:75 wt% produced highly desirable results based on its performance and quality. These results demonstrate the significance of blending polymeric membranes to modify their specific properties for the desired function and highlight the possibility of more commercial applications.

Furthermore, the best-performing blended membrane obtained from the previous experiment was then embedded with pure CNTs (pCNTs) to investigate if CNTs will further enhance the quality and separation performance of the membrane due to the unique physicochemical and antifouling properties of pCNTs. The pCNTs were also functionalized using acid treatment to enhance their hydrophilicity, mechanical strength and dispersion capability, and then dispersed into the best-performed blended membrane. The best-performing blended membrane was loaded at different concentrations of pCNT, e.g. 0.5% pCNT, 1% pCNT, 1.5% pCNT and one with 1% functionalized CNTs (fCNTs). The same characterization methods used to evaluate the blended membranes were applied. The performance of these membranes was also tested through pure water permeation and separation of phenol and benzene from synthetic wastewater containing 20 ppm of phenol and 20 ppm of benzene using a dead-end filtration cell at a feed pressure of 100-300 kPa.The results show that embedding CNTs in the blended polymer (PSF/PES) increased both the porosity and water absorption capacity of the membranes, thereby resulting in enhanced water flux up to 309 L/m^2h for the 1.5 wt.% pure CNTs loaded membrane and 326 L/m^2h for 1 wt.% functionalized CNT-

loaded membrane. Infusing the PSF/PES membrane with CNTs enhanced the thermal stability, and mechanical strength as well. Results from AFM indicate enhanced hydrophilicity of the membranes, translating in the enhancement of the anti-fouling property of the membranes. The % rejection of benzene and phenol in membranes with CNTs decreased with an increase in pCNTs concentration and pressure, while it increased in membranes embedded with fCNTs. The % rejection of benzene in pCNTs membrane decreased with 13.5% and 7.55% in fCNT membrane while phenol decreased with 55.6% in pCNT membrane and 42.9% in the FCNT membrane. This can be attributed to poor CNT dispersion resulting in increased pore size observed when CNT concentration increased. Optimization of membrane synthesis might be required to enhance the separation performance of the membranes.

DEDICATION

To my dad, M.K Rameetse,

To my mom, M.M Rameetse,

To my siblings, Tshepo, Sammy and Karabo,

To Flora,

To Kholofelo

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PUBLICATIONS AND CONFERENCE PRESENTATIONS FROM THE STUDY

1. Rameetse, M.S., Aberefa, O., **Daramola, M.O.** (2020) Effect of loading and functionalization of CNT on the performance of blended PSF/PES membrane during treatment of wastewater containing phenol and benzene, Membranes, 10(3): 54, https://doi.org/10.3390/membranes10030054
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3. **Rameetse, M.S.,** Aberefa, A.O, and Daramola, M.O. (2019) Synthesis and characterization of PSF/PES composite membranes for use in oily wastewater treatment, 10th Cross-faculty postgraduate symposium, University of the Witwatersrand, South Africa (poster presentation).
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Nomenclature

PSF	Polysulfone
PES	Polyethersulfone
CNTs	Carbon Nanotubes
SWCNT	Single-Walled Carbon Nanotube
DWCNT	Double-Walled Carbon Nanotube
MWCNT	Multi-walled Carbon Nanotube
p-CNTs	Pure Carbon Nanotubes
f-CNTs	Functionalized Carbon Nanotubes
VA-CNTs	Vertically Aligned Carbon Nanotubes
AC	Activated Carbon
GAC	Granular Activated Carbon
MOF	Metal-Organic Frameworks
NP	Nanoparticles
UF	Ultrafiltration
MF	Microfiltration
NF	Nanofiltration
RO	Reverse Osmosis

BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
UV	Ultraviolet
EPA	Environmental Protection Agency
NMP	N-Methyl-2-pyrrolidone
PVA	Polyvinyl Alcohol
PEG	Polyethylene Glycol
EWC	Equilibrium Water Content
PWF	Pure Water Flux
TGA	Thermogravimetric Analysis
AFM	Atomic Force Microscope
SEM	Scanning Electron Microscope
W_d	Weight of dry membrane
w_w	Weight of wet membrane
C_f	Concentration of feed
C_P	Concentration of permeate
TMP	Transmembrane Pressure

CHAPTER 1

1. Introduction

1.1 Background and Motivation

According to the US Department of energy, produced water is defined as water formed in reservoirs extracted below the ground with oil and gas (Clark and Veil, 2009). It is naturally made up of formation water as well as water that has been injected into the reservoir and any substances that are added during the oil and gas production. The physical and chemical properties of produced water differ dramatically according to the geographic location of the field because different geologic formations produce different chemical components (Veil, 2004). Produced water is reported to be the largest waste byproduct during oil and gas exploration and production (Phasha, 2017). Oil and gas operations are reported to yield about 15 - 21 billion barrels of this water annually (Clark and Veil et al., 2009). Figure 1.1 shows the five-year changes in fluid production reports conducted in the United States between 2007 and 2012 where oil and gas production showed an increase of 29% and 22%, respectively. Water being the largest by-product showed a slight increase of just over 1% and still remains the highest by-product, hence the petroleum industry is starting to consider it as a possible profit stream.

Produced water constitutes different compounds such as hydrocarbons, phenols, salts, dissolved minerals, and metals, which are considered as toxic water pollutants. Produced water can either be reused or disposed of; however, it must be treated before disposal in order to meet regulatory limits (Neff et al., 2011). If the water is discharged untreated, it may damage the surrounding

environment (Guerra et al,2011). Since the volume of produced water in oil wells increases with time, the cost of managing it also follows suit. It is reported that once the management costs of produced water exceed that of the hydrocarbon produced, the well is usually shut down (Clark and Veil, 2009). With suitable treatment and application to advantageous beneficial use, produced water can assist as a new water source (Guerra et al, 2011). Benefits of treated produced water include crop irrigation, drinking water for livestock, streamflow, and wetland augmentation, and for instrument cooling purposes in industries (Hagström et al., 2016).

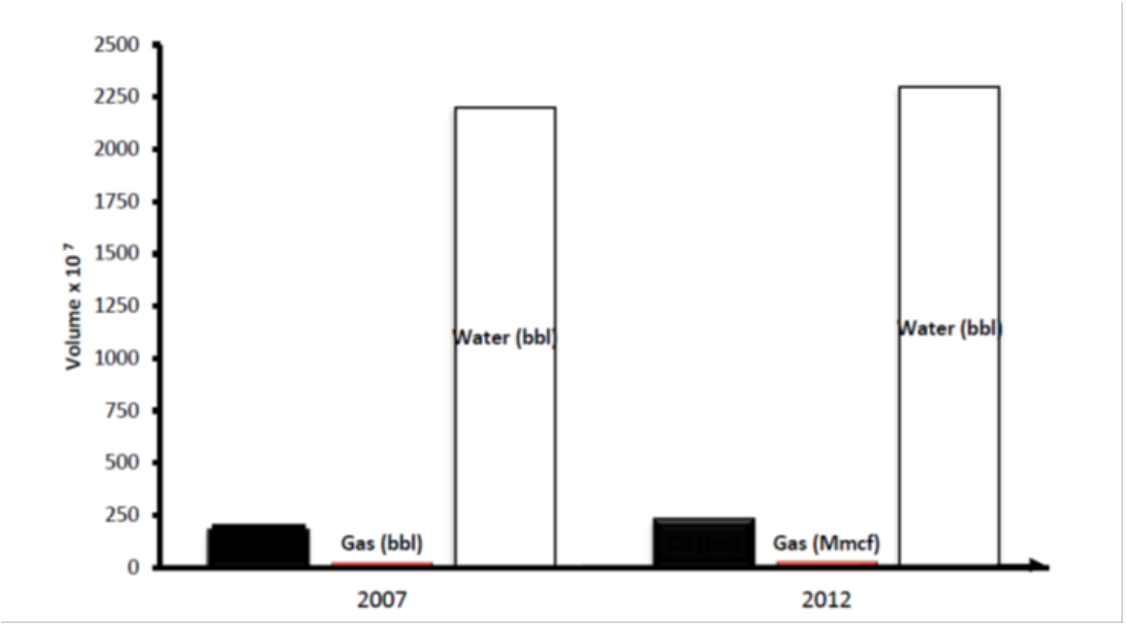


Figure 1.1. Five-year change in fluid production in the US (Veil, 2004)

Various technologies have been developed in the previous years to treat produced water, but membrane technology has shown greater separation efficiency as compared to other technologies (Das et al., 2014). Membrane technology also has comparative advantages over other technologies, such as compactness and lightweight, easier expansion to increase capacity due to modular system,

low maintenance, low energy requirements as it does not require phase transition for separation to occurs, low cost, and environmentally friendly (Ismail et al., 2017). Under membrane filtration technologies, there is ultrafiltration (UF), microfiltration (MF), reverse osmosis (RO) and nanofiltration (NF) which have been successfully used to separate water from oil (Maphutha et al, 2013). Reverse osmosis, ultrafiltration, nanofiltration, and microfiltration are pressure-driven methods (Das et al, 2014). Among the above-mentioned membrane filtration methods, the major challenges faced are fouling and concentration polarization, which influences the membrane operational performance to separate oil from water and stability. These challenges culminate in regular need to replace equipment. This motivated various researches to develop more effective and simple methods to improve membrane hydrophilicity.

Recently, the application of carbon nanotube (CNT) filled membranes as oil-containing water separation materials have attracted wide-ranging attention due to their properties which include low density, high porosity, electrical and thermal conductivity (Xia et al., 201; Daramola et al., 2017). Other properties include tensile strength, higher elastic modulus, and strain to fracture, the capability to endure twisting together with cross-sectional distortions, and high compression without breakage (Du et al, 2007). These properties stabilize and strengthen membranes; they also enhance their separation performance. However, to increase the hydrophilicity of the membranes, CNTs have to be functionalized to improve the surface property of the membrane. Functionalization also improves the dispersion of CNTs in the polymer matrix during fabrication to obtain composites with intrinsic properties. This step is important because the more hydrophilic

a membrane is, the better its fouling resistance based on the fact that most fouling agents are naturally hydrophobic (Kochkodan et al., 2014).

In this study, the aim was to synthesize blended polysulfone (PSF) and polyethersulfone (PES) composite membrane and embed CNTs within the membrane. Generally, the primary objective of polymer blending is to obtain products with unique improved properties at a lower cost. These properties include increased toughening, improved barrier property, and flame-retardant property (Thomas et al., 2015). PSF is an excellent polymer for membrane fabrication because it is reported to possess properties needed for efficient water treatment. The properties include good solubility, excellent heat stability, high mechanical strength, electrical and chemical stability (Hamzah et al., 2014). PES, on the other hand, shows excellent thermal stability, other properties include oxidative resistance, visual transparency, and good solubility as well (Mendez et al., 2013). Therefore, the blending of these two polymers will improve the modulus, mechanical and thermal stability of the membrane. The optimum composition of these two polymers was evaluated to give better separation efficiency of the membrane. A further modification was made to the membrane by dispersing functionalized CNTs within the polymer to enhance the hydrophilic property of the membrane.

1.2 Problem Statement

Membrane technology, especially the application of polymeric membrane is reported as the most feasible commonly used method for produced water treatment (Ismail et al., 2017). However, the challenge faced with this method is membrane surface fouling resulting in pore plugging and insufficient mechanical strength, hence the limitation in the application of membranes in various

industries to treat wastewater (Sheppard, 2013). To overcome this problem, further modifications have to be made to the membrane surface. This can be achieved by producing highly robust and hydrophilic membranes by polymer blending and embedding CNTs which can improve their separation performance by enhancing the surface property of the membrane. The increased mechanical strength of the membrane can also be obtained by using polymers with high mechanical strength properties.

Therefore, this study sought to answer the following questions:

i. Will the separation performance of the blended PES/PSF membrane be greater than the membranes with each polymer?
ii. Will the functionalization of the CNTs increase the separation performance of the membrane?
iii. How much loading of functionalized CNT in the blended membrane will give the highest separation performance during phenol-containing wastewater?
iv. Will the addition of functionalized CNTs to the blended membrane enhance the performance of the membrane, compared to the addition of pure CNTs?

1.3 Research Objectives

The main aim of this research was to synthesize blended PES/PSF polymer composite membrane and embed them with CNTs at different loading. Then, evaluate the separation performance of these membranes during the treatment of phenol and benzene-containing wastewater. This aim was achieved by satisfying the following objectives:

i. To prepare a PSF, PES, and blended PES/PSF composite characterize and evaluate them for the treatment of phenol and benzene-containing wastewater.

ii. To investigate the effect of CNT loading on the physicochemical properties, thermal stability, mechanical strength, and separation performance of CNT PES/PSF membranes during the treatment of phenol-containing wastewater.

iii. To functionalize CNTs and embed the functionalized CNTs in the best performing blended PES/PSF membrane from (ii), characterize the membranes and evaluate them for the treatment of wastewater containing phenol.

1.4 Dissertation layout

Chapter 1: This chapter addresses the motivation, aims, objectives of this research as well as questions expected to be answered by the end of this research project.

Chapter 2: This chapter focuses on the literature review of this study and gives an overall introduction of CNTs and polymers used to fabricate the UF membranes. It also gives a brief understanding of polymer blending and roots of membrane fouling. The literature also includes the effect of the functionalization of CNTs and other traditional methods used to modify polymeric membranes to enhance membrane performance.

Chapter 3: In this chapter, thin-film composite membranes were prepared by blending PSF with PES. The polymers were blended at different compositions and were characterized and tested for the treatment of phenol and benzene containing wastewater. The best performed blended membrane with desirable physicochemical properties was selected for further modification in chapter 4.

Chapter 4: In this chapter, the best-performed membrane (25PSF:75PES) was embedded with pCNTs and fCNTs at different compositions. The formed membranes were then evaluated for their separation performance and quality to investigate the effect of CNT functionalization.

Chapter 5: This chapter summarizes the findings of this research and recommendations for further developments in this area.

CHAPTER 2

2 Literature Review

2.1 Produced water and its pollutants

Produced water represents the largest volume of waste by-product produced during the extraction of oil and gas. Having a better understanding of its constituents and how much of it is produced is vital when selecting the correct method of treatment. The majority of the constituents are labeled priority pollutants due to the negative impact they have on the environment. Some of the components found in produced water include metals and complex organic chemicals such as; monocyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), phenols, and alkylphenols. Monocyclic aromatic hydrocarbons are 6-carbon ring structures such as benzene, toluene, ethylbenzene, and xylene (BTEX). BTEX are carcinogenic priority pollutants and have been reported to be more abundant in the environment than PAHs (Fayemiwo et al., 2017). BTEX are highly volatile and water-soluble, and upon exposure, they can result in acute toxicity and health hazard to humans. PAHs are known as organic pollutants with 2 to 7-carbon rings, often causing environmental degradation. Compounds in this group include; naphthalene, fluorene, pyrene, and phenanthrene (Zheng and Richardson, 1999; Neff et al., 2011). The concentration of PAHs usually ranges from 0.04-3 mg/L in produced water. Phenols are water-soluble compounds with very high reactivity tendencies. Their peak concentration in produced water is usually 20 mg/L. They are classified into different phenol groups based on the number of carbon chains present (De Silva et al., 2017; Neff et al., 2011).

The toxicity of these compounds motivated the development of various wastewater treatment methods to achieve the accepted discharge limit concentrations. This study was limited to the removal of phenol and benzene due to their toxicity and abundance in produced water.

2.1.1 Phenol

Recently there has been a rising concern among environmental scientists regarding the negative impact of the environment and human exposure to chemical compounds such as Phenol. Phenol is a colorless compound with stronger hydrogen bonds, thus making it more soluble in water than in alcohol. It is also reported to be more acidic than other alcohols due to the stable phenoxide ions that form in aqueous solution (Derosa, 2006). It is an organic water pollutant found in produced water from oil and gas industries (De Silva et al., 2017). Phenolic compounds in produced water come from biodegradation of oil underground and are transported over to the surface by formation water, which is a naturally occurring phenomenon (Neff et al., 2011). Its concentration in produced water is usually between 0.4-23 mg/L and is reported to be lethal even at lower concentrations. When discharged into the environment, specifically in the air and soil, it tends to degrade rapidly, while it persists for longer periods in water, affecting animals and people who might consume it. However, this compound may remain for longer periods in all these mentioned mediums if continuously discharged. This semi-volatile compound poses a serious threat to human health in cases of long-term exposure resulting in severe effects such as damaged red blood cells, kidney, and liver. and the ecosystem if exposed to the environment (Raza et al., 2019). This compound also has a negative impact on aquatic organisms when discharged to the oceans without proper treatment; it suppresses the growth of the aquatic biological system (Raza et al., 2019). According to the United States-Environmental Protection Agency (EPA), it's level of toxicity depends on the

type of phenol and its concentration. When highly concentrated it is classified as a priority pollutant. The EPA has set a maximum limit of phenol for disposable wastewater at 0.1 mg/L. For this reason, many traditional treatment methods such as chemical/ biological oxidation, steam distillation, and adsorption were used for the removal of water pollutants such as phenol; however, they are unable to remove phenol compounds at concentrations higher than 20mg/L, consumes a lot of energy, produces secondary pollutants in the process and are environmentally unfriendly (Villegas et al., 2016). These drawbacks motivated the specific emphasis on research to develop more innovative technologies to remove this compound in effluent water produced in these industries to meet the stringent standards laid by the EPA. When present in water, phenol tends to interact with other organic compounds to form chlorophenols which are also as toxic (Kulkarni and Kaware, 2013).

Phenol is a versatile organic compound commonly used in lower concentrations in households and in slightly higher concentrations in industries as an intermediate for the production of commercial products. Some of its uses include;

- Surgical antiseptic for sterilization,
- Disinfectant in detergents,
- Plastic manufacturing,
- Phenolic resins for electrical switches,
- Cosmetic formulations,
- Manufacturing of explosives,
- Pharmaceutical drugs formulation,

- Extraction of biomolecules.

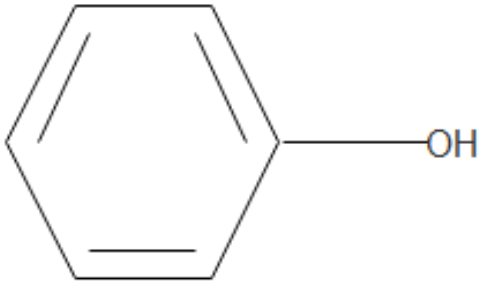


Figure 2.1. The molecular structure of phenol (Wang and Zhang, 2012)

2.1.2 Benzene

One-ring aromatic hydrocarbons are the most abundant compounds found in crude oil as a by-product of extraction processes (Smith, 2010). Benzene concentration in produced water usually ranges from 0.01-50 mg/L, and it is one of the hydrocarbons among the BTEX (Benzene, toluene, ethylbenzene, and xylene) family reported to be highly volatile. It is a colorless, highly flammable molecule with six carbon-rings, with each of these carbons attached with hydrogen and has a boiling point of about 80.1˚C and can remain stable at a high temperature of up to 1000˚C depending on the heating time (Smith, 2010; Moldoveanu, 2019). Benzene occurs as a result of incomplete fossil fuel combustion and is classified as a priority pollutant according to the EPA. Exposure to very high concentrations of benzene can lead to death even if it's for a brief period of about a few minutes. In most cases, this compound is absorbed into the human body through inhalation then travels into nervous and fatty tissues (Kasemy et al., 2019). According to the World Health Organization, the effects of benzene can be both acute and chronic. Acute exposure may

result in migraine, loss of consciousness, dizziness and skin irritation if one is in contact with the pollutant, whereas chronic exposure results in more severe effects such as neurological complications, damaged bone marrow, as well as increased risk of leukemia development. Studies have shown that the risk of leukemia is more susceptible at cumulative exposure of the pollutant when its above 2mg/L, therefore risk increases with an increase in concentration (Smith, 2010). However, the effect is not always immediate and can accumulate over time (Viotti et al., 2019). Therefore, wastewater containing benzene requires proper treatment upon production to protect workers' health.

Many industries rely on benzene to produce some of the commonly used products in our everyday life which includes, glue, plastics, dyes, and pesticides; it has been in use since the 19th century as;

- Solvent for the formulation of products such as paint, glue and nail polish,
- Rubber and metal lubricant,
- Plasticizer,
- Aftershave in the 19th century due to its pleasant smell,
- Laboratory chemical to perform experiments,
- Fuel additives,
- Additive to cleaning detergents,
- Intermediate to produce other related chemicals like cyclohexane and ethylbenzene.

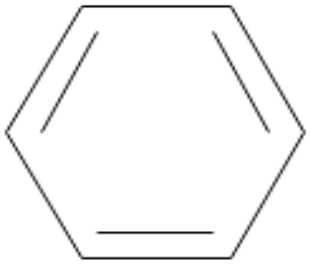


Figure 2.2. Molecular structure of benzene (Tamagawa et al., 1976).

2.2 Treatment of produced water

The treatment of produced water before disposal or recycling is a mandatory requirement as per the regulatory standards set by the EPA. The treatment of this wastewater is required to prevent possible exposure to the environment, humans, and animals. To achieve this, different treatment methods have been studied, developed, and modified. The ideal strategy is to develop an inexpensive method, preferably moveable treatment units that do not take large spaces and most importantly assure the achievement of targeted output criteria in terms of separation performance.

