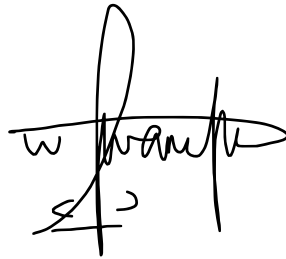


Declaration

I, Kwame Owusu-Ansah, declare that this dissertation is my own work. It is being submitted for the degree of Master of Science to the University of the Witwatersrand. It has not been submitted before for any degree or examination to any other university.

A handwritten signature in black ink, appearing to read 'Kwame Owusu-Ansah', with a stylized flourish at the end.

Kwame Owusu-Ansah

October 28, 2014

Executive summary

Membrane technology is widely used for water treatment purposes in a wide array of industries. This research focused on the use of this technology in the oil and gas industry. This is primarily because of its low cost and low energy requirements, its environmental friendliness and its ability to treat large quantities of waste water. The ability to scale membranes makes them very attractive for use on offshore platforms where space is limited. This research focused on the use of polymeric membranes in the treatment of produced water primarily from enhanced oil recovery (EOR) processes. This is when the energy of the oil or gas reservoir is boosted using chemicals, heat, biological or technical techniques. Water is a highly used resource in this process and this contributes to the large quantities of produced water waste from this industry.

Carbon Nanotubes (CNTs) were first produced and characterized. CNTs are widely studied nano-materials due to their good qualities and vast applications. Numerous techniques have been developed for the synthesis of this material with chemical vapor deposition method (CVD) being most common. This involves the growth of CNTs, usually in the presence of a catalyst at a high temperature. The effect of the catalyst support (zeolite and CaCO_3) on the synthesis of CNTs was first studied. It was observed that CNTs that were grown from zeolite supported catalysts (CNT-z) had smaller outer diameters ranging from 10nm to 50nm, while CNTs grown from CaCO_3 supported catalysts (CNT-c) had larger outer diameter of 20nm to 80nm. This disparity in the outer wall diameter was still evident after functionalization with HNO_3 . Another difference between the two supports was the CNT purity achieved after synthesis. Functionalized CNT-z (fCNT-z) had more catalytic impurities than functionalized CNT-c (fCNT-c), which was almost clean of any residual catalyst. The impurities in the fCNT-zs were found to be SiO_2 . This was removed by HF treatment to give very pristine CNT-zs. The CNTs were characterized with Raman, Fourier transform infrared radiation (FTIR), thermogravimetric/derivate weight loss analysis (TGA/DTG), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The fCNT-cs were used in the membrane preparation because of their larger size, which meant better interaction with the membrane structure.

Two techniques were used in the production of the membranes: the solution casting method (SC method), which produced non-porous, dense and isotropic membranes, and the phase inversion method (PI method), which produced micro-porous anisotropic membranes. The membranes were modified using fCNTs and a polyester non-woven fabric (NWF). The membranes were characterized using the SEM, atomic force microscopy (AFM), contact angles, FTIR, TGA/DTG and tensile

strength analysis. The surface morphologies clearly revealed the surface pores while the cross sections showed voids. The pore sizes ranged from $1.598\mu\text{m}$ for the membranes with the NWF, to 0.191mm for the CNT imbedded membranes without the NWF. The surface pores were not as evident in the solution cast membranes. The dense nature of these membranes meant they had significantly higher tensile strengths and Young's moduli. Rougher membranes were produced with the PI method and this confirmed the presence of pores with lower contact angles. TGA/DTG showed that SC membranes were more thermally stable at higher temperatures than the membranes produced *via* PI.

Functionalized CNTs interacted with the hydrophobic membranes to enhance its physical, chemical and mechanical properties. CNTs reduced the contact angles, increased the surface roughness, pore and void sizes and the tensile strengths for both kinds of membranes. It however reduced the thermal stability and rigidity of the membranes. The addition of the NWF support also decreased the pore sizes of the membranes by PI and introduced voids into the membranes by SC.

The PI membranes were tested for performance using a synthetically made produced water. It was shown that increasing pressure increased permeate flux. Functionalized CNTs also increased permeate flux while controlling fouling via pore blockage. The addition of NWF also resulted in flux decline by providing additional resistance to the flow of permeate through the membrane. Water and oil permeates were then collected and tested for oil concentrations. The results showed oil rejections ranging between 78% and 90% with the mixed matrix PI membranes supported on a polyester NWF having the highest oil rejections.