2.2.1 Adsorptive treatment

Adsorption is defined as the adhesion of solutes to a thin film surface that has pollutant-binding capabilities. The intermolecular forces of attraction result in the accumulation of organic solutes found in wastewater when they come in contact with the absorbable surface (Ismadji and Bhatia, 2001). The accumulation of absorbates in this process is what defines the separation performance of this technique. The separation efficiency of this method depends on the surface area of the absorption surface, the larger the surface, the higher the absorption. Another dependent factor is the type of adsorbent used. There two types of adsorbents, synthetic (activated carbon) and natural

(clays and zeolites) adsorbents. Activated carbon (AC) is a commonly used adsorbent due to its large surface area and porosity, making it more effective to remove organic water pollutants (Ismadji and Bhatia, 2001). Activated carbon is produced from agricultural products and the production method is reported to be expensive. This method is commonly used as tertiary wastewater treatment for the removal of bacteria and organic toxins (such as phenol and fluorine) found in water (Heijman and Hopman, 1999). Lopez et al., (2018) used granular activated GAC to treat phenol-containing wastewater, the obtained results showed 93% of phenol absorbate. This method is mainly employed in drinking water purification processes and industrial effluent water treatment. It is reported to be a fast, inexpensive method (Ali and Gupta, 2006). The disadvantage of this method is, it is not effective for the removal of metals, inorganic, and microbial pollutants. This was observed in a study conducted by Fiore and Babineau, (1977), they used activated carbon filter to remove microbial in water and the analysis showed no retention. This method also requires frequent replacement of filters due to the cake formation of absorbates.

2.2.2 Biological treatment

Biological treatment is also known as the activated sludge process and it is widely used in various industries for the removal of organic water pollutants. Its economic advantage in terms of operating costs is the reason behind its wide application in municipalities and industries. Biological treatment can be applied using two different types of processes, which are aerobic and anaerobic treatments. These processes are self-explanatory, the aerobic process takes place in the presence of oxygen while the anaerobic process takes place in the absence of oxygen (Freire et al., 2001). During the aerobic process, wastewater is transferred to a tank pumped up with oxygen which allows microbial growth which will result in the decomposition of the organic pollutants in the

wastewater. Anaerobic treatment is usually applied when treating wastewater with more concentrated contaminants. This treatment is carried out by microorganisms that digest organic waste and convert it to carbon dioxide or methane. The anaerobic treatment has several advantages as compared to the aerobic treatment, such as net energy recovery, reduced production of sludge and its ability to apply higher feed volumes (Sadmalis et al., 2018; Rincon et al., 2003). The limitations of anaerobic filters are mostly associated with the deterioration of the bed structure caused by the accumulation of non-biodegradable solid particles. The accumulation of these solid particles, in turn, affects the flow of the treated solution (Anderson et al., 2003). The degradation of organic pollutants during anaerobic treatment is slower and less efficient than in aerobic treatment. Hence the Aerobic treatment remains the preferred method for most applications (Sadmalis et al., 2018).

2.2.3 Membrane-based treatment

Membranes are permeable substrates able to transport substances through their pores. This method is classified into different paths with different separation mechanisms, which include UF, MF, NF, and RO. During wastewater treatment, water is forced through a selective barrier on the membrane, thereby blocking the diffusion of the targeted solutes (Maphutha et al., 2013; Das et al., 2013). The separation efficiency of membranes depends on its characteristics and operating conditions. They are easy to operate and exhibit high selectivity during separation, they are cost-effective and less energy intensive. Hence the membrane market is expanding rapidly, industries are always looking for ways to cut costs to ensure profitability (Velu et al., 2015; Raza et al., 2019).

Polymers such as polysulfone and polyethersulfone are the most popular membrane material due to their good membrane forming performances. However, the life span of polymeric membranes is usually shortened by their fouling nature (Sheppard, 2013; Alenazi et al., 2017). To solve this problem, more work has been done and still is, to improve the hydrophilicity of polymeric membranes (Shi et al., 2014). Various modification techniques such as adding nanoparticles, grafting, and coating with materials that have hydrophilic properties have been widely used.

2.2.3.1. Polysulfone polymer

The selection of polymer plays a vital role in the performance of the membrane because various factors such as membrane morphology depend on it. Polysulfones are a family of engineering thermoplastics that display excellent properties and are also cost-effective, making it an ideal polymer of use in diverse markets such as membrane manufacturing (Akkapeddi, 2014). This is because it allows easy fabrication of membrane with pores sizes as small as 0.4 nm, thus making them more selective and suitable for application in water treatment/ recovery processes (Ji et al., 2017). Polysulfones are known as good membrane materials due to their excellent chemical and physical stability. Hamzah et al, (2015) reported that polysulfone can remain relatively constant at higher temperatures just over 200˚C. They also show excellent flame retardancy, low creep, and high dimensional stability. This polymer is also known to be highly resistant to mineral acids, alkali, and electrolytes, and are chemically inactive in pH ranging from 0 to 14 (Ji et al., 2019). These are the properties that make polysulfone membranes the preferred choice in separation processes, however, the only drawback reported is fouling which impacts the longevity of the membrane. This happens due to the extreme hydrophobic nature of the polymer. The membranes

are commonly used for a wide variety for various applications such as gas and wastewater separation, desalination, and biological processes (Albu et al., 2011). The porosity of the formed membrane can be controlled and is dependent on the concentration of the polymer in the membrane solution (Hamzah et al., 2014). Despite all these good qualities, the polysulfone membrane tends to foul easily due to its hydrophobic surface nature that attracts fouling agents. For this reason, there has been considerable interest in the blending of this polymer with other materials to modify its surface and make it less hydrophobic (Kim et al., 1992).

2.2.3.2. Polyethersulfone polymer

Polyethersulfone is a transparent commercially available amorphous type of polymer containing both ether and sulfone groups. It has relatively high water absorption Because of its outstanding properties and simple fabrication, this polymer is commonly used for fabrication of membranes such as the ultrafiltration and microfiltration with pore sizes as averaging from 0.05-10 microns for gas separation, water treatment, pretreatment of reverse osmosis and blood purification in medical fields (Alenazi et al., 2017; Yu et al., 2011). However, the pore structure of this polymer always relies on the technique and conditions carried out to prepare the membrane Some of its desired properties include, exceptional thermal stability withstanding high temperatures, mechanically stable in terms of strength especially between -50˚C and 180 ˚C, good electrical characteristic, transparency, hydrolytic strength, excellent chemical resistance to acids and alcohols, making it tolerant to a wide pH range (Giesa and Schmidt, 2001). Other properties include good oxidative stability, simple processing, and environmental endurance (Zhu et al., 2014). Its hydrophobic nature is considered as one main concern with limitations that are similar

to the polysulfone. Frequent cleaning is required to remove the accumulation of foulants on the surface to maintain the integrity of the membrane and it is usually an expensive exercise (Alenazi et al., 2017). It has a harder benzene ring as well as a softer ether bond.

2.3 Benefits of treated produced water

Produced water is a waste byproduct; however, with suitable treatment and application to beneficial use, produced water can aid as a new water source. Multiple technologies are employed to treat this waste product to make it obtainable as a resource for farm-owners and environmental programs in need of a new source of freshwater. The use of produced water can assist lessen the stress on freshwater resources; this will allow groundwater to be utilized for other valuable purposes. Past literature has reported on several potential benefits of treated produced water, which includes, livestock watering, crop irrigation, streamflow and wetland augmentation, and general water-based industrial uses. The treated wastewater also can be stored for future use in aquifers (Guerra et al., 2011; Hagström et al., 2016). Irrigation purposes require large volumes of water, but also have the strictest water quality criteria, especially with produced water containing large amounts of salts which can prevent vegetation growth and also affect the quality of the soil; therefore, thorough treatment is required before use. With livestock, the water requirements are not very strict, it depends on the type of animal and numerous factors such as activity, type of feed intake, and the surrounding temperature. Also, animals can endure lesser quality water than human beings (Guerra et al., 2011). Produced water can also become a substantial alternative resource for many industrial processes if treated to the acceptable quality and can be reused in various petroleum operations. Other uses can include soil or cement dust suppression, firefighting, and cooling equipment in industries (Hagström et al., 2016).

Produced water can also be used as a source for pressure maintenance purposes. These are applied as alternatives to discharging the wastewater into streams as well as on the environment because it contains pollutants such as hydrocarbons, dissolved salts, suspended metals, production chemical additives, and organic acids which are also introduced into the environment (Onojake and Abanum, 2012).

2.4 Membranes for wastewater treatment

2.4.1 Organic membranes

2.4.1.1. Ultrafiltration membrane

Modern ultrafiltration was originally developed as a fractionation technique in the late 1960s. Ultrafiltration is a pressure-driven filtration process similar to microfiltration where the liquid is forced to travel through a semipermeable membrane to remove larger solids particles that a bigger than the pore sizes (Warsinger et al., 2016). Their first major application was for the filtration of electro coat paint. Recently, ultrafiltration membranes are commonly employed for water treatment purposes in industries such as refineries, medicine, and food production, mainly to remove colloidal materials, proteins, and suspended solids. These membranes are categorized as semipermeable membranes because they allow macro-molecules and ions to permeate through while retaining/ rejecting macromolecules (Ji et al., 2017). These are polymer-made membrane filters with pore sizes that range between 0.01-0.1 μm, only capable of rejecting colloidal molecules with diameters greater than 0.1 μm. They are usually made of polymers (such as polysulfone, polyethersulfone, and polystyrene) and inorganic materials in rare cases (Warsinger et al., 2016). The separation mechanism of this type of membrane is size exclusion. Their

separation performance depends on multiple factors which include the physicochemical properties of the membrane, amount of pressure applied, temperature, and feed composition (Ji et al., 2017). These membranes are usually operated at lower pressures between 1-10 bar, still sufficient enough to obtain high flux rates and good rejection. Chakrabarty et al, (2008) treated oily wastewater using an ultrafiltration membrane prepared from polysulfone and modified it with polyethylene and polyvinylpyrrolidone. The obtained rejection rates were desirable (>90%). There are two types of ultrafiltration systems, the point-of-use system, which has the smallest pores, and is employed in common drinking water taps for pre-treated water and the point-of-entry system which is installed at the source to pre-treat raw wastewater.

2.4.1.2. Microfiltration Membrane

During microfiltration (MF), feed solution enters through the membrane at a higher pressure than the permeate. The difference in pressure is what facilitates the permeation of water through the membrane pores while retaining the targeted solutes. This process uses a dead-end mode where the feed solution is passed through the membrane but has no reject recycle stream. The pore size of MF membranes usually varies from 0.1 to 10 μm (Moslehi and Mahdavi, 2019). The separation mechanism of MF is different from that of UF. For UF separation, the targeted solutes in the feed are deposited and absorbed into the surface of the membrane, plugging the pores and reducing the pore size (Nakamura and Matsumoto, 2013). These membranes are usually used for the treatment of potable water, oil-containing wastewater, and pretreatment of RO systems (Zaidi et al., 1992; Nakamura and Matsumoto, 2013). Unlike other organic membranes, MF systems operate under low pressure less than 2 bars (Abdel-Fatah, 2018). The drawback of MF is that it can only separate

suspended solids and bacteria and is sensitive to oxidative chemicals. Like other membrane processes, MF is also prone to severe fouling during potable water processing due to the forming cake by suspended solids on the membrane surface. Effects of polymer blending in membranes (Padaki et al., 2015).

2.4.1.3. Nanofiltration

Nanofiltration is a pressure-driven membrane process used for the separation of organic and inorganic substances from solution. During NF feed solution diffuses through a membrane, under pressure differentials that are usually less than those for reverse osmosis, but still significantly greater than those for MF and UF (Abdel-Fatah, 2018). This process is deemed to be a green, convenient, and effective method due to its small footprint and low costs of maintenance. Typically, nanofiltration membranes have pore sizes ranging from 1-10 nm, they are smaller than pores in UF and MF membranes, but they are larger than those in RO membranes.NF applications are increasing rapidly in water and wastewater treatment, separation of suspended solutes from solution, production of bio-materials, and in the food industry. Although NF membranes are employed for various applications, membrane fouling is a challenging factor that many industries are still trying to overcome. It also uses highly intensive energy because it operates under high pressure ranging from 5-35 bars, which can be costly (Abdel-Fatah, 2018). However, the flexibility of preparation with various materials to choose from is what increases and spreads its application in different processes.

2.4.1.4. Reverse Osmosis

Reverse osmosis (RO) is a water treatment process that uses porous membranes to separate unwanted solutes from water under higher pressure as a driving force. It uses the concept of osmosis phenomenon, where the osmotic pressure distinction between the pure water and saltwater facilitates the separation of solutes from water (Saleem and Zaidi, 2019). RO was initially developed for the desalination of seawater and brackish water for rural areas to have access to drinking water. However, currently, it is employed for various applications and not only does it remove water pollutants of great concern, but it also removes ion particles and dissolved minerals (Greenlee et al., 2009). RO systems are commonly installed in homes for two functions which are; water softening and water purification. They require simple maintenance. Which can be done even when the machine is still operational.

Although there have been significant developments in membrane materials for RO, the application of this treatment is also limited by the occurrence of fouling which leads to deterioration of membrane performance and shortened lifetime (Ahmed et al., 2019; Greenlee et al., 2009). It is also not a cost-effective process because it requires high-pressure levels of up to 150 bars, especially for deionization (Abdel-Fatah, 2018).

2.4.1.5. Blended polymer membranes

The commercial application of polymeric materials as membranes remains technically limited; therefore, there is a serious need for new membrane materials that have fundamentally different properties from polymeric membrane materials (Kim, 2007). Different approaches are employed to modify the performance of the polymeric membrane to endure the required duties. This introduced polymer blending, which is a mixture of two or more polymers. It is a time and cost-

effective technique used to develop materials with unique anticipated properties depending on the type of membrane needed (Mushtaq et al., 2013). The advantages of polymer blending include, increased toughening, extended service temperature range, improved barrier property, and flame-retardant property (Thomas et al., 2015). PES and PSF are reported to be widely used for water treatment purposes due to their good membrane forming performances, outstanding heat stability, visual transparency, and excellent solubility. However, they are both known to be hydrophobic (Mendez et al., 2013). This problem can be solved by both physical and chemical modification (Aberefa, 2015). Another problem usually encountered with polymer blending is the inability of polymers obtain a miscible composition, which is commonly due to very low influence of the mixing entropy, however, this drawback can be overcome by the development of definite interactions, such as electrostatic interactions, hydrogen bonding, ion-dipole, and transfer of charges by introducing specific functional groups to the polymers (Albu et al, 2011).

Another solution to commercial ultrafiltration membranes that are commonly prepared from hydrophobic polymers is by surface modification, improving membrane hydrophilicity by blending with hydrophilic copolymers (Ariono et al, 2017). The concentration of the polymer is known as one of the significant parameters tailoring the membrane properties, thus it is essential to determine the optimum concentration of the polymer for the improvement of membrane performance (Ismail et al, 2017). The concentration influences the characteristics of the membrane such as membrane morphology, thickness, pore size, and viscosity of membrane solution, which has an effect on the membrane performance in terms of permeability and selectivity (Hamzah et al, 2014). Zhang et al. (2013) used polysulfone to develop their membrane and reported that the selectivity if water on these membranes increases with an increase in the number of hydrophilic

groups on the membrane surface, which was prepared by addition of functionalized polystyrene which contains a smaller molecular weight. Maphutha (2013) also used polysulfone for his membrane synthesis and found that the mechanical strength of the polymer support increased with increasing CNT addition to 7.5%.

Types of Polymer Blending

i. Miscible polymer blends have a ΔH less than 0. The blended polymers often result in a single-phase structure at a particular temperature and are usually optically transparent. Miscibility can be influenced by several factors such as morphology, and reduction of surface tension (Thomas et al., 2015).
ii. Immiscible polymer blends find it difficult to form a single phase. They have a coarse morphology, sharp interface, and poor adhesion between the blend phases. Immiscibility may be limited to certain ranges of temperature, pressure, and composition. It depends on the chemical structures, molar-mass distributions, and molecular architectures of the components (work et al., 2004). These types of polymer blends are useless without compatibilization.
iii. Partially miscible polymer blends have two phases, which exhibits properties amid immiscible and miscible polymer blends. These polymer blends appear homogeneous and are compatible (Khan et al., 2018).

2.4.2 Inorganic membranes

Inorganic membrane materials include ceramic, nanoporous carbon, zeolites, and palladium alloys. These membranes are chemically resistant to organic solvents, and this makes it easier to clean the membrane regularly with solvents without damaging. They are mechanically robust, thermally

stable, and have good permeability, selectivity, and anti-fouling properties. However, their stiffness and high cost are their main drawbacks limiting their application in most industries.

2.4.2.1. Ceramic membranes

Ceramic membrane processes are a rapidly emerging technology for water treatment. Ceramic membranes are porous filters with an asymmetric structure, made out of a ceramic material such as alumina, zirconia, titania, and silica (He et al., 2019). The choice of materials used for the fabrication of these membranes plays a critical role in determining membrane function and performance. The use of ceramic membranes ensures maximum mechanical and chemical stability (Nandi et al., 2009). These properties allow ceramic membranes to operate under high pressure without damaging and to offer long term effective performance, thereby, giving them more advantages over traditional organic membranes. These membranes have also shown high thermal stability, excellent resistance to acidic chemicals. They are mostly applied in MF and UF, on some occasions in NF and RO for wastewater treatment and gas separation (He et al., 2019; Sondhi et al., 2003). The challenge faced with these membranes is they require very high initial investment cost, in terms of membrane production and operation (Park et al., 2015; Ihsanullah, 2019).

2.4.2.2. Carbon-based membranes

Carbon-based membranes were introduced due to limitations that polymeric membranes have, such as membrane fouling and low mechanical strength. Incorporation of CNTs ensures enhanced surface hydrophilicity, antifouling properties, fast water flux, thermal and mechanical stability (Berber et al., 2000; Das et al., 2014). Carbon-based membranes are made from carbon nanomaterials like graphene or nanotubes. To fabricate carbon-based membranes, CNTs are mixed

with a polymer matrix, using various methods such as phase-inversion, interfacial polymerization, and polymer grafting. They are classified into two categories depending on the fabrication method used, free-standing CNT membranes which are also known as vertically aligned CNT (VA-CNT) membranes, and mixed CNT membranes. Mixed CNT membranes are the commonly used membranes compared to VA CNT membranes because they are easy to fabricate and require a simple operating system (Ihsanullah, 2019). These membranes are usually employed for applications such as desalination, wastewater treatment, and gas separation; and previous studies have demonstrated that carbon-based membrane separation is a promising technology (Das et al., 2014).

2.4.3 Mixed matrix membranes (MMM)

The vast majority of commercial membrane systems are polymeric because of processing feasibility and low cost (Kim, 2007). However, numerous defects experienced with polymeric membranes have led to the development of membranes by focusing on three major challenges: high perm-selectivity for water and numerous contaminants; low surface fouling; and higher mechanical strength to withstand any arising tension (Chan et al., 2015). The development of polymeric membranes led to the introduction of mixed matrix membranes, which are normally defined as the incorporation of functional fillers (dispersed) into a polymer matrix (Noble, 2011). The addition of fillers into a polymer matrix is to prevent fouling while retaining superior membrane performance is desirable, with the goal of minimizing cleaning frequency and energy costs associated with cleaning and membrane replacement (Ahmed et al., 2019). Some of the popular functional fillers include CNTs, zeolites, silica, and metal-organic frameworks (MOFs).

Table 2.1 represents a few studies that have used different inorganic fillers to prepare MMM for water treatment.

Table 2.1. Types of inorganic fillers for water treatment

Fillers	Membrane type	Advantage	Reference
Silica	MF	Improved hydrophilicity	Gandashtani et al., 2015
Silica	UF	Improved hydrophilicity	Rakhshan and Pakizeh, 2016
Zeolite	RO	100% rejection of salt ions	Liu and Chen, 2013
CNTs	UF	Improved hydrophilicity	Phasha, 2013
CNTs	RO	Improved hydrophilicity	Zhao et al., 2014
CNTs	UF	Improved hydrophilicity	Chan, 2015
MOFs	NF	Improved rejection of dye	Meng et al., 2019

2.4.3.1. Types of fillers

Carbon nanotubes (CNTs)

Carbon nanotubes have intensively attracted a lot of attention as additives to polymeric membranes used in water treatment facilities because of their outstanding mechanical, thermal, electrical, high porosity, and high-density properties, which can be a solution to the above-mentioned challenges. Properties such as the high electrical and thermal conductivity are commonly used to advance functional equipment with heat resistance, electrical conducting, and chemical sensing. Embedding CNT's in membranes offers desirable properties such as surface hydrophilicity,

improved rejection capability, and anti-fouling properties. Depending on how many tubular nanostructures they have, they come in different forms, namely; single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT) and multi-walled carbon nanotubes (MWCNT) (Aberefa, 2015). Berber et al, (2000) reported that CNTs are the best heat-conducting nanomaterials, with a thermal conductivity as high as 6600W/mK SWCNTs and 3000W/mK for MWCNTs at room temperature. More properties are compared in Table 2.2. They are also reported to possess greater chemical reactivity, lower chemical mass, energy, and less environmental impact (Das, 2017).

Table 2.2. Difference between SWCNT and MWCNT (Ihsanullah, 2019; Phasha, 2017)

SWCNT	MWCNT
Single layer of graphene	Multiple layers of graphene
Low purity	High purity
The specific gravity of 0.8 g/cm^3	The specific gravity of 1.8 g/cm^3
Moderate mechanical strength	High mechanical strength
Easy to twist	Difficult to twist
High thermal stability	Moderate thermal stability
Difficult to synthesize in bulks	Easy to synthesize in bulks
Requires catalyst for the synthesis	Does not require a catalyst for the synthesis

Analysis of CNT properties demonstrate that their performance depends on several factors, such as the types of CNTs used (SWNTs or MWNTs) and their morphology (Du et al., 2007). Literature states that open-ended SWCNTs are more fit for the adsorption of multiple adsorbents due to their analogous sizes, unlike MWCNTs. SWCNTs stimulates these adsorption phenomena because of

their lower diameter (Das et al., 2014). Introducing CNTs to a polymer matrix can result in an alteration of the morphology and properties of the membrane. The integrity, hydrophilicity, and stability of the resulting membrane are important factors to consider for the overall membrane performance, which sturdily relies on good CNT dispersion in the casting solution (Chan et al., 2015).In most cases, agglomeration, which is the inability of CNTs to disperse in a polymer matrix is due to van der Waals forces, which limits their application. This is where the functionalization of CNTs was introduced, which is the acid treatment used to enhance CNT dispersion in the polymer matrix. The dispersed nature of these nanoparticles favors hydrophilicity, thus facilitating the fast transportation of water molecules with minimum or no energy consumption as compared to reverse osmosis and micro-filtration membranes (Ihsanullah, 2019). Phasha, (2017) reported that infusing functionalized CNTs into polymeric membranes also helps to make the membrane less susceptible to fouling thus increasing the membrane performance during filtration due to its hydrophilic and mechanical strength properties.