Dedication

This work is dedicated to God Almighty who provided the will, energy and wisdom to complete this work successfully. I also dedicate it to my parents and siblings, Alex, Matilda, Yaw and Akosua Owusu-Ansah for their continual support.

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A large group of people assisted me with this work in one way or the other and it would be impossible to list each and every one of them. But to all those who helped, I would like to say a huge thanks!

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Nomenclature

A	Membrane area in m^{-2}
A_l	Load bearing area
AFM	Veeco Di3100 atomic force microscope
CNT	Carbon nanotubes
CM	Solution cast membranes using the casting machine
CVD	chemical vapor deposition
CNT-c	As-grown CNTs on Fe Co on $CaCO_3$ catalyst
CNT-z	As-grown CNTs on Fe Co on zeolite catalyst
C_f	Concentration of feed synthetic oil in mg/l
C_p	Concentration of permeate in mg/l
δ_d	Dispersive component of the Hansen solubility parameters
δ_h	Hydrogen bonding component of the Hansen solubility parameters
δ_p	Polar component of the Hansen solubility parameters
δ_t	Total solubility component of the Hansen solubility parameters
DMAc	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DTG	Derivative weight loss analysis
E	Young's modulus
EDS	Energy dispersive spectroscopy

EOR	Enhanced oil recovery
fCNT-c	Functionalized CNTs on Fe-Co on CaCO ₃ catalyst
fCNT-z	Functionalized CNTs on Fe-Co on zeolite catalyst
fCNTs	Functionalized/ acid treated carbon nanotubes
FD _t	Flux decline in
FTIR	Bruker TENSOR 27 fourier transform infrared radiation
HF	Hydrofluoric acid
HiPCO	High pressure carbon-mono-oxide disproportionation method
I _{D/G}	Intensity ratio for Raman
J _o	Initial flux in $lm^{-2}.h^{-1}$
J _p	Flux of permeate in $lm^{-2}.hr^{-1}$
J _r	Relative flux
J _t	Flux after every 15min in $lm^{-2}.h^{-1}$
MARS	Membrane aromatic recovery system
MF	Microfiltration
MWCO	Molecular weight cut off
NF	Nanofiltration
NMP	1-Methyl-2-pyrrolidinone
NORM	Normally occurring radioactive materials
NWF	Polyester non-woven fabric
PI	Phase inversion membranes
PAH	Polycyclic aromatic hydrocarbons
PES	Polyether sulfone
PSf	Polysulfone
R	Percentage oil rejection
R _a	Mean roughness

RO	Reverse osmosis
SEM	FEI Nova Nanolab 600 scanning electron microscope
σ	Stress in kPa
TEM	FEI Tecnai Spirit G2 transmission electron microscope
TGA	TA SDTQ 600 thermogravimetric analysis
Δt	Running time fore filtration in <i>hrs</i>
UF	Ultrafiltration
US EPA	United States environmental protection agency
UTS	Ultimate tensile strength
V	Volume of permeate in L
XRD	Bruker D2 phaser X-ray diffraction

Chapter 1

Introduction

1.1 Background and motivation

The search for crude oil has reached new heights with oil explorers delving into increasingly harsh and dangerous terrains, employing even more complex processes in order to find this highly essential resource. The advances in exploration technologies and processes have been closely followed by stringent environmental laws, forcing explorers to come up with ways that thoroughly treat their waste or devise techniques that are less harmful to the environment (Muehlenbachs et al., 2013). Produced water or industrial oil wastewater is the largest waste stream from oil and gas exploration and production processes, making it the focus of treatment processes in middle and downstream activities (Ebrahimi et al., 2010).

Underground saline water is denser than crude oil. Saline water settles in reservoir rocks and it comes out with some oil and gas during the drilling process. The water that comes out is known as produced water or formation water. Water, injected into the oil wells during exploration also forms produced water when it comes to the surface with the oil and saline water mixture. Produced water contains various organic and inorganic impurities dissolved in the dispersed oil or in the water (Fakhru'l-Razi et al., 2009). These impurities cannot be discharged directly to the environment. Typical concentrations of oil in produced water ranges from 50 mg of oil per liter of produced water (50 mg/l) to 1000 mg/l or more, depending on the oilfield (Chakrabarty et al., 2008a). This has the potential to adversely affect the environment. Contaminants in dispersed oil include polycyclic aromatic hydrocarbons (PAHs), heavy alkyl phenols (both of which are very harmful carcinogens), dissolved minerals that contain trace amounts of heavy metals and normally occurring radioactive materials (NORMs) such as radium 226 and 228 (Bakke et al., 2013). Some chemicals used in the drilling process end up in produced water and are also generally unfriendly to the environment (Fakhru'l-Razi et al., 2009).