Zeolites

Zeolites are highly porous crystalline aluminosilicates with a tetrahedrally-connected 3-dimensional structure. They contain uniform pores that able to pass through molecules up to 1 nm in size. Zeolites are known as versatile materials used for various applications in the industry due to their unique structure and outstanding properties. Some of the properties include excellent thermal and mechanical stability. Unlike MOFs, zeolites are stable in water and at high temperatures, which can be attributed to the fact that they are prepared under a higher temperature

of up to 100˚C (Cao et al., 2018). Because of these properties, researchers explored the behavior of MMM with zeolites as fillers.

The incorporation of zeolites in the polymer matrix has gained a lot of interest in water treatment studies. This is because zeolite membranes are able to remove dissolved organic solutes and ions. The separation mechanism in zeolite membranes is based on size exclusion and selective sorption. Zeolite membranes have shown improved hydrophilicity and high selectivity during separation processes, which can be explained by their molecular sieving (Li et al., 2013). They are also commonly used as ion-exchange beds for water softening and water treatment systems, catalysts for organic reactions, and for gas separation.

Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are hybrid inorganic-organic solid compounds of inorganic secondary building units connected by multitopic organic ligands. MOFs are considered as promising materials for the fabrication of MMMs because of their ease of functionalization, high porosity, framework flexibility, large surface area, and good compatibility with the polymer matrix (Sorribus et al., 2013; Sun et al., 2019). They have been used in many industries such as desalination and gas separation. Sorribus et al, (2013) reported that the incorporation of MOFs in polymeric membranes enhances the hydrophilicity of the membrane. The crystalline nature of MOFs also leads to increased pure water permeation and selectivity of targeted contaminants. However, their application in water treatment membranes is still limited because majority MOFs are unstable in water (Meng et al., 2019). Therefore, various developments to synthesize MOFs that are stable in water have been explored. Another challenge with raw MOFs is that they are

difficult to disperse in the polymer matrix (Cao et al., 2018). They are also vulnerable to humidity and high temperatures. More efforts are put into finding suitable MOFs for water treatment membranes and optimization of synthesis methods (Li et al., 2013).

2.5 Dispersion Enhancement of mixed matrix membranes (MMMs) via functionalization

CNT membranes have intensively gained a lot of attraction in the wastewater treatment community; however, their application is limited due to the hydrophobic nature of pure CNTs which tends to form membranes that foul easily due to that limiting factor (Yang et al., 2016). Another challenge faced by researchers with these nanoparticles is they tend to agglomerate in the polymeric matrix. This is the reason why even after a decade of research, the full potential of employing CNTs as reinforcements still remains limited because of the difficulties associated with CNT dispersion during membrane fabrication processing. The reason behind this is poor interfacial interaction between the polymer and CNTs (Ma et al., 2010). This motivated researchers to direct their efforts in exploring more ways to modify the CNTs to make the membranes more robust and hydrophilic, thus improving their antifouling property. For this purpose, the functionalization of CNTs was explored to introduce new functional/hydrophilic groups on the surface of the CNTs in order to enhance their incompatibility with polymers (Singh et al., 2008); (Choi et al., 2006). Comparison studies have been performed to investigate the effects of pristine and functionalized CNT incorporation into the polymer matrix. Generally, functionalized MWCNT are found to be smaller in size and less compact and tougher as compared to the pristine MWCNTs, which might

explain why pristine CNT tend to agglomerate due to Van der Waal forces and not disperse well in polymer matrix membranes as compared to functionalized CNTs (Ugarte et al., 1996). Furthermore, the treatment of CNTs with acids such as HNO3 or H2SO4 has been reported to open the tips of the nanotubes and introduce oxygen-containing groups (Hussain et al., 2012).

2.5.1 Acid treatment

The acid treatment method uses various types of oxidizing agents or acid mixtures such as HNO_3, H_2SO_4/HNO_3, H_2O_2, KMnO4, $K_2Cr_2O_7/H_2SO_4$, $HCl/H_2SO_4/HNO_3$, oxygen gas, ozone, and $KMnO_4/H_2SO_4$. This method involves a chemical reaction between the oxidizing agents and the nanotube bundles, these agents aggressively disrupt the aromatic ring by substituting one carbon atom from the CNTs with one or more oxygen atoms to form functional groups such as hydroxyl (–OH) and carboxylic acid (–COOH) that breaks the Van-der Waals forces on the surface of CNT (Sezer and Koç, 2019). Multiple researchers have used the H_2SO_4/HNO_3 concentrated acid mixture (Tsai et al., 2013), (Hoa, 2018) This is also known as wet chemical oxidation; it is recognized as one of the most widely employed treatment methods due to its flexibility and proficiency (Hoa, 2018). For this reaction, CNTs added to the acid mixture are sonicated for a period of time; this causes a rise in temperature of the acid allowing rapid breakage of carbon nanotube structures. However, the time it takes for these CNTs to break depends on the size and structure.

2.5.2 Chemical grafting

This treatment can be carried out through various chemical processes such as anhydridation, esterification, or amidization of oxygen functional groups formed on the surface of CNTs, thus transforming their nanocrystals. The choice of solvent for this process plays a vital role, acetone

has been reported as the preferred solvent due to its desirable results (Laachachi et al., 2008). Song and Kim, (2013) prepared ultrafiltration membranes from PSF composites with poly(1-vinylpyrrolidone) grafted silica NPs, the results showed increased flux and also improved the hydrophilicity of the membrane, which showed enhanced fouling resistance.

2.5.3 In situ polymerization

During this treatment, peroxide groups are grafted onto the surfaces of carbon nanotubes thus functionalizing them and ensuring uniform dispersion in the polymer matrix and various solvents. In situ polymerization also ensures stronger covalent interactions between polymer and CNTs, high mechanical strength, thermal stability (Wang et al., 2012). There are various types of in situ polymerization methods which include atom transfer radical polymerization (ATRP), ring-opening, reversible addition-fragmentation chain transfer, and direct electrophilic substitution. ATRP is probably the most practical technique because it offers the advantages of radical polymerization (Coessens et al., 2001)

2.5.4 Plasma oxidation

The main purpose of this treatment is to remove metallic particles used as a catalyst for the amorphous carbon generated during the production of CNTs. The functionalization of CNTs with this treatment is used to incorporate OH and COOH functional groups on their surface and results in enhanced mechanical robustness and structural integrity suitable for practical applications. (Chen et al., 2009) functionalized their MWCNTs with a microwave-excited Ar/O2 surface-wave plasma treatment and obtained similar results. Time is very important during this treatment; over-treating may result in morphological defects of the CNTs. Scaffaro et al, (2012) use a Tucano

Gambetti radio-frequency apparatus to functionalize their CNTs at different exposure time intervals from 2 to 10 minutes and used air and oxygen as their choice of gas. After functionalization, the elasticity and tensile strength of the CNTs doubled as compared to the non-functionalized CNTs. They also showed enhanced interfacial interaction with the polymer, which is mainly due to the negatively charged carboxylic groups. This treatment is currently used for various application such as bonding and printing on to the material surface

2.5.5 Hydrothermal treatment

This is a controlled surface functionalization of CNTs by nitric acid (HNO_3) hydrothermal oxidation which forms oxygen functional groups (Likodimos et al., 2014). This is also known as heat treatment, usually conducted at higher pressure and temperature of up to 700˚C. Hydrothermal treatment controls the chemistry and morphology of treated nanoparticles, thus altering and enhancing their properties. Upon functionalization, increased surface area, thermal stability, and conductivity are evident in treated CNTs. The improved properties allow potential applications of these nanoparticles (Dalod et al., 2017). There are four aspects that go into this treatment, which are mixed solvents, materials with high crystal structures, capping reagents, and reactions at high pressure and temperatures. For this treatment to be successful, the nanoparticles have to be completely pure. The drawbacks of this process are cost ineffectiveness due to expensive autoclaves needed, there are also safety issues throughout the reaction process (Asim et al., 2014).

2.6 Factors affecting separation performance of polymer and mixed matrix membranes (MMM)

2.6.1 Nature of membrane materials.

The type of materials used to produce membranes has an effect on the flux and the overall performance of a membrane. It impacts on the mechanical strength, chemical and thermal the stability of the membrane, therefore polymers with the mentioned properties are often used as well as other additives which includes PEG400 to enhance other properties such as water flux and porosity to prepare the membranes (Ariano et al., 2017). The mechanical strength of membranes is very important, polymers and nanocomposites containing higher mechanical strength property are often fabricated to reinforce the membrane making them strong and less susceptible to damage. By infusing CNTs into the polymer solution to make nanocomposite increases the life usage of the membranes. For oil-water treatment, the membrane surface has to be as hydrophilic as possible to avoid fouling which affects the performance of the membrane. As a result, several methods such as the application of ultraviolet radiation, treating with low-temperature H_2O plasma blending with hydrophilic materials like PVA layers and adding nanoparticles such as functionalized CNTs have been employed to improve the hydrophilicity of membranes (Steen et al., 2002). The reason for this is that the hydrophilicity of a membrane surface offers improved antifouling resistance due to the hydrophobic nature of most foulants which in turn affects the water flux due to foulants that plug into pores (Kumar and Ismail, 2015). CNTs owing to several properties which include, robust antimicrobial activity and higher water flux pose as improved materials used to modify the surface of membranes, however, they have to be functionalized to improve their hydrophilic property and

to promote good CNT dispersion by forming higher interfaces with the polymer matrix. (Liu et al., 2013).

Polymer concentration also plays an important role during membrane preparation as it controls the viscosity of the dope solution. This has a resulting impact on the morphology of the membrane when it comes to pore sizes, which further affects the permeation flux. Ariono et al., (2017) investigated the effect of polymer concentration on the performance of the membrane using polysulfone, he found out that the water permeation flux decreased with an increase in polysulfone concentration. Increased polysulfone concentration increases the dope solution viscosity, which results in smaller membrane pore sizes. When polysulfone concentrations are low, the dope solution viscosity decreases, thus resulting in larger pore sizes. This affects the selectivity of the membrane, allowing substances meant to be rejected to easily pass through (Sheppard, 2013). This is because the permeability is directly proportional to the fourth power of the pore radius (Ln D rp4) according to the Hagen-Poiseuille equation. However, membrane selectivity towards substances can actually be improved by the addition of volatile solvent into the membrane solution during membrane preparation. Velu et al, (2011) used PES to prepare his membranes and reported that the increase in PES concentration decreased the water flux and water content while the membrane hydraulic resistance increased.

2.6.2 Process conditions

During the operating time, the feed pressure is usually adjusted to compensate for the fluctuation of the temperature of the feed. However, increasing the transmembrane pressure may result in blockage of pores as well as compaction of the membrane. As a result of compaction, higher

pressure has to be applied to maintain the design permeate flow. This impact on the membrane performance due to an increased protein fouling, making the membrane less efficient (Phasha, 2017). Therefore, the operator needs to be aware of the optimal transmembrane pressure. Any pressure value above the optimal trans-membrane pressure will lead to a decrease in permeate flux (Sheppard, 2013).

Change in feed temperature results in the change in the rate of flux through the membrane. It is generally common for the viscosity of the permeate to decrease as temperature increases, making it easier for the feed to disperse on the surface of the membrane during filtration. This will result in increased permeate flux (Sheppard, 2013).

2.6.3 Concentration polarization

Concentration polarization is defined as the accumulation of solutes/ suspended colloids on the surface of the membrane. These are solutes that are rejected during the separation process in UF, MF, NF, and RO membranes (Bian et al., 2000). The solute accumulation on the surface of the membrane results in a concentration difference between feed bulk and polarized layer on the membrane surface. This phenomenon is always associated with decreased flux and membrane performance. The decline in water flux is a result of a cake layer that forms when there is a high concentration of solutes deposited on the membrane surface (Jonsson, 1995; Sablani et al., 2001). The cake layer plug into the pores of the membrane, thereby, blocking the pathway for water diffusion. Concentration polarization also acts as a precursor for membrane fouling as a result of solute adsorption. The accumulated solutes often lead to high osmotic pressure which consumes a lot of energy (Wijmans et al., 1985). Studies have been conducted to gain a full understanding of

this phenomenon in membranes, hence researchers are now looking into more innovative ways of reducing concentration polarization. This is done by exploring several approaches such as membrane surface modification (Bian et al., 2000). The use of dispersants and filtration systems with a mixing feed tank also reduces the potential of concentration polarization by increasing the fluid flow rate past the surface of the membrane (Jonsson, 1995).

2.6.4 Membrane fouling

Besides chemical attacks, fouling is a major problem faced by polymeric membranes, it is defined as the resistance appearing during the filtration of wastewater due to the cake formation or oil concentration layer on the membrane surface, creating defects in membrane pores (Das et al.,2014). It alters the properties of the membrane and this also potentially alters the surface charge, pore size, hydrophilicity, and surface morphology. This is an important factor to consider when designing membranes because it affects operations, costs, and performance of the system (Azuri, 2014). According to Sheppard (2013), there are three different types of membrane fouling which are: reversible fouling, irreversible fouling, and irrecoverable fouling. Reversible fouling can be defined as fouling that can be removed by physical membrane cleaning and it is commonly caused by foulants that are poorly adsorbed onto the membrane surface. Whereas irreversible fouling is fouling that cannot be removed by physical cleaning but however, can be removed by chemical cleaning. This type of fouling may be caused by hydrophobic interactions, hydrogen bonding, van der Waal's attractions that take place between the surface of the membrane and foulants. And lastly, irrecoverable fouling, which is fouling that cannot be removed by any of the existing cleaning methods. These methods of cleaning further increase cost and maintenance requirements; hence it is of importance to develop ways of mitigating this problem.

According to Field (2010), membrane fouling occurs in different forms listed below:

- Pore blockage – During filtration, membrane pores can be blocked, resulting in a reduced influx of permeate.
- Adsorption – This arises when there are definite interactions between the solute particles and the membrane surface, a layer of these solutes can develop even in the absence of permeation flux further causing extra hydraulic resistance.
- Deposition – A deposit of particles can grow to form a cake on the surface of the membrane, this also causes additional hydraulic resistance.
- Gel formation –This is caused by an increased level of concentration polarization which may result in the formation of gel in the vicinity of the membrane surface.

Pollutant concentration reduces the lifetime and modules of the membrane resulting in pore narrowing or blocking. This becomes a problem since the membrane filtration method is incapable of self-cleaning, therefore recycling or chemical treatment is required for the removal of the cake to unblock the pores (Das et al., 2014). To mitigate this problem, several methods have been employed to modify membrane surfaces to make them more hydrophilic, including the application of ultraviolet radiation, blending with hydrophilic materials, graft polymerization, and plasma grafting (Sheppard, 2013). Despite their great increase in hydrophilicity, some of the modifications result in a significant drop in water permeation flux; this is due to the extra thickness formed when coating the surface with these hydrophilic layers (Chan et al., 2015). Optimizing operating conditions also helps prevent fouling. The tendency of oil cake forming on the membrane surface will decrease because of the repulsive interaction among negatively-charged-hydrophilic

membranes (Sianipar et al., 2017). This promotes a more unstable attachment of the oil on the membrane's surface and makes it simple to clean and wash off the cake in industrial applications.

2.6.3.1. Strategies to control fouling

Pre-treatment of feedwater is a necessity prior to filtration to reduces the number of foulants that could potentially be suspended on the membrane surface. However, the selection of a pre-treatment method depends on the source of water and the type of contaminants found (Mansouri et al., 2010). It is reported in the literature that these pre-treatment methods are not as effective because they are not capable of removing foulants completely. The chemicals could also contribute to membrane fouling when they react with some of the foulants in the feed water (Azuri, 2014). Table 2.3 shows the different chemical pre-treatment techniques for feed water.

Table 2.3. Chemical pre-treatment of feed (Azuri, 2014; Singh, 2005)

Techniques	**Purpose**
Coagulants	Destabilizes colloidal particles via chemical reactions thus Improving the elimination of solids and precipitation.
Antiscalants	Delays the crystallization of scale mineral compounds of the membrane, allowing water to pass through before any chemical reaction can occur thus increasing the solubility of the compounds.
Acids	Altering the pH to the acidic range to delay the scaling and adsorption potential of some compounds on the membrane surface
Dispersant	Prevents solid compounds from being suspended on the surface of the membrane.
UV	This technique exposes microorganisms to UV radiation thus enabling biological activities or replication.
Ozone	This is applied as a gaseous form to reduce biological activities and eliminate organic compounds.

2.7 Polymer and mixed matrix membranes MMMs for treatment of phenol wastewater.

Polymeric and MMMs have recently been employed for the removal of priority pollutants such as phenolic compounds, benzene, toluene, and fluorene from wastewater produced during industrial operations. This water is treated in order to avert the looming water crisis faced all around the world, therefore, water is recycled and recovered to increase the availability of potable water. Previous studies have demonstrated polymeric membrane as effective separation techniques, owing to their high selectivity, easy fabrication, low energy consumption, and environmental friendliness. Collectively, these advantages facilitate the recovery of gallons of wastewater produced in industries.

The effectiveness of the membranes depends on the membrane material; therefore, the choice of polymer and additives is important for extended life and application of the membrane. Even though polymeric membranes have achieved massive technological innovation and remain the most commonly used materials for commercial membranes, they are naturally hydrophobic. The hydrophobic interactions between membrane material, solutes, and microbial cells often result in protein adsorption, making them more susceptible to fouling of membrane pores (Sheppard, 2013). As a result, researchers continue to discover and develop various techniques to alter the surface properties of these membranes. These techniques include the incorporation of nanoparticles, coating (PVA), graft polymerization, the addition of surfactants, plasma treatment, and polymer blending (Sinha and Purkait, 2013). Out of the mentioned methods, incorporation of nanoparticles

is reported as the most preferred method as it doesn't drastically alter the morphology and pore size of the membrane (Wu et al., 2008).

Less has been reported on phenol removal using polymeric membranes and MMM. Raza et al. (2019) presented a study based on the removal of phenolic compounds from industrial wastewater using membrane technology. From this review, polymeric membrane such as PES and PSF show desirable phenol rejection of up to 95%. However, the membrane performance in all the studies reviewed is affected by the hydrophobic interaction between the solute in the feed and the surface of the membrane. Mukherjee and De, (2016) incorporated titanium dioxide in a PSF membrane for the removal of phenol, their results showed phenol rejection of 75%. In their next study, Mukherjee and De, (2016) incorporated CNTs in a PSF membrane for the removal of benzene and the results showed a significant rejection of 97%. These results demonstrate that MMMs are a promising separation technology in industries producing effluent water with organic compounds. Future research on the incorporation of blended polymeric membranes and suitable nanoparticles can improve the industrial application of membrane-based separations for wastewater treatment. Table 2.4 summarizes the performance of polymeric and MMMs.

Table 2.4. Recovery of phenol and benzene using polymeric and mixed matrix membranes.

Membrane Material	Target pollutant	Rejection %	Reference
PSF	Phenol	81	Raza et al., 2019
PSF/Titanium-dioxide	Phenol	75	Mukherjee and De, 2016
PSF/CNT	Benzene	97	Mukherjee and De, 2016
PES	Phenol	94.9	Sun et al., 2015
PSF	Phenol	81	Galanakis et al., 2013
Composite fluoropolymer	Phenol	56	Galanakis et al., 2013
Polyamide	Phenol	94.9	Sun et al., 2015
Polyamide	Phenol	75	Raza et al, 2019

2.8 Concluding remark

Produced water from refineries can be recycled and reused using different separation technologies such as adsorption, biological and membrane treatment. However, adsorption and biological methods have shown low separation efficiency and high operational costs. These challenges directed research focus on the development of membrane-based processes, owing to their outstanding properties. The developments in membrane technology coupled with other advantages of polymeric membranes have encouraged increased applications of membranes in various industries. The current developments that have been done are summarized in the literature review, addressing various limitations of polymeric membranes such as fouling and low mechanical strength. One of the popular modification processes is polymer blending and the addition of nanoparticles such as zeolites, MOFs, silica, and CNTs. However, CNTs have been touted as the next big leap in membrane technology owing to their excellent chemical stability, mechanical

strength, high flexibility, low mass density, frictionless water molecule transport, and ease of functionalization.

CHAPTER 3

3 Synthesis and characterization of PSF/PES composite membranes and application to phenol-containing wastewater treatment

3.1 Introduction

The rapid growth in the oil, gas, and petrochemical industry has led to the large production of oily wastewater made up of different harmful organic compounds (Padaki et al., 2015). Phenol and benzene are major pollutants largely found in produced water that pose human fatality and threat to the environment. According to the US Environmental Protection Agency, phenol is ranked the 11th most hazardous chemical out of 126 (Raza et al., 2019). Benzene is also reported to be volatile and highly soluble in water, which substantially impacts the health of humans and wildlife that are exposed to the water (Reddy et al., 2012). Therefore, there is a need to develop a cost-effective technique that will effectively purify water contaminated with these compounds. Therefore, the ultimate aim of this study is to apply the blended membrane to the treatment of this wastewater. One of the objectives of this study as presented in this chapter, was to synthesize blended polysulfone (PSF) and polyethersulfone (PES) composite membrane and test them for treatment of phenol-containing wastewater.