Various environmental organizations strictly regulate the contents of discharged produced water. The United States environmental protection agency (US EPA) for example, has a daily discharge limit of produced water of 42 mg/l and a monthly discharge limit of 29 mg/l while the Nigerian government sets the daily and monthly discharge limits at 72 mg/l and 40 mg/l respectively (Veil,

2006). The quantity of produced water from offshore and onshore activities is approximately three times that of oil that is refined: 250 million bbl. of oil/d to 80 million bbl. of oil/d (de Figueredo et al., 2014). This puts a lot of pressure on oil explorers to conform to these regulations by either developing technologies that reduce wastewater production, recycling treated wastewater or safely dispose them off.

The huge quantities of this wastewater produced make it difficult to simply dispose off. However, the reuse of treated produced water is a very viable option. Treated produced water can be used as an injection fluid to enhance oil production, for irrigation and even as drinking water for animals and wildlife (Veil et al., 2004). It also has a number of useful industrial applications like fire control, plant makeup water *etc.* Produced water from onshore processes is treated using physical and chemical treatment methods. However these methods are not suitable for wastewater from offshore processes. This is because of spatial limitations on offshore platforms. These treatment processes are costly and toxic chemicals are often employed in the process (Fakhru'l-Razi et al., 2009). Biological treatment processes, unlike physical and chemical treatment processes, are less costly and are better at removing dissolved and suspended compounds from the wastewater. However, like physical and chemical treatment processes, it is not suitable for offshore platforms because of the limited space on offshore platforms (Fakhru'l-Razi et al., 2009; Kołtuniewicz and Field, 1996). These limitations of physical, chemical and biological treatment methods can be overcome by membrane treatment processes.

Membrane treatment processes are suitable for medium to large offshore platforms as well as the treatment of produced water onshore. They are able to retain dispersed oil droplets from the produced water and permeate the continuous water phase. They also have lower capital costs, lower energy requirements, make no use of toxic chemicals and can treat large flows of waste to produce high quality permeates (Wu et al., 2008). Membrane filtration often requires a driving force such as a pressure difference or a concentration difference but this can sometimes deform the oil droplets, allowing it through the membrane pores to contaminate the permeate (Chakrabarty et al., 2008a). The major problem with membranes however is fouling (Liu, 2014; Kang and Cao, 2012). Fouling significantly increases the cost of wastewater treatment using this technology. One way of controlling fouling is by increasing the hydrophilicity of the membrane. Membranes can be made hydrophilic by modifying them with materials like CNTs or polyvinyl alcohol Maphutha et al. (2013); Li et al. (2006); Phao et al. (2013).

The aim of this research was to investigate how modified membranes can be used in the treatment of produced water specifically from oil and gas drilling activities. The membranes were modified with fCNTs and a polyester NWF fabric. Numerous studies have been done on the use of CNTs in water treatment, however very few have been done on the combined effects of fCNTs with NWF Chakrabarty et al. (2010); Arockiasamy et al. (2013); Celik et al. (2011); Maphutha et al. (2013). It was hypothesized that these alterations can be effective in separating the oil from the water from produced water. This would be especially useful for deep offshore platforms where large quantities of produced water are produced and space is limited. Crude oil was used in the

production of synthetic produced water to simulate the characteristics of produced water. The performance of the membranes in the treatment of the produced water is reported. The effect of CNTs and the NWF support on the membranes properties and also on oil rejections was studied in detail.

1.2 Research objectives

The aim of the research was to explore the performance of modified membranes in the treatment of synthetically made waste-water (produced water). It also explored the physical and chemical properties of the CNTs and the membranes, investigating how well the membranes reduced the oil content in the wastewater to acceptable discharge levels.