Polymeric membranes are continuously being developed through different techniques to improve their performance and quality. One of the approaches being explored by researchers is the polymer blending technique, both in academic and industrial perspectives (Albu et al., 2011). This is because the commercial application of polymeric materials as membranes remains technically

limited; therefore, there is a serious need for new membrane materials that have different properties from basic polymeric membrane materials (Kim, 2007). However, polymer blending is limited by the complete incompatibility of certain polymer blends, making it difficult to obtain miscible compositions.

A great majority of polymer blends have been reported to be multiphase, basically partially or completely immiscible. Immiscible polymer blends find it difficult to form a single phase. They have a coarse morphology, sharp interface, and poor adhesion between the blend phases. Miscibility can be influenced by several factors such as morphology, and reduction of surface tension (Thomas et al., 2015). Thus, it seems very attractive to blend PSF and PES to investigate its effect on the separation performance, mechanical and thermal stability of the fabricated membranes resulted from the blending.

3.2 Materials and methods

The materials employed in the study were polysulfone (PSF) pellets (average molecular weight 35, 000 Da) from Sigma Aldrich, South Africa; polyethersulfone (PES) crystal (0.025mm x 150 mm x 150 mm) from GIC Scientific, N-Methyl-2-pyrrolidone (NMP) (99%; from ACE, South Africa), Phenol (Molecular biology) and Benzene (≥ 99.7%) both from Sigma Aldrich, South Africa.

A standard procedure was applied when preparing the membranes, using the phase inversion technique induced by immersion–precipitation (Mulder, 2000). 10% of Polysulfone and polyethersulfone pellets measured by weight at different compositions of (100:0, 0:100, 50:50, 80:20, 20:80, and 75:25) respectively, were dissolved in NMP under continuous agitation at room

temperature for 12 h. The casting solution was cast using a casting blade set at 180 μm on smooth glass. The glass, together with the dope, was then immersed in distilled water for the phase separation step. The formed membranes were left to dry at room temperature for 24 hours. The membranes were then characterized.

3.2.1 Characterization of membranes

Equilibrium water content (EWC) is directly related to porosity and is defined as the moisture level where the membrane neither loses nor gains moisture (jasiewics and Pietrzak, 2013). This is usually done to check how much water a membrane can absorp.. It was calculated using equation (3.1), where Ww is the weight of the membrane when wet while Wd is the dry weight of the membrane.

$$\text{EWC} = \frac{Ww - Wd}{Ww} \times 100\% \quad (3.1)$$

The porosity of the membrane was determined by the mass loss of the wet membrane after drying up (jasiewics and Pietrzak, 2013). It also measures up the void spaces created by pores within the membrane. It was calculated using equation (3.2), where ρ is the density of water and V is the total volume of the membrane (Sinha and Purkait, 2013).

$$Porosity = \frac{Ww - Wd}{\rho \times v} \times 100\% \quad (3.2)$$

Atomic Force Microscopy (AFM) was used to capture topographic images of the membranes and provide some information on the roughness of the samples. It is a versatile microscopy technology that was established in 1986 by Nobel Prize Winner Gerd Binnig who worked with Christoph

Gerber and Calvin Quate (Rugar and Giessib, 2019). It is a type of high-resolution scanning probe microscope that has a resolution that can be measured in fractions of a nanometer. It is versatile because it is able to record topographic images and provides some information on nano-scale chemical, physical (roughness and pore size distribution), mechanical (modulus, stiffness, viscoelastic, frictional), electrical and magnetic properties. Information is collected with a sharp tip that scans the surface of the membrane. According to Hooke's law, the forces that exist between the tip and the membrane surface result in a deflection of the cantilever, producing valuable data about the surface of the membrane (Sheppard, 2013). The microscope was operated in non-contact mode, at a resonance frequency between 75-100 kHz and 1μm×1μm images were obtained.

The membrane's degradation ability was investigated using a thermogravimetry analysis (TGA) instrument. Thermogravimetric analysis (TGA) is one of the most common techniques used to investigate the thermal behavior of membrane samples in which changes in chemical and physical properties of materials are measured as a function of increasing temperature. It measures the amount of weight change when a sample is heated. It analyzes a range of materials such as polymers, metals, glasses, plastics, and ceramics. For this study, measurements were carried out under a nitrogen atmosphere and in temperature ranging from 25 to 800 °C at 10˚C/min, at a flow rate of 50 mL/min. The thermal stability of both PSF and PES membranes was measured to serve as a reference point for the blended membranes.

Figure 3.1. Model di3100 AFM instrument.

Figure 3.2. Thermogravimetric analyzer, TGA-model Perkin Elmer.

A tensile test was conducted on the membrane using a nano-tensile test machine, the machine works on the stress and strain gathered from thermographs to determine the mechanical strength of the membrane. Three samples of each membrane with a dimension of 10 x 30 mm^2 were cut and tested. The force applied and change in length at the break for each sample were obtained. Finally, the tensile strength and the young modulus values were calculated using Equation (3.3) and Equation (3.4), respectively.

$$\text{Tensile Strength} = \frac{Force}{Area} \quad (3.3)$$

$$\text{Young Modulus} = \frac{Tensile\ Strength}{Strain} \quad (3.4)$$

3.2.2 Performance evaluation

Pure water flux is expressed as the volume of permeate that passes through a membrane per unit membrane surface per unit time and it is related to water permeation which is a pressure-driven process (Sheppard, 2013). The pure water permeation of the synthesized composite membranes was measured using a dead-end filtration unit. The flux was calculated using equation (3.5) where Jw represents pure water flux ($Lm^{-2}h^{-1}$), V is the volume of water (L) that permeated through the membrane, A is the area of the membrane (50 m^2) while t stands for water permeation time, which was 20 minutes for all the membranes.

$$Jw = \frac{V}{A\triangle t} \quad (3.5)$$

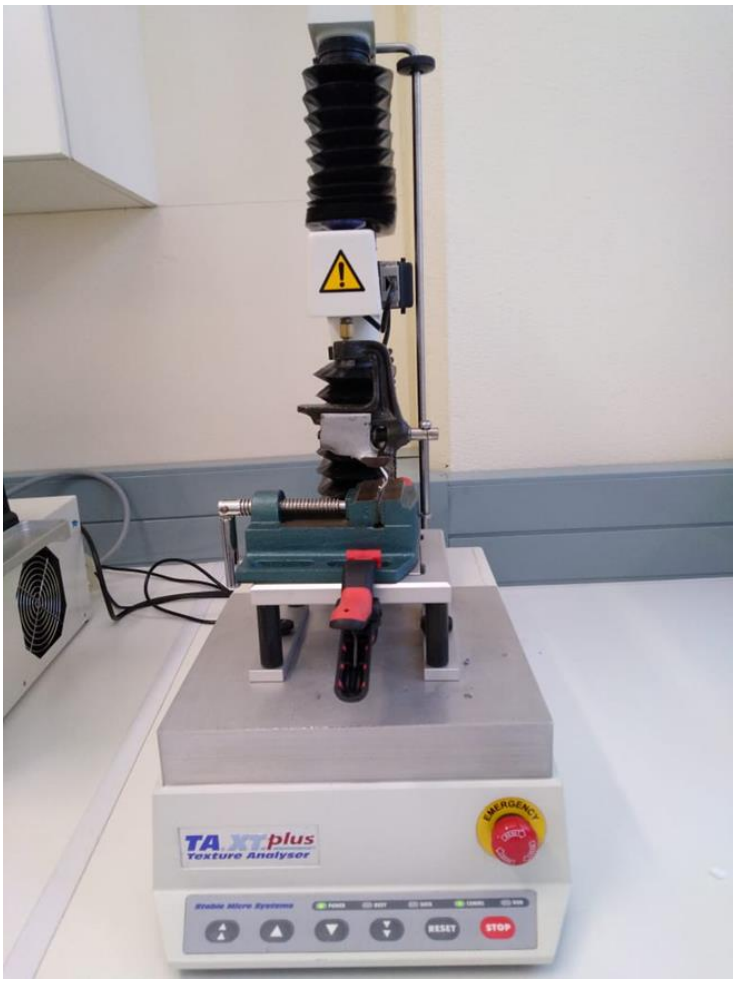


Figure 3.3. Nano-tensile tester/ Texture Analyzer, XY plus.

3.2.3 Phenol and benzene wastewater separation

The ultrafiltration experiment was conducted using a dead-end filtration unit to evaluate the separation performance of PSF/PES blending for phenol and benzene wastewater. To prepare the feed, phenol and benzene were dissolved in deionized water at a concentration of 20 mg/L and 20 mg/L, respectively. The feed was filtered through each membrane and the permeate was analyzed using pre-calibrated high-performance liquid chromatography (HPLC). Rejection ratio was calculated using equation (3.6), where C_p is the concentration of the permeate while C_f is the

concentration of the feed. For each membrane, three permeation tests were conducted, and the average rejection values are reported.

$$R = (1 - \frac{C_p}{C_f}) \times 100\% \quad (3.6)$$

Figure 3.4. Dead-end filtration cell.

3.3 Results and discussion

3.3.1 Membrane characterization

The equilibrium water content of the prepared membranes was measured as shown in Table 3.1 using equation (3.1). This is an important parameter for membrane characterization and has a close

relationship with pure water flux because flux relies on the number of pores on the membrane surface. These pores allow the membrane to accommodate water molecules. The results in Table 3.1 show that the water content of pure PES membrane is greater than that of pure PSF, and when the two polymers are blended, the water content increased. This is evident with the 50%PSF-50%PES which has the highest water content followed by the 25%PSF-75%PES membrane.

The porosity of the membranes was determined by analysis of its weight in the wet and dry state and calculated from Equation (3.2). The results are presented in Table (3.1). As observed, the porosity of PES, 43.15% is greater than that of PSF, which is 38.66%. Blending PSF with PES enhanced its porosity when the wt% of PES is greater or equal to PSF, 50%PSF-50%PES membrane showed the highest porosity of 55.39%.

Table 3.1. Effect of polymer blending on the characteristic of membranes

Membrane	EWC (%)	Porosity (%)
100% PSF	55.83	38.66 ±6.0
100% PES	61.94	43.15 ±4.8
20% PSF -80% PES	54.95	48.66 ±3
25% PSF – 75% PES	61.58	55.39 ±5.6
50% PSF - 50% PES	72.52	58.87 ±3.7
80% PSF – 20% PES	53.10	37.70 ±2.0

The Thermo-Gravimetric Analysis of PSF, PES, and PSF/PES blend membranes is shown in Figure 3.5 and Figure 3.6.

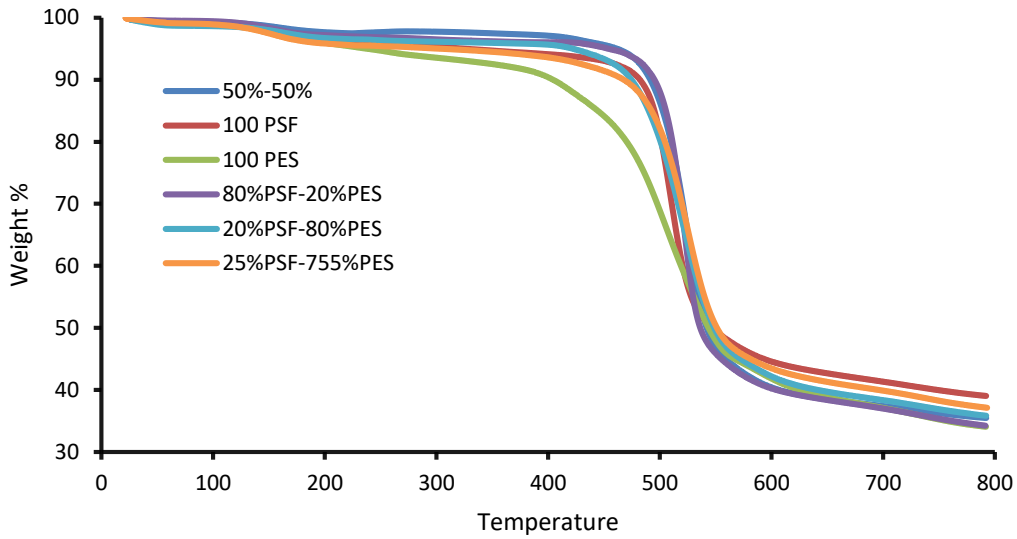


Figure 3.5. The TGA curves of 100% PES, 100% PSF, and PSF/PES blend membranes

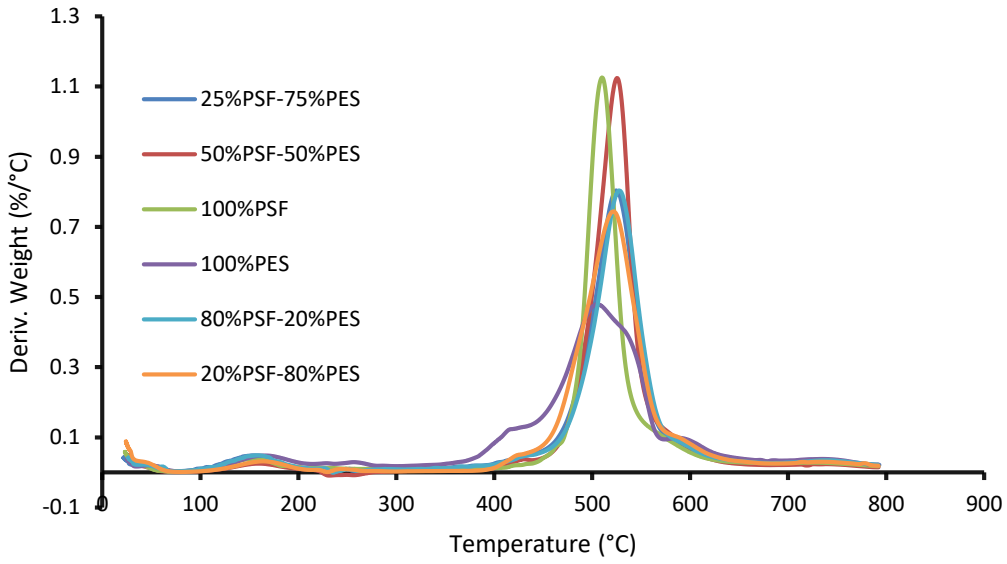


Figure 3.6. Thermograms of 100% PSF, 100% PES and PSF/PES blended membranes

The thermal stability potential of the membrane was studied using a thermo-gravimetric analysis (TGA) instrument. As observed in Figure 3.5, the PES membrane displayed the least thermal

stability. Loss in weight of PES is significant at a temperature of >400 °C, as compared to the PSF membrane at about 500 °C. However, the thermogram of the PES membrane agree with the report of Ayyaru, and Ahn, (2018), their thermogravimetric analysis showed PES membrane decomposing between temperatures 400 °C and 500 °C. Figure 3.5 also shows that blending PES with PSF enhances its thermal stability. Very little weight loss was observed under 500 °C for all blended membranes, indicating good thermal stability. Amongst all, 25%PSF-75%PES membrane shows to be the most stable. Figure 3.6 shows the derivative weight loss curve of the synthesized membrane. All the curves have a single peak, which confirms the miscibility of both polymers, thereby, indicating that no phase separation occurred during blending (Mclaunchlin and Ghita, 2016).

The mechanical properties of the membranes were measured based on their tensile strength and young modulus to see how much force they can endure before tearing. The results are shown in Figure 3.7 and Figure 3.8. The blended membranes showed a higher tensile strength in the 25%PSF-75%PES membrane while the others showed a rather decreasing trend as compared to the two reference membranes (PSF and PES). Fundamentally, the increase in the tensile strength of the 25%PSF-75%PES membrane is likely due to the improvement in the morphological structure of the upon blending (Ismail et al.,2017). The decrease in tensile strength observed with 20%PSF-80PES and 50%PSF-50%PES membranes can be attributed to the incompatibility of the blends at these compositions (Jin et al., 2018). Figure 3.8 depicts the young's modulus results; these results describe the elastic properties of the membranes when under tension. As observed in Figure 3.8, PES displayed a higher young modulus than PSF, blending the two polymers to enhance the membranes' elasticity. The elasticity increases with an increase in PES concentration

in the blended membranes, making the 20%PSF-80%PES the membrane with the highest young modulus.

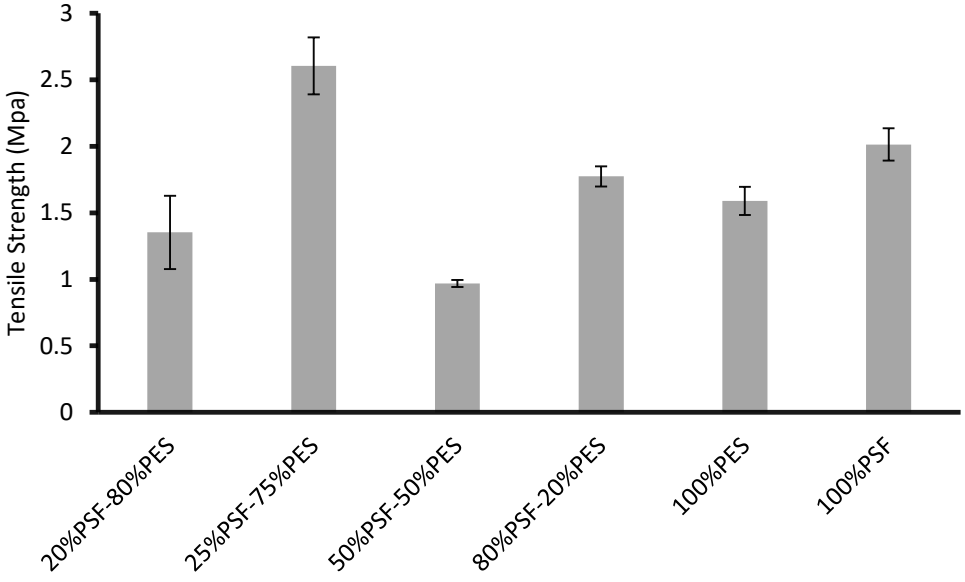


Figure 3.7. Tensile strength of PSF/PES prepared membranes

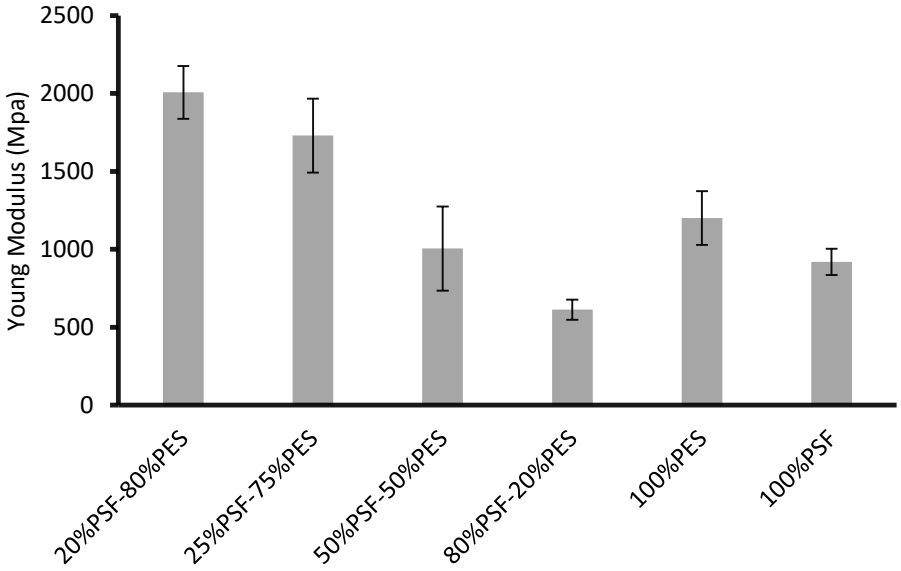


Figure 3.8. Young modulus for PSF/PES blended membranes

AFM was used to study and evaluate the surface nature of the membranes. Figure 3.9 shows the three-dimensional height images of all synthesized membranes. Table 3.2 shows the different roughness parameters of all membranes. It was observed that PES roughness is greater than that of PSF and blending PES with PSF reduced its roughness. Even after blending PES and PSF, the surface roughness of the blend was greater than that of PSF. This is evident in Figure 3.9f, The PSF membrane appears smoother than the other membranes, making it the least susceptible to fouling. The 50%PSF-50%PES membrane in figure 3.9c showed greater roughness, this weakens the hydrodynamics on the membrane surface, which in turn facilitates concentration polarization as well as fouling (Cuperus and Smolders, 1991).

Table 3.2. Surface roughness parameters of the prepared membranes

Membrane	Mean surface roughness (Ra-nm)	Mean surface roughness (Ra-nm)
100% PSF	11.66 ±0.67	13.46 ±0.34
100% PES	5.73 ±0.51	7.05 ±0.16
20% PSF -80% PES	10.88 ±0.19	13.31 ±0.42
25% PSF – 75% PES	7.16 ±0.25	9.01 ±0.32
50% PSF - 50% PES	18.33 ±0.50	24.79 ±0.72
80% PSF – 20% PES	10.73 ±0.51	13.39 ±0.52

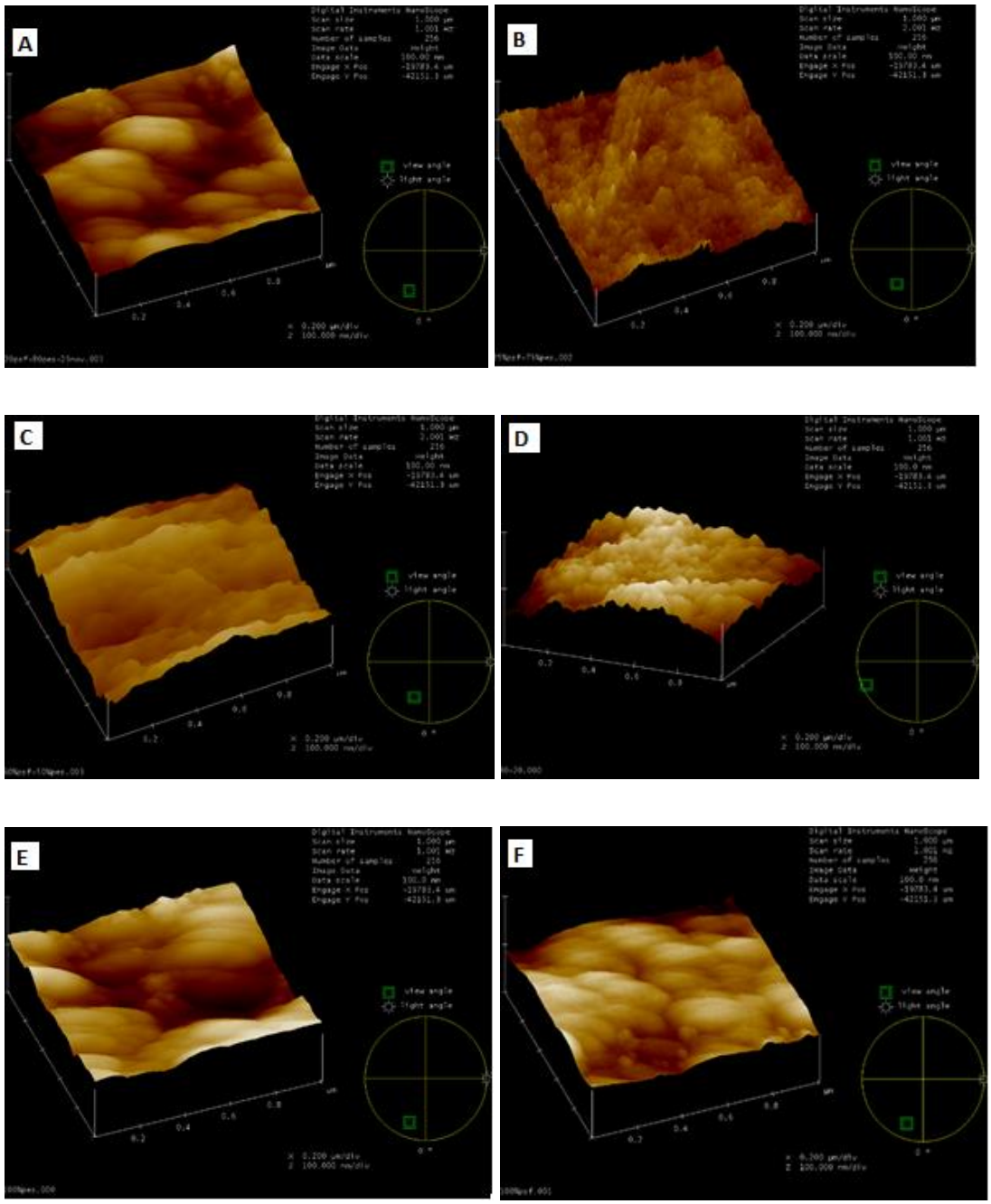
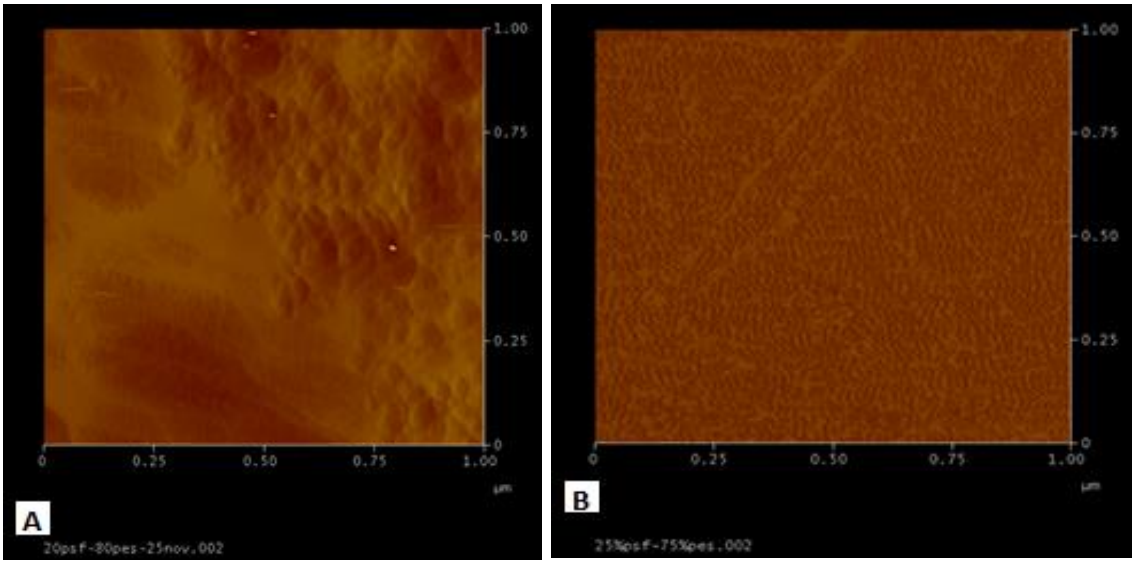


Figure 3.9. AFM 3D surface morphology images of a) 20PSF:80PES, b) 25PSF:75PES, c) 50PSF:50PES, d) 80PSF:20PES, e) 100PES and f) 100 PSF.

Literature has reported that membrane fouling is influenced by the physical roughness of a membrane surface (Vrijenhoek et al., 2001). The bright areas on AFM images exhibit the highest points and dark areas portray the pores of the membranes (Rezaee et al., 2015). From this information, it is observed in Figure 3.10b that 25%PSF-75%PES has more pores than all the membranes which confirm its high flux rate, the pores also appear much smaller than that of the other membranes. However, there is no regular geometry of the surface sections for their pores. The 50%PSF-50%PES membrane in Figure 3.10c showed the highest surface roughness than all the other membranes as presented in Table 3.2. Ayyaru and Ahn (2018) reported that membranes with higher surface roughness often showed high porosity. This is further corroborated by the high porosity of 50%PSF-50%PES membrane as discussed in section 3.3.1. High roughness is also associated with membrane fouling due to foulants being able to deposit easily in the valleys on the surface (Ayyaru and Ahn, 2018).



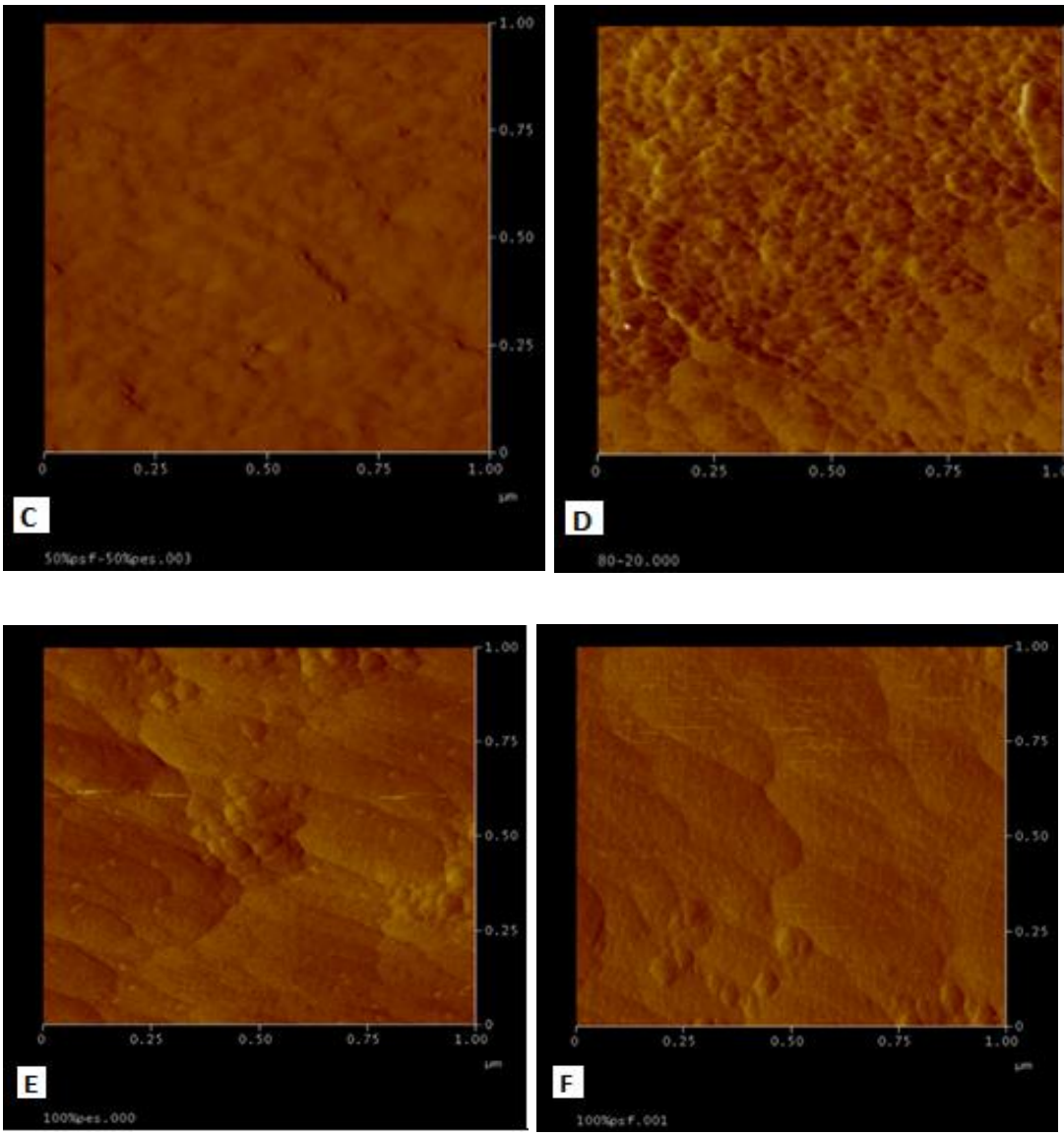


Figure 3.10. AFM 2D surface images of a) 20PSF:80PES, b) 25PSF:75PES, c) 50PSF:50PES, d) 80PSF:20PES, e) 100PES and f) 100PSF.

3.3.2 Treatment performance evaluation

Pure water flux (PWF) was determined by allowing deionized water to permeate through the membrane at a constant transmembrane pressure of 0,7 bar. The flux values were obtained using

equation (3.5) and the results are represented in Figure 3.11. As observed, the flux of the PES membrane is greater than that of the pure PSF membrane. This explains the increasing pure water permeation in blended membranes with the higher PES concentration (20%PSF-80%PES, 25%PSF-75%PES, and 50%PSF-50%PES) as compared to the membrane with the lower PES concentration, 80%PSF-20%PES membrane in this case. The results obtained also agrees with the porosity results in section 3.3.1 The increased water permeation can be attributed to the increased number of pores after blending the polymers. PWF results represent the membrane's hydraulic permeability and highly depends on the thickness and porosity of the membrane (Hamza et al.,2014). It also depends on the wettability of the membrane; when it is improved, it often results in a favorable increase in water permeability (Xu et al., 2019). The obtained results indicate that blending PSF with PES increased the pore density of the membranes. However, the flux shows a slight decrease when the weight of PES is greater than 75%, making the 25%PSF-75%PES blended membrane the one with the highest flux. These results are comparable with those observed by Ravishankar et al. (2018), where the PSF membrane displayed flux of under 20 L/m^2h.

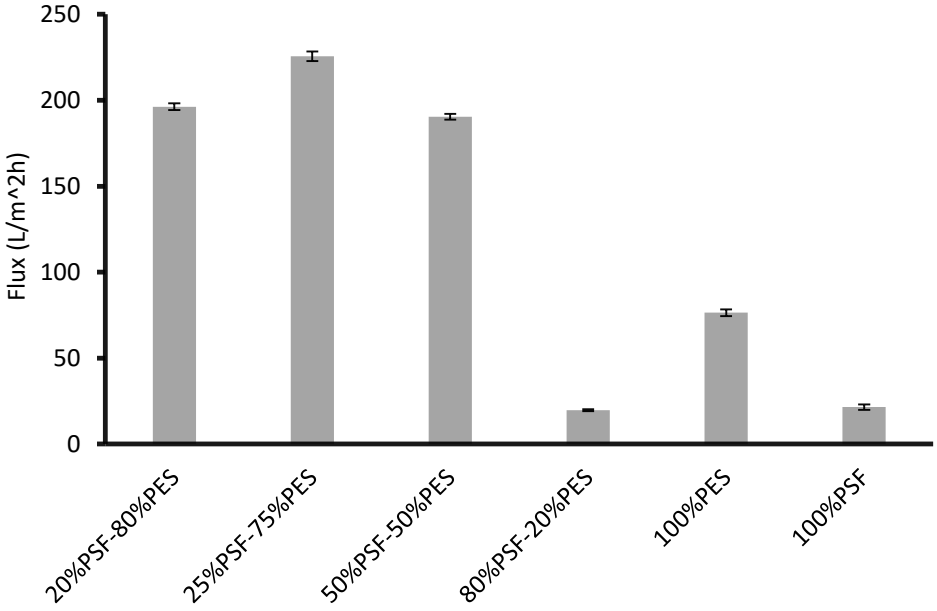


Figure 3-11. Pure water permeation through the synthesized membranes (Experimental conditions: Feed pressure=1 bar; atmospheric pressure=0.8 bar; TMP- 0.2; temperature=25˚C.

The rejection of waste during the filtration experiment depends highly on the transmembrane pressure and the morphology of the membrane (Sinha and Purkait, 2013). The separation performance experiments were conducted at a constant transmembrane pressure (TMP) of 0.2 bar. It has been reported that the most efficient waste rejection is obtained at lower pressures (Rahayu et al., 2018), hence the reason for choosing a lower pressure for the separation experiment. This may be because the trans-membrane pressure was constantly low which also results in lower capillary pressure of the membrane. At low TMP, the pores remain intact (Chakrabarty et al., 2008). This experiment was conducted using synthetic wastewater containing 30 mg/L of phenol and 20 mg/L of benzene. The % rejection of the membranes is represented in Table 3.3. All the membranes showed excellent separation efficiency, giving % rejection of over 95% for phenol and

benzene. The 25%PSF-75%PES membrane displayed the highest water flux than all the other membranes while also displaying % rejection of 99.6% and 98.9 for benzene and phenol, respectively.

Table 3.3. Effect of polymer blending on separation performance

Membrane	Benzene % Rejection	Phenol % Rejection
100% PSF	97.0	98.6
100% PES	96.0	98.1
20% PSF -80% PES	99.2	97.7
25% PSF – 75% PES	99.6	98.9
50% PSF - 50% PES	98.0	98.1
80% PSF – 20% PES	98.6	99.0

3.4 Concluding remark

The effect of polymer blending was investigated based on the performance evaluation of the membranes. The selection of the best-blended membrane was based on the performance of each of the membranes without compromising the quality. The flux and porosity showed an improvement in the majority of the blended membranes than in pure PES and PSF membranes. The 25%PSF-75%PES displayed the highest flux of 225 L/m^2h while 50%PSF-50%PES yielded the highest porosity of 58.87% followed by 25%PSF-75%PES with 55.39%. Ultrafiltration study was performed at low pressure and all the membranes showed excellent selectivity towards phenol and benzene. AFM images indicated lower roughness in the pure PSF membrane as compared to the blended membranes and 25%PSF-75%PES was the second lowest, which was an improvement

compared to the pure PES. The tensile strength only improved with the 25%PSF-75%PES membrane while the elasticity increased with an increase in PES concentration in the blended membranes. Therefore, from these results, 25%PSF-75%PES membrane appears to be the best-blended membrane based on its separation performance and physicochemical and thermal property.

CHAPTER 4

4 Reinforcement of PSF/PES composite membranes with CNTs and application in phenol and benzene-containing wastewater treatment.

4.1 Introduction

Ever since the discovery of CNTs by Sumio Iijima in 1991, they have attracted special attention. Researchers have concentrated their focus on studying and understanding their structure, properties, and use. These nanoparticles have enhanced and facilitated the application of membranes, especially for water treatment purposes due to their unique outstanding characteristics (Rashid and Ralph, 2017). However, the application of CNTs is still limited due to their lack of solubility in many common solvents and difficulty to disperse in polymer matrixes. To overcome this problem, intensive efforts have been put into modifying these nanoparticles to enhance their dispersion and maximize their performance (Ihsanullah, 2019.

In this chapter, four membranes embedded with CNTs were synthesized, three with pure CNTs (pCNTs) and one with functionalized CNTs (fCNTs). The CNTs were embedded into the 25%PSF-75%PES membrane, which was the best performing membrane as observed in chapter 3. The membranes synthesized were characterized and used for the treatment of wastewater containing phenol and benzene. This chapter also reports the purification and functionalization of CNTs, characterization of fabricated membranes, and their evaluation in the treatment of wastewater containing phenol and benzene. It is interesting to mention that the effect of pCNTs loading on the separation performance of the membranes was not investigated during this study.

4.2 Materials and methods

The same materials used in Chapter 3 were used for this experiment, with addition to multi-walled CNTs with a diameter of about 10 nm; length of about 3-6 μm; with a purity of 98% was obtained from Sigma Aldrich, in South Africa, 98% H_2SO_4 and 65% HNO_3 both from Sigma Aldrich, South Africa.

4.2.1 Purification and functionalization of CNTs

The CNTs were first purified because CNTs usually contain a lot of impurities, such as amorphous carbon, multi-shelled carbon particles or iron residual catalyst depending on the type of method used for production. These impurities have to be removed in order to get the desired properties of CNTs. For this purpose, 1 g of raw CNTs was added to 100 ml of hydrochloric acid and then ultrasonicated for 4 hours at 40˚C. The centrifuged residue was then washed with distilled water again and filtered using a vacuum filtration until the pH of the filtrate was neutral. The filtered CNTs were then dried at 100˚C for 24 hours.

For functionalization, 1 g of pure CNTs was mixed with a mixture of 75 ml of Sulfuric acid (H_2SO_4) and 25 ml of Nitric (HNO_3); the mixture was ultrasonicated for 4 hours at 40°C. The same protocol for washing and drying used during purification was applied. The dried CNTs were then characterized to confirm successful functionalization using the Fourier transform infrared spectroscopy (FTIR) to check the presence of functional groups (Aberefa et al., 2019). The FTIR analysis is represented in Appendix C, Figure C1.

4.2.2 Fabrication of CNT infused PSF/PES membrane

The membranes were then synthesized using the phase inversion method. Three membranes were synthesized with pure CNTs at various concentrations (0.5 wt%, 1.0 wt%, and 1.5 wt%), and one with functionalized CNTs at a concentration of 1%wt. For each membrane, the CNTs were dispersed in 15 ml of NMP, and 10%wt of 25:75 PSF/PES dissolved in another 15 ml of NMP and stirred for 20 hours using a magnetic stirrer. After 20 hours, the polymer solution was added to the CNT solution. The mixture was then stirred for 4 hours until the CNTs were completely dispersed in the polymer mixture to form a casting solution. The casting solution was then cast using a casting blade set at 180 μm on a smooth glass plate. The casted solution was then immersed in distilled water for the phase separation step and left for 30 seconds until the membrane is formed, this was done to initiate solvent evaporation (Chung et al, 2005). The formed membranes were left to dry at room temperature for 24 hours and then characterized. The same characterization methods used in chapter 3 were used for this chapter.

Scanning electron microscope images of the membranes were obtained with a transmission electron microscope as described in the literature (Stadtländer et al., 2007). Samples were coated before being scanned; to increase its conductivity between the equipment and the sample and to prevent the build-up of high voltage charges on the sample by conducting the charges to the ground. However, the type and period of coating influence the resolution and quality of the SEM image obtained thereof. For these membranes, carbon and gold-palladium were used for coating. Various images were examined and taken at magnifications of 5000× for the cross-section views at an acceleration voltage of 10kV.

Figure 4.1. Casting blade and glass used to cast membranes.

4.2.3 Separation Performance of the membrane

The separation performance of the membrane was evaluated using a dead-end filtration set-up. To prepare the feed, phenol and benzene were dissolved in deionized water at a concentration of 20 mg/L and 20 mg/L, respectively. But firstly, pure water permeation was conducted to obtain the initial flux of the membrane. This set-up uses nitrogen gas to beef-up the feed pressure through the membrane. The use of a magnetic stirrer in this set-up offers a high but indeterminate shear force required to reduce solid cake formed on the membrane surface (Munir, 2006). For this experiment, each membrane was tested at a different feed pressure of 100, 200, and 300 kPa.

Figure 4.2. SEM (model Carl Zeiss Sigma), Germany (Wits, School of Chemical and Metallurgical Engineering).

4.3 Results and Discussion

4.3.1 Effect of incorporation of CNTs on membrane quality.

The addition of hydrophilic nanoparticles such as CNTs has been commonly used to modify membrane surfaces. One of the key advantages of this approach is that the water permeability through the CNT channel is reported to be three times higher than that of the conventional membrane (Kalra et al., 2003). Table 4.1 shows EWC and porosity results, it was gathered that both the EWC and porosity of the fabricated membranes increased considerably with the increase in CNT loading. Generally, the addition of CNTs helps in the formation of a porous membrane structure by breaking down the walls of the membrane. Another reason is due to the -OH group added to the functionalized CNTs which lowers the hydraulic resistance thus increasing the capacity of the membrane to hold more water (Mehrabadi et al., 2018; Yang et al., 2016).

Table 4.1. Effect of CNT loading on ultrafiltration characteristics of membranes.