The objectives of the research were as follows:

- To synthesize and characterize Fe/Co catalysts *via* the wet impregnation method, for the preparation of CNTs. CNTs were synthesized using the CVD method.
- Investigate the effect of the catalyst support on the properties of CNTs.
- To produce polymeric membranes blended with CNTs (mixed matrix membranes), and to investigate their effect on the properties and performance of the membranes.
- Investigate the influence of membrane preparation techniques on the membrane's properties.
- Investigate the influence of the NWF on the properties of the membrane
- Investigate how fouling affects the permeate fluxes
- Investigate the performance of the membranes in separating water from crude oil in a cross flow filtration system

1.3 Outline of dissertation

Chapter 1: This chapter briefly motivates the need for membrane technology in wastewater treatment on offshore platforms. It explains how this waste comes about in the first place. It then touches briefly on how current processes fail to adequately meet the needs of oil explorers in treating this waste to the accepted levels before being discharged or recycled. The primary aim and objectives of the project is also outlined in this chapter

Chapter 2: This chapter provides an overview of the various parts of the project, looking at membrane technology and its applications in the petroleum industry. It looks briefly at nanotechnology, summarizing the various synthesis methods for CNT production and the precursors and carbon sources best suited for filtration applications.

Chapter 3: This chapter outlines the materials and various experimental procedures used to achieve the research objectives outlined in Chapter 1. These procedures include the production of synthetic oil/water wastewater, the production of the CNT catalyst, CNT synthesis, membrane preparation and the various characterization and property tests.

Chapter 4: This chapter presents and discusses the results from the experimental work, linking them to the hypotheses drawn in the Chapter 2. Results from the catalyst preparation and CNT synthesis are discussed and these results inform the CNT choice used in the membrane preparation. Results obtained from characterizing and property evaluations of the various membranes are then presented.

Chapter 5: Findings, conclusions and recommendations drawn from this work are presented in this chapter.

References

- Arockiasamy, D. L., Alam, J., Alhoshan, M., Mar. 2013. Carbon nanotubes-blended poly(phenylene sulfone) membranes for ultrafiltration applications. *Applied Water Science* 3 (1), 93–103.
- Bakke, T., Klungsøyr, J., Sanni, S., 2013. Environmental impacts of produced water and drilling waste discharges from the norwegian offshore petroleum industry. *Marine Environmental Research* 92, 154–169.
- Celik, E., Park, H., Choi, H., Choi, H., Jan. 2011. Carbon nanotube blended polyethersulfone membranes for fouling control in water treatment. *Water Research* 45 (1), 274–282.
- Chakrabarty, B., Ghoshal, A. K., Purkait, M. K., Feb. 2008a. Effect of molecular weight of PEG on membrane morphology and transport properties. *Journal of Membrane Science* 309 (1–2), 209–221.
- Chakrabarty, B., Ghoshal, A. K., Purkait, M. K., Dec. 2010. Cross-flow ultrafiltration of stable oil-in-water emulsion using polysulfone membranes. *Chemical Engineering Journal* 165 (2), 447–456.
- de Figueredo, K. S. L., Martínez-Huitle, C. A., Teixeira, A. B. R., de Pinho, A. L. S., Vivacqua, C. A., da Silva, D. R., Apr. 2014. Study of produced water using hydrochemistry and multivariate statistics in different production zones of mature fields in the potiguar basin – brazil. *Journal of Petroleum Science and Engineering* 116, 109–114.
- Ebrahimi, M., Willershausen, D., Ashaghi, K. S., Engel, L., Placido, L., Mund, P., Bolduan, P., Czermak, P., Jan. 2010. Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment. *Desalination* 250 (3), 991–996.
- Fakhru’l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., Abidin, Z. Z., Oct. 2009. Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials* 170 (2–3), 530–551.
- Kang, G.-d., Cao, Y.-m., Mar. 2012. Development of antifouling reverse osmosis membranes for water treatment: A review. *Water Research* 46 (3), 584–600.
- Kołtuniewicz, A. B., Field, R. W., Jun. 1996. Process factors during removal of oil-in-water emulsions with cross-flow microfiltration. *Desalination* 105 (1–2), 79–89.
- Li, Y. S., Yan, L., Xiang, C. B., Hong, L. J., Sep. 2006. Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes. *Desalination* 196 (1–3), 76–83.
- Liu, C., 2014. Advances in membrane technologies for drinking water purification. In: Ahuja, S. (Ed.), *Comprehensive Water Quality and Purification*. Elsevier, Waltham, pp. 75–97.