Membrane	EWC (%)	Porosity (%)
0% CNT	61.58	55.39 ±5.6
0.5% nf-CNT	46.81	33.67 ±4.8
1% nf-CNT	60.17	57.39 ±2.6
1,5% nf-CNT	63.78	58.07 ±4.2
1% fCNT	68.36	60.89 ±4.7

TGA was used to determine the thermal stability of the nanocomposite membranes. CNT loading had a substantial effect on the thermal stability of polymeric membranes. Due to their unique

structural features, CNTs possess excellent thermal properties. The thermal stability of CNTs in general ranges from 720°C – 2000°C depending on their structure (Luo et al., 2011). Figure 4.3 presents the results of the TGA. The slight weight loss observed between 25˚C - 200˚C is due to the loss of moisture and solvent used during the fabrication of the membrane. Considering Figure 4.3, the 0 wt% membrane started degrading at 480˚C. Upon adding pCNTs, the addition of 0.5wt%, the thermal stability decreased, with degradation occurring between 400˚C and 420˚C. This can be attributed to certain defects in the polymer matrix. However, the thermal stability improved started increasing after the addition of 1%wt composition, attributable to the high level of compatibility between the CNTs and the polymer matrix. Comparable behavior in terms of thermal stability of membranes containing CNTs has been reported in the literature (Chen et al., 2009; Xu et al., 2017). Upon the incorporation of fCNTs, the thermal stability declined. It has been reported that the functionalization of CNTs tends to reduce the thermal stability of nanocomposite, which is due to the present carboxylic groups on the CNTs that are easily broken at lower temperatures (Luo et al., 2011). This could explain the observation when 1 wt% of fCNTs was added. Figure 4.4 shows a single high peak, confirming good compatibility between the blended polymers and CNTs. The shallow peak between 100˚C-200˚C represents the loss of solvent (NMP) contained in the membrane, which has a boiling point of 202˚C.

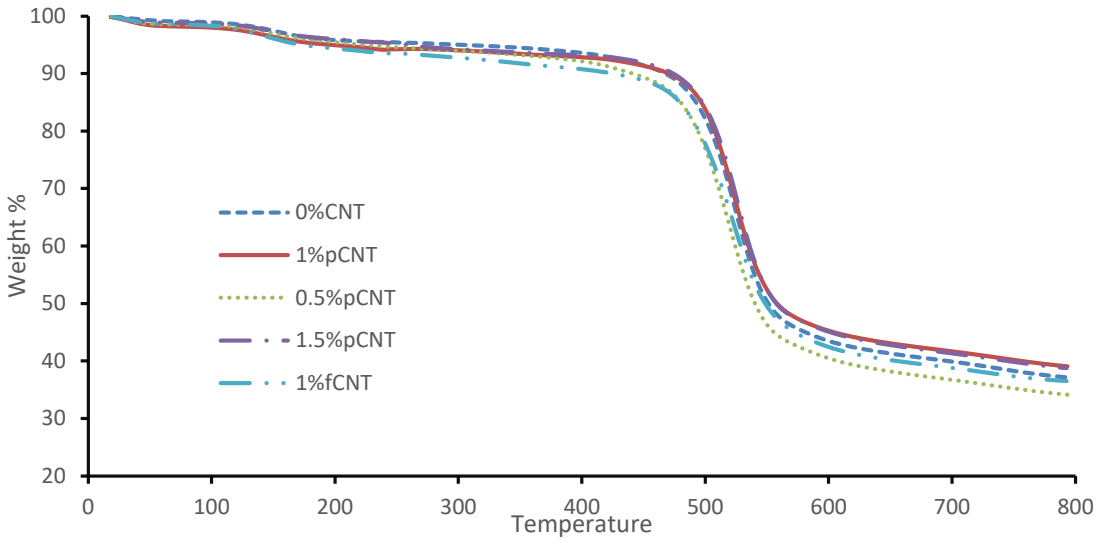


Figure 4-3. TGA curves of blended PSF/PES membranes with different CNT concentrations

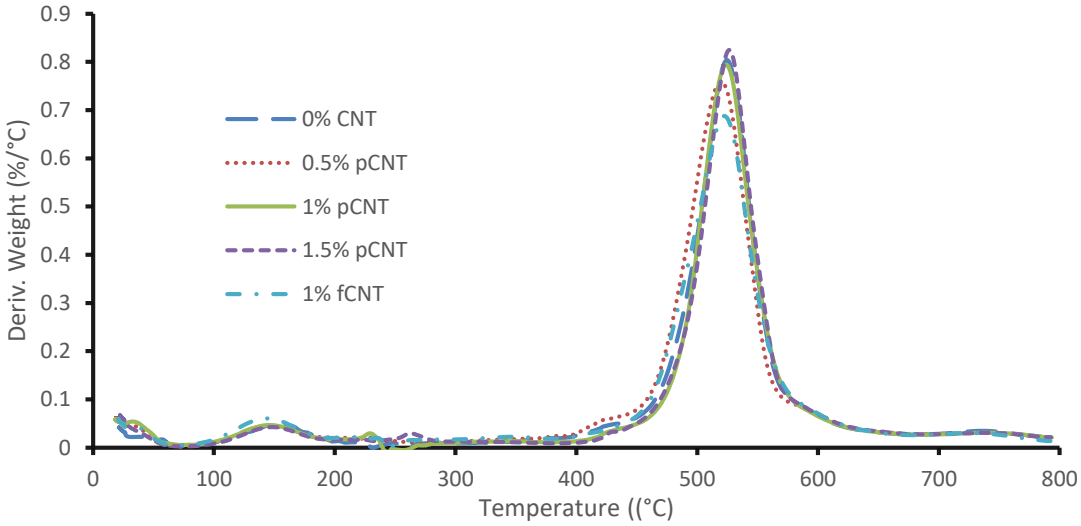


Figure 4.4. Thermographs of blended PSF/PES membranes with different CNT concentrations

Incorporation of CNTs has been reported to increase the life span of membranes by enhancing their robustness, making them less susceptible to break during operation (Esbati and Irani, 2018). This is due to the strong chemical bonds between carbon atoms found in single graphene of CNTs. Ideally, pressing on the tip of a nanotube causes it to bend rather than breaking, and usually goes back to its original shape when the pressing force is released (Shima, 2011). This improves the membrane tensile strength when incorporated in the polymer matrix. Figure 4.5 summarizes the results obtained from the nano-tensile tests. It is observed that the tensile strength of the membranes increased with an increase in pCNT concentration. The 1.5 %wt pCNT membrane is the most stable in terms of mechanical strength. The tensile strength of this membrane increased with over 35% as compared to the pristine membrane, thus making it the best membrane with excellent tensile properties in this study. Using the functionalized CNTs in the PSF/PES further maximized the tensile strength of the membrane as expected. From these results, it is seen that embedding CNTs did improve the mechanical strength of the membrane in agreement with the literature (Phasha, 2017; Collins et al., 2000; Choi et al., 2006). The improvement in the tensile strength of the membrane could be attributed to the enhanced interaction between the polymer matrix and CNTs (Mehrabadi et al., 2018).

The same phenomenon was observed for Young's modulus. The ability of membranes to be stretched under constant pressure influences their industrial applications. As shown in Figure 4.6, the elasticity and strain of the membrane are dependent on the concentration of the CNTs; it increased with an increase in CNT concentration. From these results, it can be deduced that embedding CNTs has a positive impact on the mechanical properties of the membranes, confirming good interfacial interaction between the CNTs and the blended polymers.

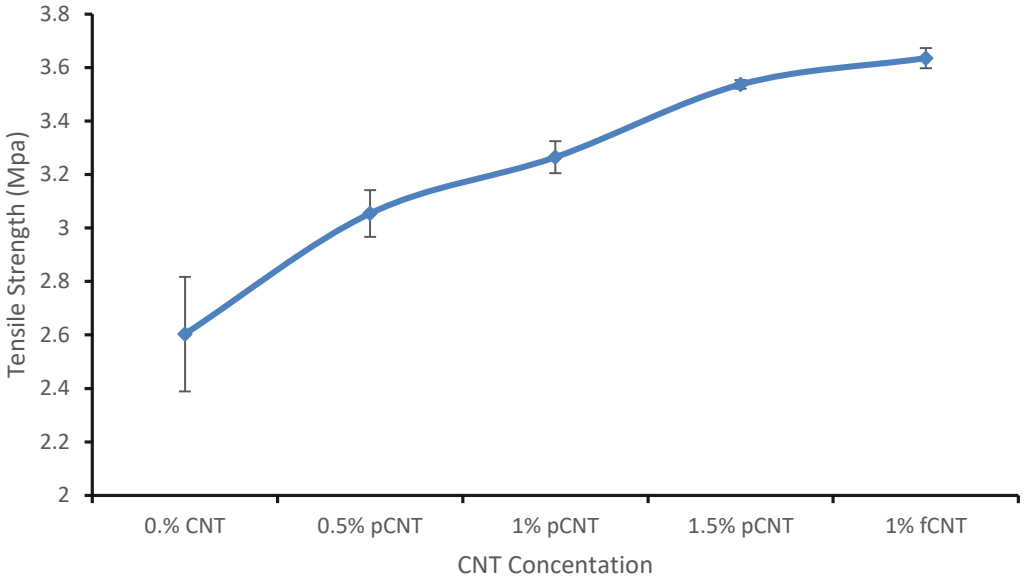


Figure 4.5. Tensile strength for CNT/PSF/PES blended membranes

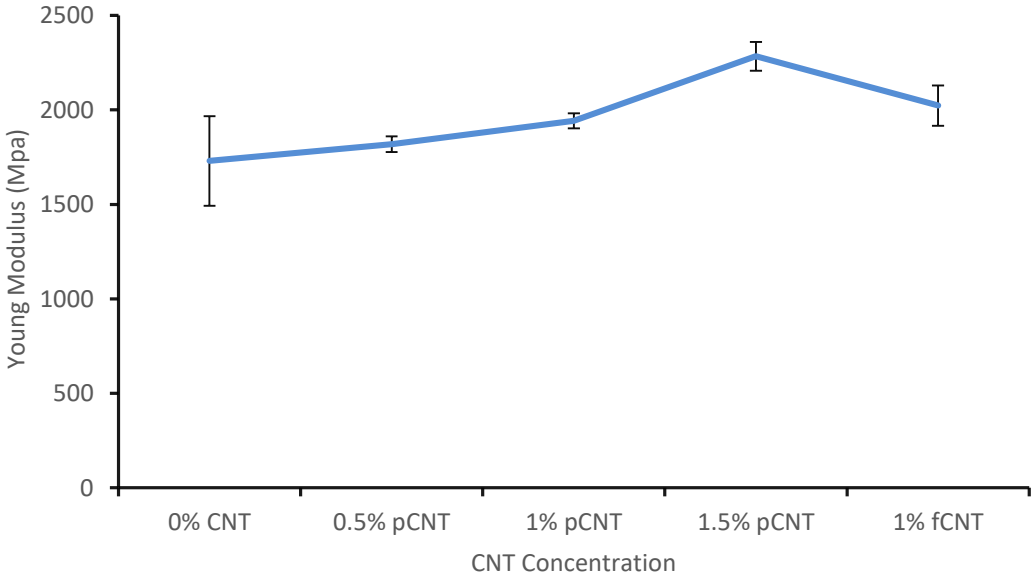


Figure 4.6. Young modulus for CNT/PSF/PES blended membranes

Generally, PSF and PES are known as hydrophobic polymers that foul easily due to hydrophobic foulant molecules that are driven toward the surface (Kumar and Ismail, 2015). AFM has become vital equipment for the membrane community when optimizing the fouling properties of membranes used for separation processes (Powell et al., 2017). The rougher the surface of the membrane, the more susceptible it is to foul over time. This is because a rough surface serves as microhabitats for foulants to flourish and form a cake layer, thus reducing the integrity of the membrane (Najjar et al., 2019). Therefore, a decrease in surface roughness reduces the ability of contaminants to accumulate on the membrane. For this study, the AFM was used to analyze the effect of CNT loading in the PSF/PES membrane by looking at the peak to the valley and surface roughness measurements of the prepared membranes. In general, imbedding CNTs alters the properties of the membrane surface, thus generating electrostatic forces between polymer chains (Mehrabadi et al., 2018). As observed in Table 4.2, it is shown that the roughness of the membranes decreased with an increase in CNT loading, making the membranes smoother compared to blended polymers. This is due to the hydrophilic nature of CNTs as comparable with the study conducted by Choi et al, (2006). The membrane with fCNT further reduced the roughness as compared to that of pCNTs, this is due to the added carboxylic acid groups on the CNTs surface which reduce the adhesion of fouling agents. Previous literature has reported that during phase inversion, fCNTs tend to travel towards the surface of the membrane, thus inducing the hydrophilic nature of the surface as expected. (Mehrabadi et al., 2018) Additionally, an increase in the hydrophilicity of a membrane provides more opportunity for water to chemically associate with the membrane surface, rather than foulants (Kumar and Ismail, 2015). These results indicate that

the composite membranes embedded with CNTs possess smoother surfaces, further improving their anti-biofouling property

Table 4.2. Effect of CNT loading on membrane roughness.

Membrane	Mean surface roughness (Ra-nm)	Root mean surface roughness (Rq-nm)
0% CNT	7.160 ±1.5	9.010 ±1,6
0.5% p-CNT	3.523 ±2.1	4.594 ±2.8
1% p-CNT	3.402 ±1.9	4.315 ±2.6
1,5% p-CNT	2.736 ±2.8	3.572 ±1.2
1% fCNT	1.865 ±0.7	2.420 ±1.7

Membranes need to demonstrate non-adhesive properties in order to be considered as robust hydrophilic membranes and be applied in wastewater treatment processes. Increased hydrophilicity of the CNT membranes changes the surface absorption properties, thereby improving the antifouling properties of the membrane (Kumar and Ismail, 2015). Generally, fouling agents are negatively charged, so adding negative functional groups to the CNTs increases the negative charge density of the membrane, therefore repelling the fouling agents introduced to the membrane during production (Yin and Den, 2015). The first sign of membrane fouling is decreased flux overtime

It is evident that the addition of CNT did have an effect on the surface nature of the membrane by altering the charge, hydrophilicity as well as roughness (Kumar and Ismail, 2015). The same membrane behavior was observed by Zhang et al., (2013). These results confirm the potential of incorporating CNTs to improve the overall performance of commercial membranes by preventing fouling, thereby reducing operational costs and increasing membrane lifespan.

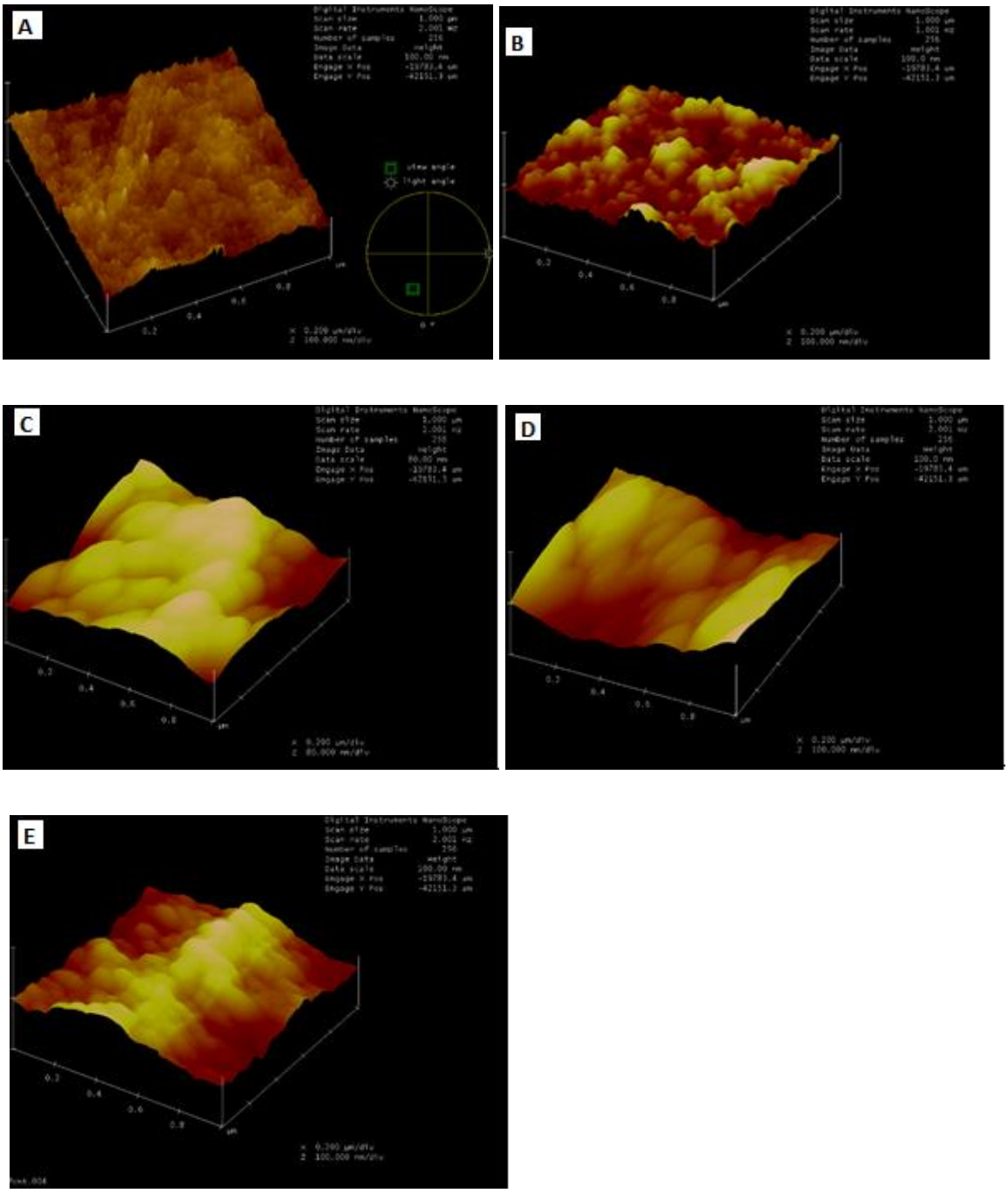
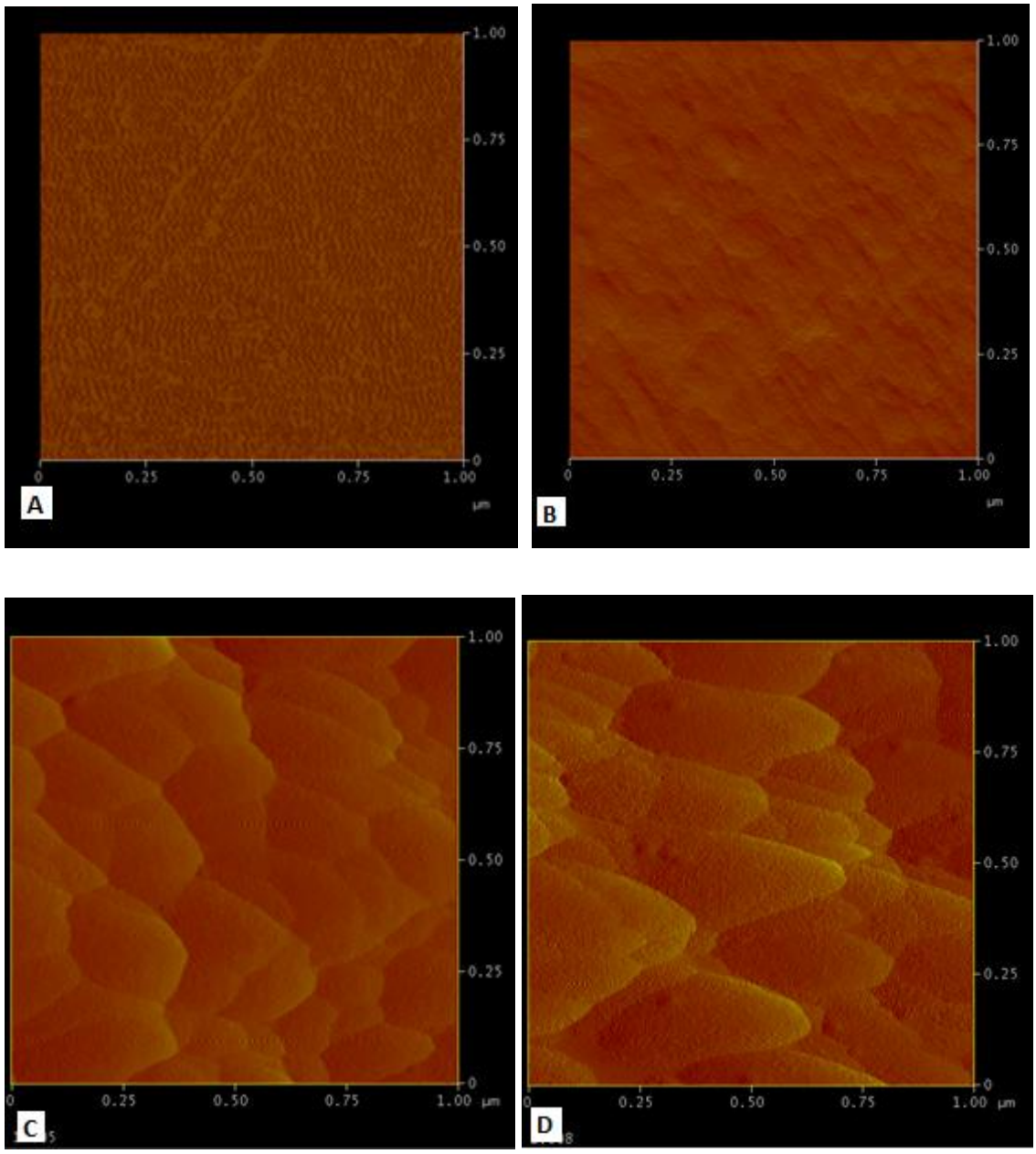


Figure 4.7. AFM 3D surface morphology images of a) 0%CNT, b) 0.5% p-CNT, c) 1%p-CNT, d) 1.5%p-CNT and e) 1%f-CNT


A
B
C
D
0
0.25
0.50
0.75
1.00
µm

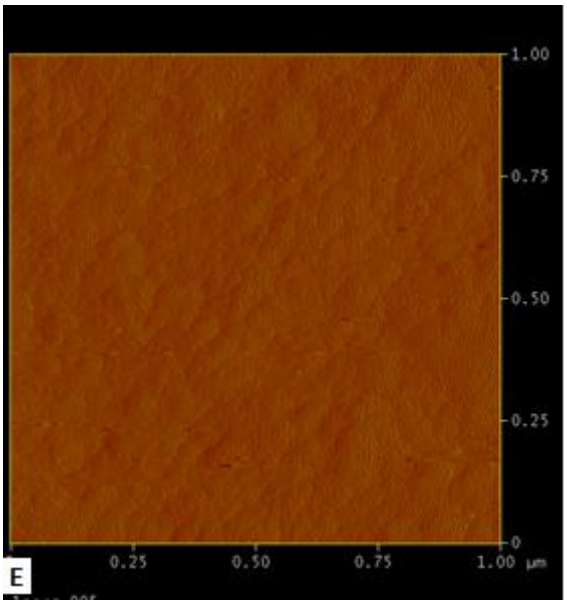
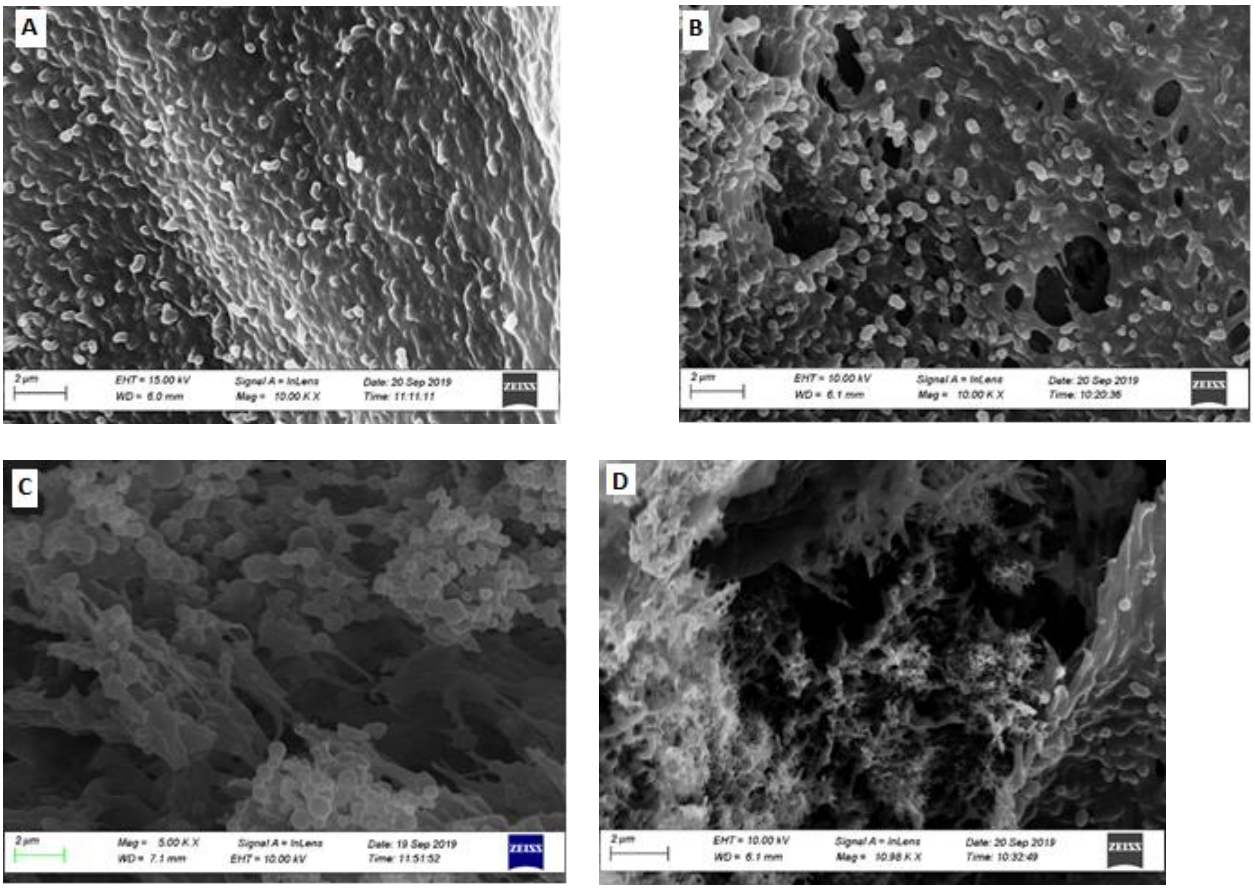


Figure 4.8. AFM 2D surface morphology images of a) 0%CNT, b) 0.5% p-CNT, c) 1%p-CNT, d) 1.5%p-CNT and e) 1%f-CNT

In order to evaluate the effect of CNT addition on the blended membrane, morphological analysis was conducted using SEM. Images of a cross-sectional view of the membrane were taken. The images were taken at a higher magnification of ×5 000. Figure 4.9 represents a high magnification cross-sectional image of PSF/PES/CNTs membranes. These images show an asymmetric porous structure with CNTs tangled with the polymer. It is clearly seen that the CNTs are arranged in a disorderly manner forming tangled threads. As seen from Figure 4.9a, the pores are very small and are not visible from the magnification used. However, after the addition of 0.5% pCNTs in Figure 4.9b, a few CNT strands are visible between the macro-voids. Macro-voids were also formed and increased significantly as the CNT concentration increased. Interfacial defects between the untreated nanoparticles and the polymer solution were expected. It is observed that by increasing the CNT concentration, the agglomeration effect is increased and thus more microvoids are

formed. The membranes with pure CNTs showed multiple localized aggregation which usually happens when the CNTs are not uniformly dispersed. This happens, as untreated CNTs tend to agglomerate due to van der Waals forces. Feng et al, (2015) reported that incorporating inorganic nanoparticles increases pore sizes when compared to pristine membranes. Figure 4.9e represents the blended membrane embedded with fCNTs, very little CNT agglomeration is observed from the matrix. This shows that functionalizing the CNTs improved the CNT dispersion as well as the pore formation in the membrane. These observations are in full agreement with the flux and porosity results presented in Figure 4.10 and Table 4.1.



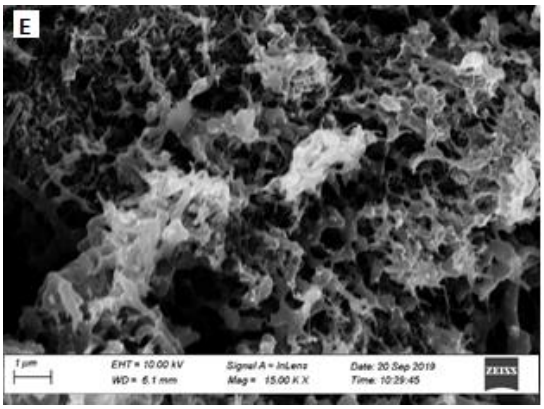


Figure 4.9. Cross-section SEM images of PSF/PES/CNT membrane (a) 0% pCNT, (b) 0.5% pCNT, (c) 1% pCNT, (d) 1.5% pCNT and (e) 1% fCNT

4.3.2 Performance evaluation of the membranes.

The flux of the membrane depends on its physicochemical properties, especially the hydrophilicity of the surface. The effect of CNT loading on CNT/PSF/PES membranes was investigated through a pure water permeation test. The water flux through the membranes was recorded and compared. As depicted in Figure 4.10, the membranes flux increased with an increase in pressure because of the increased driving force which raises the capillary pressure of the membrane, thus the pores (Sinha and Purkait, 2013). CNTs are reported to improve flux due to their hydrophilic walls which are able to interact with water molecules creating a frictionless passage. It is observed that adding 0.5wt% pure CNTs to the blended PSF/PES showed a decline in flux as compared to the pristine membrane. The reason for this could be due to the reduced frictional free volume of the polymer matrix. It was only after adding 1wt% and 1.5wt% pure CNT that the flux was enhanced and increased dramatically as the pure CNT concentration increased reaching a maximum flux of 309 $Lm^{-2}h^{-1}$ at a pressure of 300 kPa. One membrane was prepared with functionalized CNTs to

compare its performance with the pure CNT membrane. The functionalization of CNTs is generally known to influence both the chemical and physical properties of membranes, where the addition of these modified nanoparticles tends to further increase the surface pore sizes or the number of pores (Yang et al., 2016). Mehrabadi et al, (2018) reported that by functionalizing CNTs, some walls of the pore channels tend to breakdown, thus forming larger pores due to the accelerated phase separation during the phase inversion process. Nguyen et al, (2019) argued that the increase in flux after functionalization is due to hydrogen bonding between water molecules influenced by oxygen elements from the added functional groups, thus forming a thin hydration layer on the membrane surface. This confirms why the flux of the fCNT was higher than that of all pure CNTs with a maximum flux of 326 L/m2h at a feed pressure of 300 kPa.

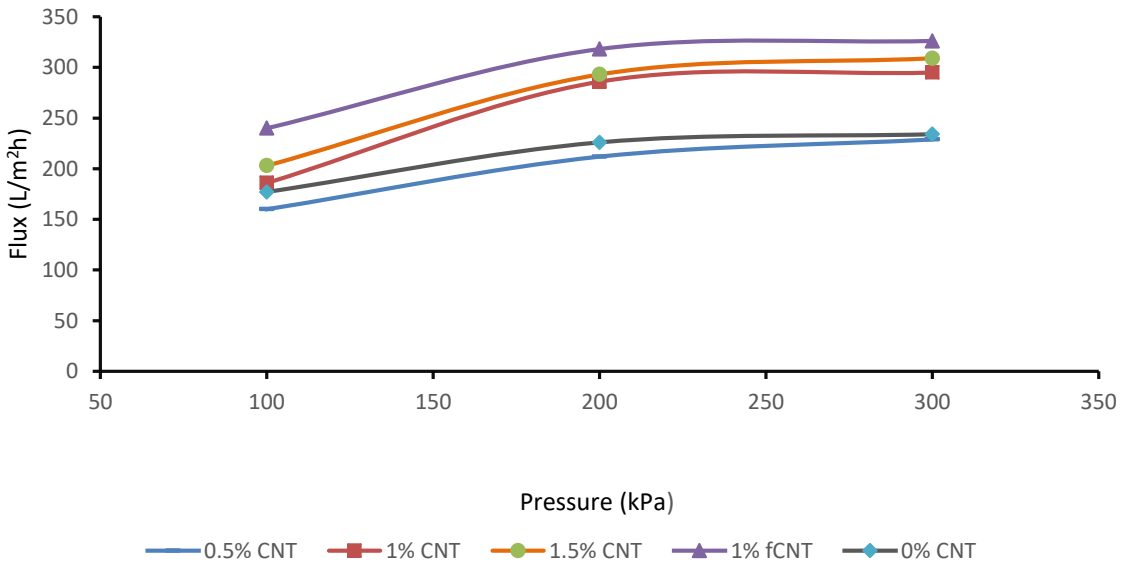


Figure 4.10. Effect of pressure and CNT concentration on membrane flux

The separation performance test was conducted to evaluate the effect of CNT concentration and CNT functionalization on the separation performance of the blended membrane at different pressure readings. The addition of CNTs not only influences the membrane flux, but it also has an effect on its selectivity. The effect of CNTs loading on phenol and benzene rejection was investigated during the treatment of synthetic wastewater containing 20 mg/L benzene and 30 mg/L phenol. Figure 4.11 and Figure 4.12 show the PSF/PES membrane has a higher rejection for both phenol and benzene than the PSF/PES/CNTs membranes. The reason for this is due to poor CNT dispersion and poor compatibility between polymer matrix and CNTs which results in increased macro voids, creating pores larger than phenol and benzene molecules. The membrane with fCNT showed enhanced % rejection as compared to that of pCNTs for both phenol and Benzene, confirming enhanced CNT dispersion as expected after functionalization. These results agree with the analysis obtained from the SEM as illustrated in Figure 4.9. Even at reduced feed pressure, % rejection of membranes with CNTs tends to decrease with an increase in pCNT loading, which is a result of an increasing number of pores as CNT concentration increases. This also explains the enhanced permeation flux of these membranes as illustrated in Figure 4.10. These results are comparable to what Phasha., (2013) reported. A decrease in the selectivity of phenol and benzene was observed as the feed pressure increased, this can be attributed to the increased driving force that pushes phenol and benzene molecules through the membrane pores.

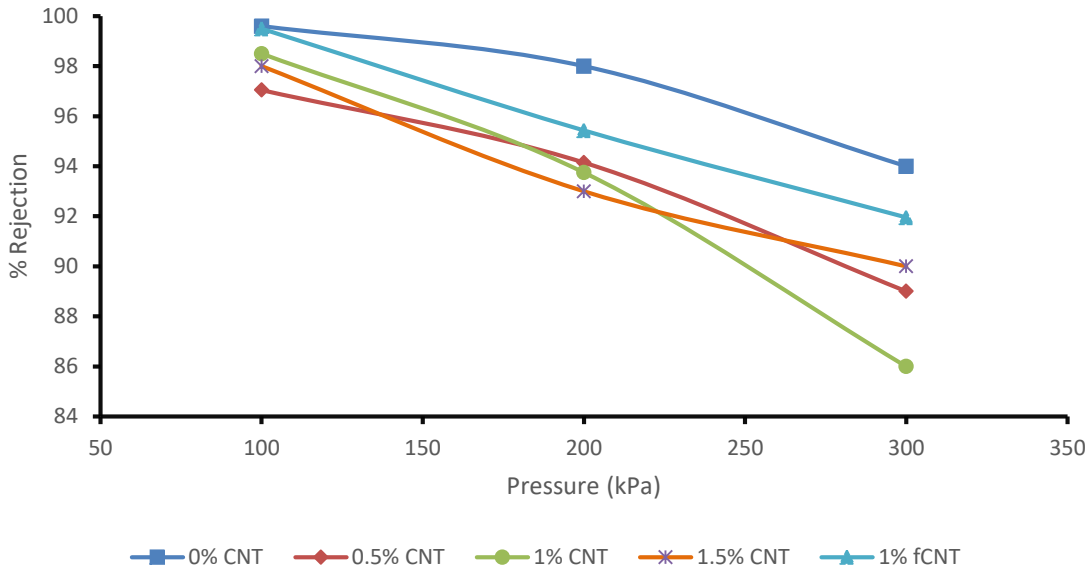


Figure 4.11. Effect of pressure and CNT concentration on Benzene rejection

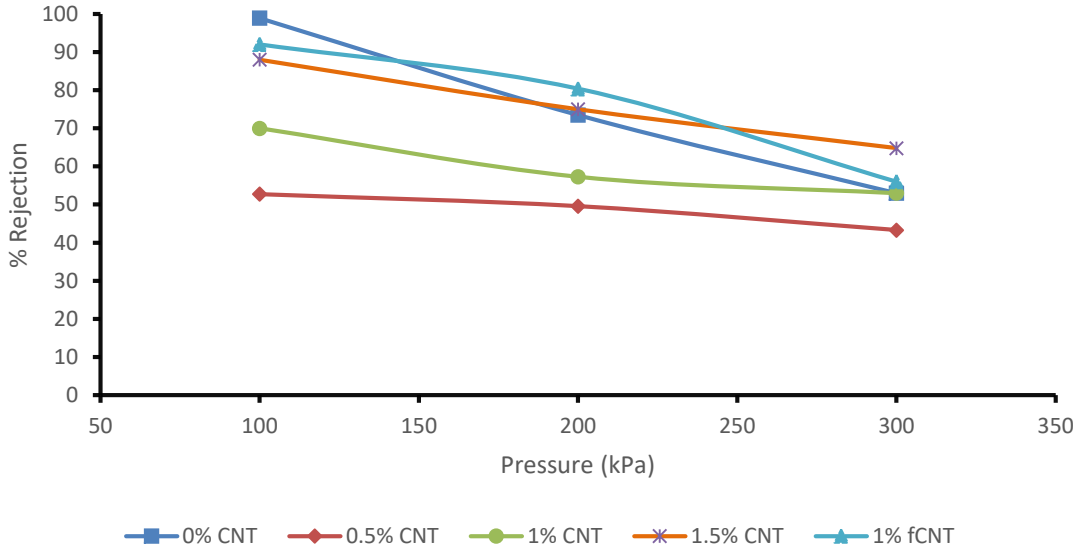


Figure 4.12. Effect of pressure and CNT concentration on Phenol rejection

4.4 Concluding remark

PSF/PES membrane embedded with pCNTs and fCNTs were prepared successfully via the phase inversion method. These membranes were tested during the treatment of synthetic wastewater containing phenol and benzene. The addition of CNTs enhanced both the porosity and the membranes' ability to absorb water from 1%wt CNT onwards. The flux of the membrane was 309 L/m^2h for 1.5% pCNT membrane and 326 L/m^2h for fCNTs membrane. However, as flux increased, % rejection decreased as compared to the pure membrane with no CNTs. This is due to the opening of pores and macro voids observed from the morphological analysis of these membranes. Though the % rejection decreased, all membranes showed acceptable benzene rejection while only two membranes (1.5% pCNT and 1% fCNT) produced desired results for phenol rejection. The effect of feed pressure on the performance of the membrane was also evaluated. Increase in feed pressure enhanced membrane flux. However, %rejection was inversely proportional to the increasing pressure. The morphological analysis of the membranes obtained from the SEM confirmed the presence of CNTs, with a noticeable agglomeration of CNTs within the membranes. However, the functionalization of the CNTs improved the dispersion of CNTs, attributable to improved interfacial interaction between the polymer and the nanoparticles. The mechanical strength, thermal stability, and surface nature of the membrane also improved drastically after adding CNTs, with optimum results obtained from the membrane with fCNTs which was expected. The roughness of the membrane decreased with an increase in CNT content, thus enhancing the antifouling properties of the membrane. According to the results obtained, reinforcing fCNT in the blended membrane produced a desirable membrane material with good separation performance.

CHAPTER 5

5 Conclusions and Recommendations

5.1 Conclusions

The main aim of this research was to synthesize blended PES/PSF polymer composite membrane and embed them with CNTs at different loadings. Furthermore, the study arrived at evaluating the separation performance of these membranes during the treatment of synthetic wastewater containing phenol and benzene. To achieve this, the first objective was to synthesize PSF, PES, and blended PSF/PES membranes, characterize and evaluate their separation performance. The blended membranes were prepared with PSF and PES at different compositions. Then, the prepared membranes were tested for the treatment of synthetic wastewater after characterizing the membranes. The separation performance of the membranes was tested using a dead-end filtration cell for the removal of phenol and benzene from wastewater. Characterization of the membranes shows a miscible blend of PSF and PES, with no sign of phase separation, resulting in enhanced thermal stability, mechanical strength, and separation performance. From these findings, the best performed blended membrane (25%PSF-75%PES) was selected for further studies. The limitations observed with the blended membranes were their hydrophobic nature, which was revealed from the AFM roughness analysis.

The next objective was to load CNTs in the blended membrane and investigate their effect on the physicochemical property, hydrophilicity, thermal stability, and separation performance. CNTs were embedded into the membrane at different loadings. Results showed a further improvement in the porosity, hydrophilicity, thermal stability, and mechanical strength of the blended

membrane, especially when the 1.5 wt% CNTs were loaded. However, there was a slight decrease in % rejection of both phenol and benzene by the CNT infused PSF/PES membranes, due to poor CNT distribution, thus forming interfacial defects such as microvoids between the CNTs and polymer matrix. This also had an effect on the increased pure water flux of the membrane (Shawky et al., 2011). The increase in feed pressure during separation filtration also had an effect on the rejection and water flux of the membrane. The higher the feed pressure, the higher the flux due to the forceful opening of pores by the transmembrane pressure, which also resulted in lower phenol and benzene rejection. Another membrane was embedded with functionalized CNTs to compare their effect with the pure CNTs. The SEM images of the membrane with fCNTs showed improved CNT dispersion as compared to the membranes with pCNTs. An improvement in CNT dispersion increases its reinforcement effect. This explains why the fCNT membrane showed desirable results, with increased mechanical strength, hydrophilicity, porosity, flux, and % rejection of both phenol and benzene as compared to the membranes with pCNTs.

5.2 Recommendations

Further research can be done on optimizing the synthesis protocol towards enhancing the separation performance of the membrane, by looking at the effect of polymer concentration and CNT dispersion. It would be interesting to see what polymer concentration gives better mechanical strength without compromising the separation performance. It would also be helpful to use real wastewater from industry to test the membrane to get an adequate sense of separation performance of the membrane pollutants of concern. The separation of real wastewater can be done to also check if there is a need to apply pre-treatment methods. The regeneration of the blended membranes can also be explored.