- Maphutha, S., Moothi, K., Meyyappan, M., Iyuke, S. E., Mar. 2013. A carbon nanotube-infused polysulfone membrane with polyvinyl alcohol layer for treating oil-containing waste water. *Nature* 3.
- Muehlenbachs, L., Cohen, M. A., Gerarden, T., Apr. 2013. The impact of water depth on safety and environmental performance in offshore oil and gas production. *Energy Policy* 55, 699–705.
- Phao, N., Nxumalo, E. N., Mamba, B. B., Mhlanga, S. D., 2013. A nitrogen-doped carbon nanotube enhanced polyethersulfone membrane system for water treatment. *Physics and Chemistry of the Earth, Parts A/B/C* 66, 148–156.
- Veil, J. A., 2006. Comparison of two international approaches to controlling risk from produced water discharges. In: 70th PERF meeting, Paris, France.
- Veil, J. A., Puder, M. G., Elcock, D., Redweik, R. J., Jan. 2004. A white papre describing produced water from production of crude oil, natural gas, and coal bed methane. Tech. rep., US Department of Energy, National Energy Technology Laboratory.
- Wu, C., Li, A., Li, L., Zhang, L., Wang, H., Qi, X., Zhang, Q., May 2008. Treatment of oily water by a poly(vinyl alcohol) ultrafiltration membrane. *Desalination* 225 (1–3), 312–321.

Chapter 2

Literature review

2.1 Overview of carbon nanotubes

Sumio Iijima first reported the synthesis of needle-like tubes grown on electrodes using a direct current arc-discharge method (Iijima, 1991). Since then, various research into this material has been explored extensively. These graphitic helically shaped structures Iijima reported were a few nanometers in diameter and possessed extraordinary mechanical, chemical and physical properties (Ghiazza et al., 2014). These qualities make CNTs useful in a number of industries such as the electronics industry, in a field known as CNT-electronics (Sharma and Ahuja, 2008), water treatment industry as membrane reinforcement for water treatment purposes (Gohil and Ray, 2009; Maphutha et al., 2013; Phao et al., 2013; Choi et al., 2006a; Ren and Wang, 2008) and in the medical field for drug delivery (Lacerda et al., 2006; Ghiazza et al., 2014; Liu, 2014). Endo et al. (2008) discuss extensively the various uses of CNTs across a wide range of industries.

The carbon-carbon bonding of the walls of nanotubes make them very stable and inert. As-grown CNTs usually possess a lot of impurities and this is dependent on the synthesis method used (Motchelaho et al., 2011). Acid treatment or functionalization removes these impurities and introduces defects into the CNTs wall structure. These defects are functional groups such as carboxylic groups, which are inserted into the graphene wall structure of the nanotubes. Functionalization makes CNTs more useful for applications such as membrane separation technology, production and drug delivery in the medical field (Lacerda et al., 2006; Gohil and Ray, 2009). The common procedure is to soak the tubes in a strong acid for a while under a heating reflux (Baudot et al., 2010).

New techniques have been developed in synthesizing CNTs. A few include the arc-discharge method, the laser ablation process, the high pressure CO conversion (HiPCO) and the CVD method (Kumar and Ando, 2010).

Arc-discharge method

This is the oldest method for producing CNTs (Iijima, 1991). Iijima discovered CNTs using this method. This method involves the electronic breakdown of carbon gas using electrodes. The electrodes are charged through an arc at a constant current and at high temperatures to breakdown the gas (Arora and Sharma, 2014). The arc-discharge method produces very high quality CNTs. However the growth mechanism by which the CNTs are grown is yet well understood.

Laser ablation method

This technique is similar to arc-discharge. A piece of graphite target is vaporized by laser IR radiations at high temperatures and in an inert environment. The structural quality of the CNTs is dependent on the reaction temperature. High reaction temperatures of about 1200 °C result in high quality CNTs. The vaporized carbon is deposited onto a substrate. This method produces bundles of SWCNTs with small diameter distributions (Mubarak et al., 2014).

HiPCO

The HiPCO method is primarily used to make SWCNT with diameters that can be varied by varying the operating conditions. Catalysts are in-situ grown iron pentacarbonyl, thermally decomposed with carbon mono oxide flowing over it at high pressures and temperatures Nikolaev et al. (1999). This method is a very promising method with potential to produce high SWCNT yields (Kumar and Ando, 2010).

CVD

The CVD method is the most widely used method in CNT synthesis. In this method, a carbon source is decomposed under high temperatures usually in the presence of a catalyst. Compared to the other methods, CVD has a lower heat requirement and gives the highest yields (Hou et al., 2008). Important factors to consider in CNT synthesis *via* this method include the source of carbon, catalyst precursor used and its support. Other factors like the reaction temperature and gas flow rates also play an important role. A lot of work has been done on the optimal conditions for the best CNT yield (Triantafyllidis et al., 2008; Mukhopadhyay et al., 1999; Hernadi et al., 1996).

Typical liquid and gaseous carbon sources include benzene, ethanol, acetylene *etc.* Ethanol produces relatively pure nanotubes compared to acetylene and benzene. The latter decomposes at a high temperature to form carbonaceous compounds. Acetylene is however safer to use at lower temperatures (650°C) compared to benzene (Kumar and Ando, 2010). The choice of catalyst determines the diameters of the CNTs (Pattinson et al., 2013). Iron, nickel and cobalt are the common metallic catalysts used in CNT synthesis (Motchelaho et al., 2011). Iron better decomposes the hydrocarbon precursor but has poor CNT graphitization. Cobalt on the other hand has better graphitization but has a low CNT yield (Tan et al., 2012). Tan et al. (2012) report that a mixture

of these two metals provides the best catalyst combination with adequate graphitization and CNT yield.

The metallic catalyst is usually synthesized on a support. A number of researchers have also looked at the use of various catalyst supports to improve CNT quality and yield (Hernadi et al., 1996; Tetana et al., 2012; Yah et al., 2011). These supports are typically metallic oxides like SiO_2 , Al_2O_3 , TiO_3 , zeolite or CaCO_3 depending on the application of the CNT (Mhlanga et al., 2009). SiO_2 , Al_2O_3 , TiO_2 and zeolite typically have a higher thermal stability than CaCO_3 , however, the latter produces CNTs with less impurities (Mhlanga et al., 2009). The metallic catalysts are supported by either the wet impregnation method or the ion-exchange method. In the ion exchange method, the catalyst support is immersed in separate carefully pH regulated aqueous solutions of the metal catalysts. This is left in the solution for about 24 h, washed, dried and characterized (Triantafyllidis et al., 2008). In the wet impregnation method, the aqueous solution of metal catalysts are mixed with distilled water and the slowly added to the catalyst support under constant stirring (Phao et al., 2013). The well mixed homogenous solution is calcined, dried and characterized. Triantafyllidis et al. (2008) compared these two techniques and reports wet impregnation method as the better method for CNT formation.

The problem with CNTs however, is their uncontrolled agglomeration in various solvents (Osorio et al., 2008). This is due to attractive forces between the nano-sized particles that make them difficult to blend with membrane solvents. The choice of solvent and functionalization methods improves the dispersion of CNTs during the PI method (Ham et al., 2005). Osorio et al. (2008) found that CNTs functionalized with a mixture of sulfuric acid, nitric acid and an optional hydrochloric acid provides the best dispersion in an aqueous medium for the longest period of time of more than 20 days.

2.2 Overview of membrane technology

Membrane technology has been around for centuries and has been applied in a wide range of fields. Table 2.1 adapted from Kołtuniewicz (2006), summarizes the advances in membrane technology over the past 250 years.

More recently, various new work like the membrane aromatic recovery system (MARS) for treating acid and basic aromatics (Ferreira et al., 2002), MTR's VaporSep- H_2^{TM} for very high H_2 recovery in ammonia and methanol plants (Alvarado and Gottschlich, 2005a) and Grace membrane systems, Separex and Cynara's (now NATCO) anisotropic cellulose acetate membranes for treatment of acidic gases have been introduced (Baker and Lokhandwala, 2008).