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APPENDIX A: AFM supporting data

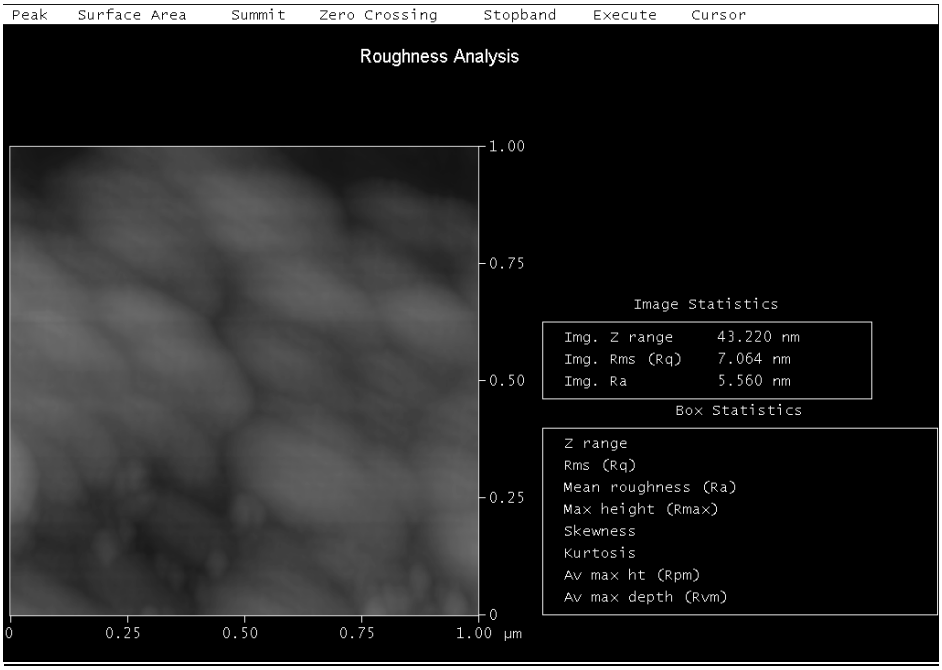

Figure A.1. Roughness analysis for 100%PSF

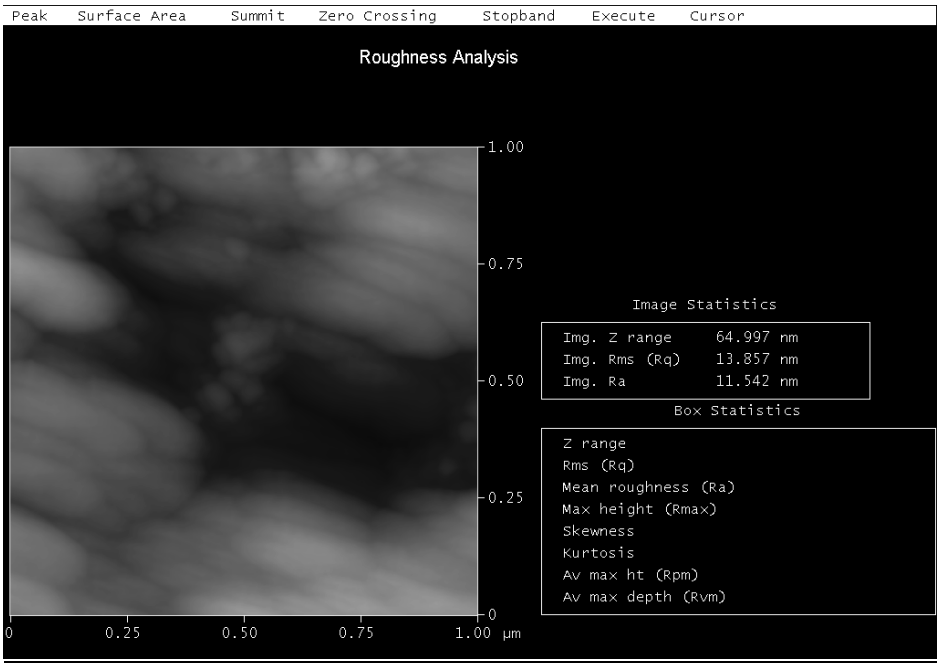

Figure A.2. Roughness analysis for 100% PES

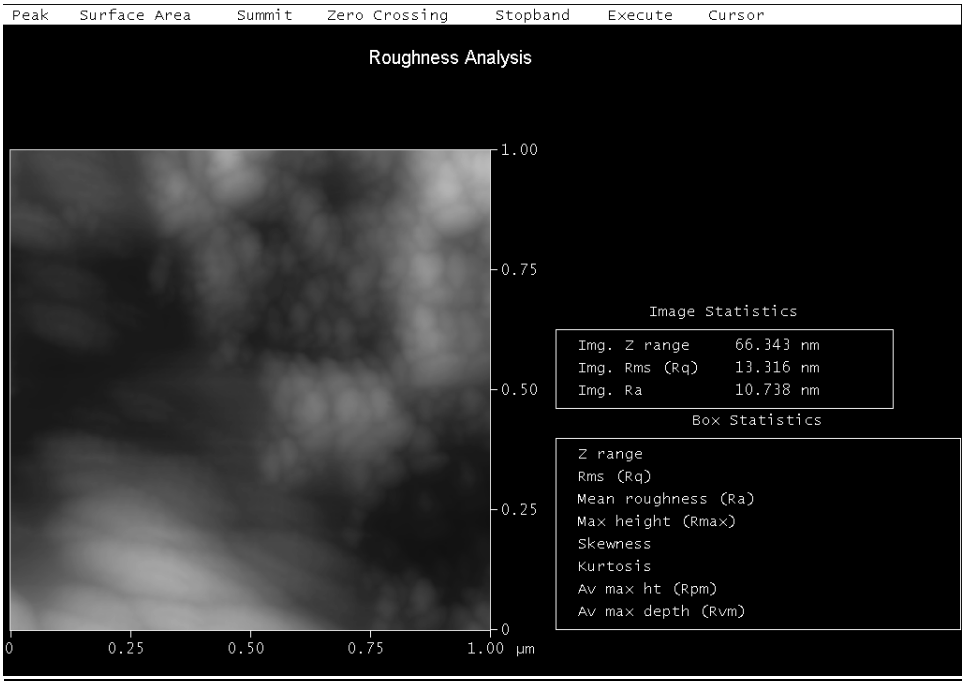

Figure A.3. Roughness analysis for 20PSF:80PES

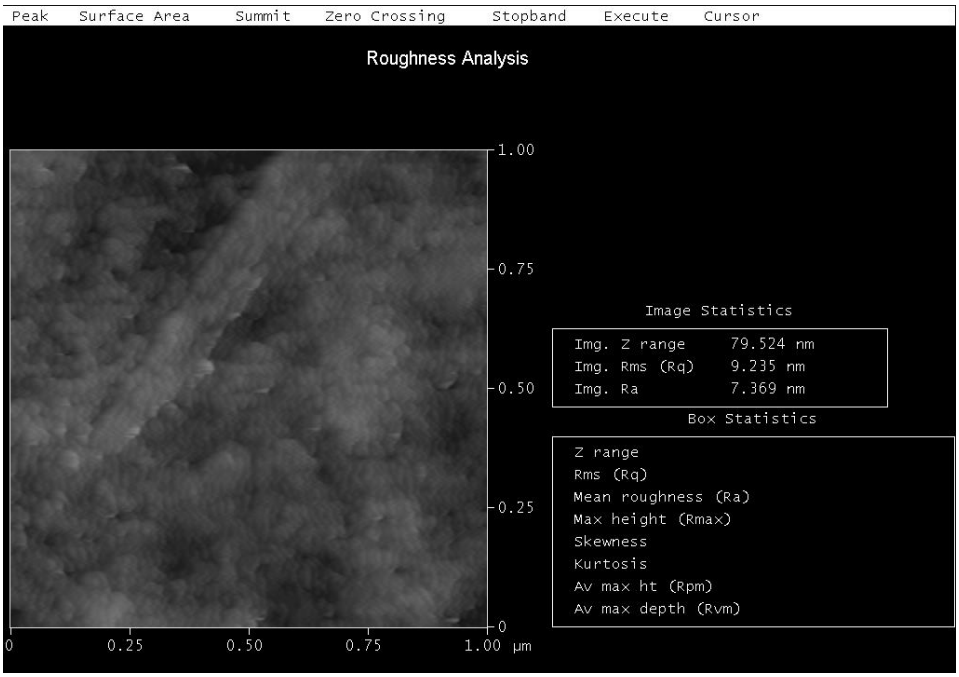

Figure A.4. Roughness analysis for 25PSF:75PES

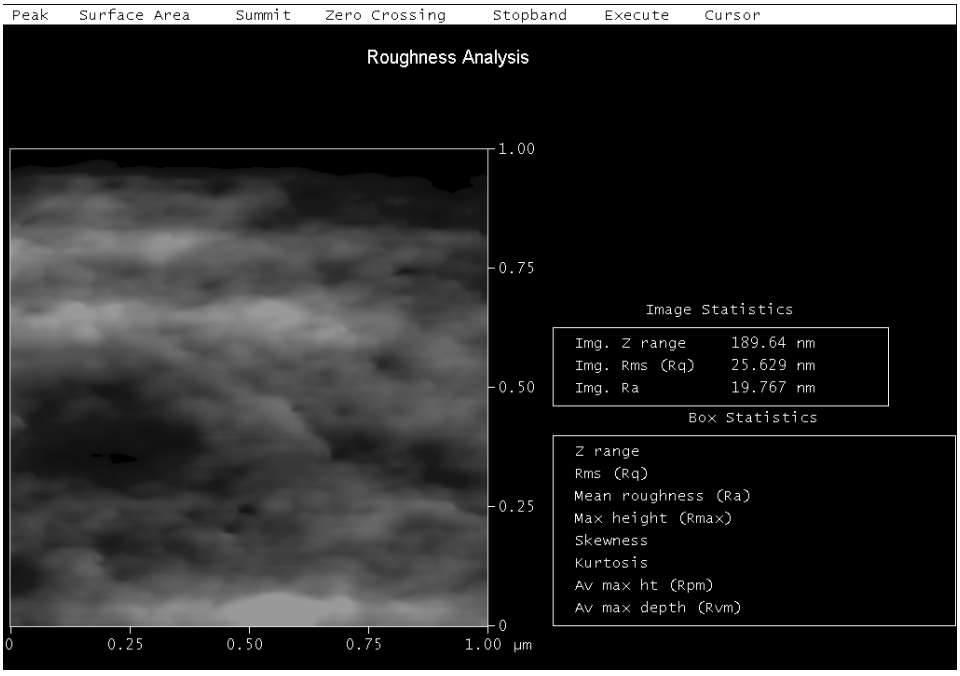

Figure A.5. Roughness analysis for 50PSF:50PES

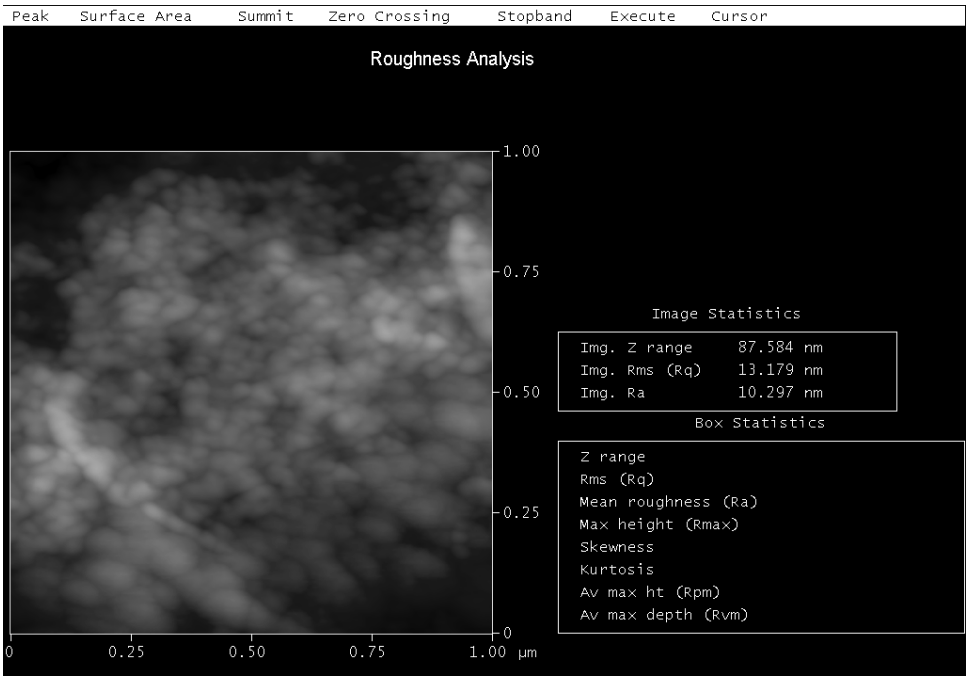

Figure A.6. Roughness analysis for 80PSF:20PES

APPENDIX B: AFM supporting data

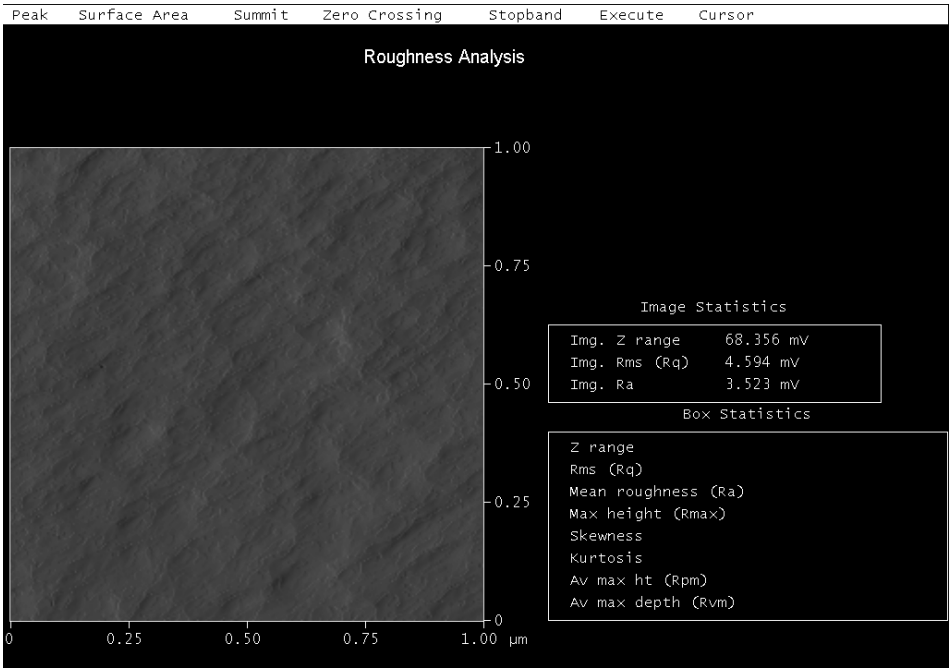

Figure B.1. Roughness analysis for 0.5% pCNT membrane

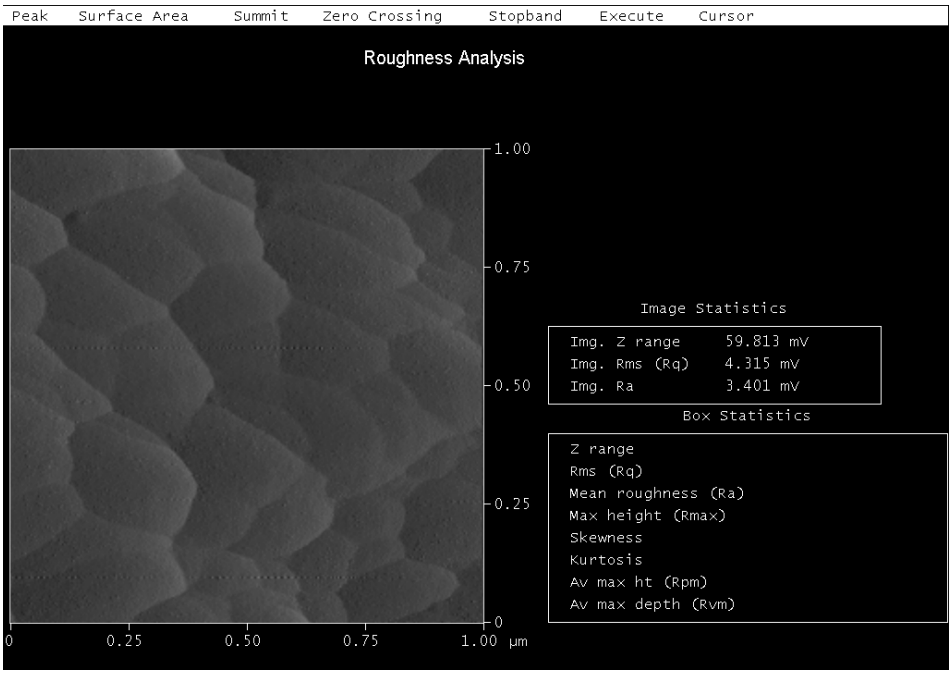

Figure B.2. Roughness analysis for 1% pCNT membrane

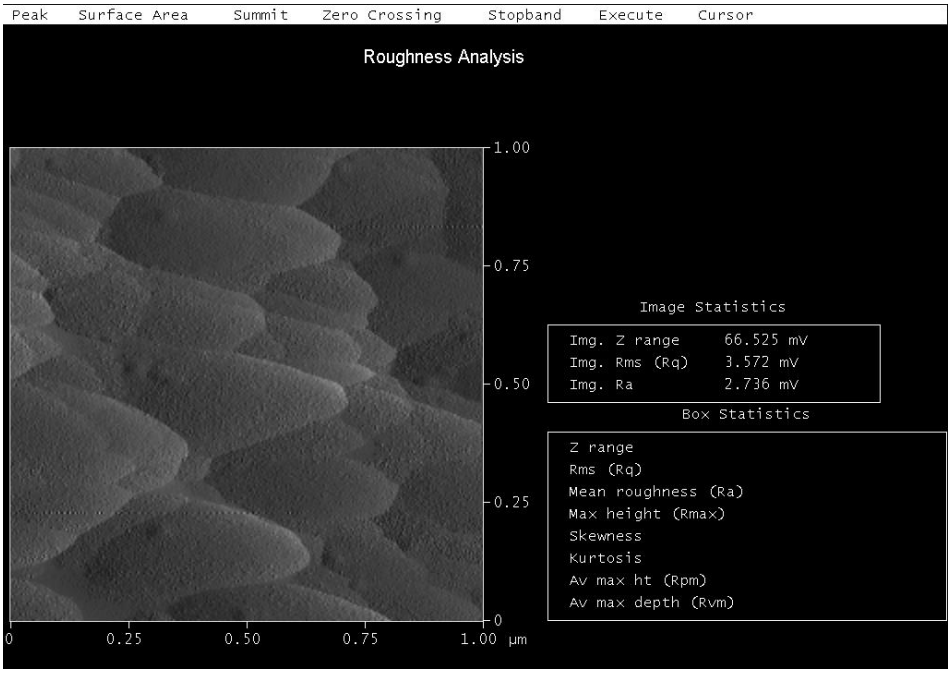

Figure B.3. Roughness analysis for 1.5% pCNT membrane

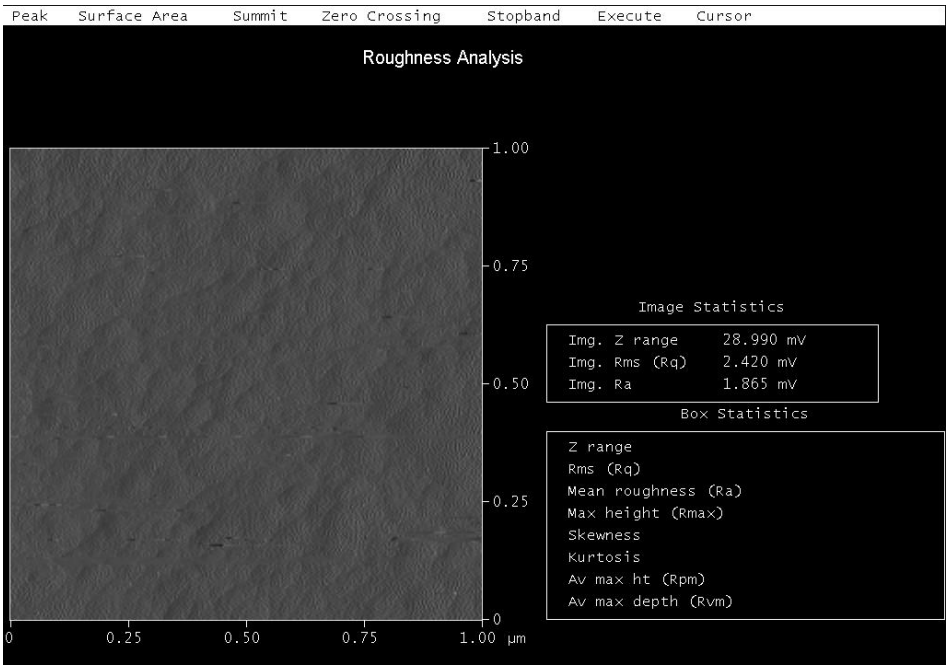

Figure B.4. Roughness analysis for 1% fCNT membrane

APPENDIX C: FTIR analysis.

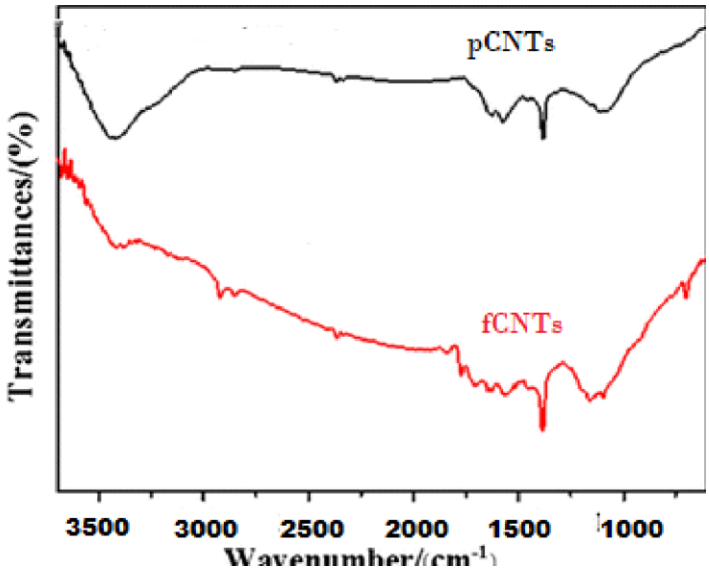

Figure C-1. FTIR spectra of pCNTs and fCNTs.