The increase in the industrial use of membrane technology is attributed to its numerous advantages. A few include its relatively low production and operating cost, its high thermal, chemical and mechanical resistances and the virtually nonexistent environmental impact of membrane filtration processes (Sonune and Ghate, 2004). All these qualities have drawn the attention of researchers and industries alike. Membranes are used widely in medical devices. Polymeric membranes are used

Table 2.1: Advances in membrane technology

Inventor	Year	Research Field
Abbe Noilett	1748	Discovering of osmosis phenomenon in natural membranes
Graham	1845	Research on anisotropy of natural membranes
Matteucci	1866	Research on dialysis
Fick	1865	The first synthetic membrane from nitrocellulosis
Graham	1866	Research on gas separation on rubber membranes
Traube	1867	Research on osmosis on synthetic membranes
Pfeffer	1877	Research on osmosis on ceramic membranes
Gibbs and van Hoff	1877	Theory of osmosis phenomena
Donnan	1911	Distribution law
Abel	1926	Research on dialysis
Michaels, Manegold, McBain	1926- 31	Research on reverse osmosis
Elder	1934	Research on electrodialysis
Kammermeyer	1957	Gas separation on silicone rubber
Kammermeyer	1957	Pervaporation of azeotropic mixtures
Londsdale	1960	Research on composite membranes
Loeb-Sourirajan	1962	Preparation of asymmetric membranes
Loeb-Sourirajan	1962	Pore size controlling in membranes
Mahon	1963	Capillary membranes
Merten	1963	Concentration polarization
Porter	1975	Classification of pressure-driven processes
Goddard	1977	Models of facilitated transport
Leblanc	1980	Membranes with immobilized carriers
Yoshikawa	1986	Membranes with active centers
Cussler, Aris, Brown	1989	The chain model of facilitated transport
Rautenbach	1990	Membrane hybrid processes

in coil, flat-plate and hollow fiber dialyzers that act as artificial kidneys, removing excess solute or water from the blood. They also play very important roles in blood pump-oxygenators used in oxidizing the blood during heart surgeries (Fournier, 2011). Pressure driven membrane filtration processes like micro filtration (MF), ultra-filtration (UF), nano-filtration (NF) and reverse osmosis (RO) are extensively used in the food and beverage industries (Peinemann et al., 2011). In the food industry, specifically the dairy industry, membranes are used to clarify, concentrate and fractionate dairy products, converting wastes from cheese production to valuable products. Membranes are also used to convert filtered milk to cheese, ice cream or yoghurt. In the beverage industry, membrane filtration is used as a clarification process for wine, beer and vinegar. In the 1980's, RO was used to remove alcohol from beer! Similarly in the pharmaceutical industry, membranes are widely employed for recovery and fractionation; recovering toxic chemicals from waste streams by NF or pervaporation, vapor recovery from N_2 /air streams or the separation of isomeric mixtures using liquid membranes (Sirkar, 2000). Table 2.2 summarizes the major membrane processes and their various applications.

The aim of this section is to provide an overview of the various parts of the project. It looks at membrane technology and its applications in the petroleum industry. It then briefly discusses nanotechnology in water treatment, summarizing the various synthesis methods for CNT production. It looks at the precursors and carbon sources best suited for CNT production. The objective is to investigate whether modified polymeric membranes are beneficial for water treatment purposes in the oil and gas industry.

2.3 Membrane application in the oil and gas industry

Membrane filtration has wide applications in both upstream and downstream processes of the oil and gas industry. They are a cost effective separation process compared to the other processes, scalable, and compact enough for medium to large offshore platforms (Wu et al., 2008; Fakhru'l-Razi et al., 2009). In the upstream sector, polymeric membranes are very effective in gas separation. It is especially useful in the separation of olefins and paraffins from conversion processes, the recovery of H_2 from hydro-treatment processes for recycling and in enhanced oil recovery (EOR) processes (Fahim et al., 2009; Faiz and Li, 2012a; Fane et al., 2008; Alvarado and Gottschlich, 2005a; Dehghani et al., 2012; Jones, 1992). Various oil and gas operators like ExxonMobil have also found polymeric membranes to have better energy requirements, better oil rejections and a lower environmental impact than the conventional flash distillation process used for wax separation (Kong et al., 2006; Gould et al., 2001). Larger membrane filtration systems are used in the downstream sector for the treatment of natural gas. This is to ensure that they meet the necessary pipeline specifications before transportation (Washim Uddin and Hägg, 2012). One of the largest markets for membranes in the oil and gas industry however is in the treatment of produced water (de Figueredo et al., 2014). This research focuses on the use of polymeric membranes in wastewater treatment in either offshore or onshore oil platforms.

Table 2.2: Summary of membrane processes

Pressure difference driving force				
	Micro filtration	Ultra filtration	Nano filtration	Reverse osmosis
Structure/ Membrane type	(An)isotropic porous	Anisotropic porous	Composite	Anisotropic/ composite
Pore size	0.05-10 μm	1-10 nm	2 nm	<2 nm
Material	Polymeric/ceramic	Polymeric/ceramic	Polyamide	Cellulose triacetate Aromatic polyamide/ polyamide
Application	Cartridge filters, sterile filtration, wine/beer sterilization,	Wastewater treatment, food processing, ultra pure water used in electronics industry	Desalination	Desalination, pollution control, food processing
Concentration gradient driving force				
	Gas separation	Pervaporation		
Structure/ membrane type	Anisotropic/ composite membrane	Composite membrane		
Pore size	non-porous	non-porous		
Material	Elastomeric & glassy polymer or cellulose acetate, polyimide	Elastomeric & glassy polymer		
Application	Dehydration of air and natural gas corrosion control of pipelines, O_2/N_2 separation, removal of CO_2 from natural gas, H_2 recovery in refineries resin degassing in polyolefin plants	Dehydration of solvents, water purification		
Temperature gradient driving force				
	Membrane distillation	Electrodialysis		
Structure/ membrane type	(An)isotropic and porous	Anion /cation ion exchange		
Pore size	0.2-1.0 μm	100-500 μm		
Material	Hydrophobic polymer	Hydrophobic polymer		
Application	Water desalination, treatment of industrial effluent, pharmaceutical purification, food processing			

2.4 Treatment of produced water

Produced water or industrial oil wastewater is the wastewater stream that comes from oil-fields' processes. They form the largest waste stream from oil and gas exploration and production and the focus of treatment processes in middle and downstream activities (Ebrahimi et al., 2010). One major source of produced water is from EOR processes.

2.4.1 Enhanced oil recovery process

Hydrocarbons are recovered *via* two main methods: the primary and supplementary recovery methods (Romeo-Zerón, 2012). The primary recovery method relies on the natural energy of the oil/gas reservoir to recover the hydrocarbons. This is always through a single wellbore. Supplementary recovery methods are usually applied when the primary energy of the reservoir runs out and the recovery of oil or gas declines. Additional energy is added to the reservoir *via* an injected fluid, through another wellbore, to complement or increase the depleting primary energy.

There are a number of recovery methods used in industry and they each employ various fluids to help with the recovery process. Chemical recovery methods include polymer flooding, chemical flooding, liquid CO₂ flooding *etc.* These polymeric, chemical or CO₂ additives are injected into injector wells along with water to lower the interfacial tension between oil and water, and to allow the oil to flow through the rock pores (Van Dyke, 1997). CO₂ and N₂, both gases miscible in the oil/gas found in petroleum reservoirs, are injected into the wells to push out the oil/gas, increasing recovery rates. These gases are then separated from the oil and recompressed to be recycled back into the well (Jones, 1992). Primary recovery methods involve the use of heat to increase the viscosity or swell of the oil to enhance recovery (Green and Willhite, 1998). They include thermal recovery and steam flooding. Other recovery methods include biological, microbial injection method and technical hydraulic fracturing and radial hydraulic jet drilling methods. Most of these recovery processes are used along with water.

Water flooding is by far the most widely used supplementary recovery method (Satter et al., 2008). Water as an injection fluid is readily available and efficiently displaces light to medium weighted oils. It is abundant and so significantly reduces the costs associated with EOR processes. Unlike the physical, chemical and technical recovery methods, water-flooding has minimal effect on the rock and geological formations of the drilling site. The EOR process (along with the other methods) contributes to the extensive waste produced water associated with the drilling operations.

Produced water is typically composed of saline water with 12 000 - 150 000 mg/l of sodium and 20 000 - 250 000 mg/l of chloride. There are also various contaminants like suspended solids, oils, bacterial growth, dissolved gases and precipitate oils (Fakhru'l-Razi et al., 2009). Environmental regulations require that these contaminants be removed, and that the pH be controlled before the wastewater is disposed off. Australia for example, has a daily discharge limit of 30 ml of contaminants per liter of produced water while that in China is 20 ml/l (Veil, 2006). Currently conventional treatment processes are used by they do not efficiently remove these contaminants,

leaving some residual oil in the treated water. They are also costly, use toxic chemicals that corrode pipelines and require large installation spaces. These make them unattractive for industrial use on oil platforms (Wu et al., 2008).

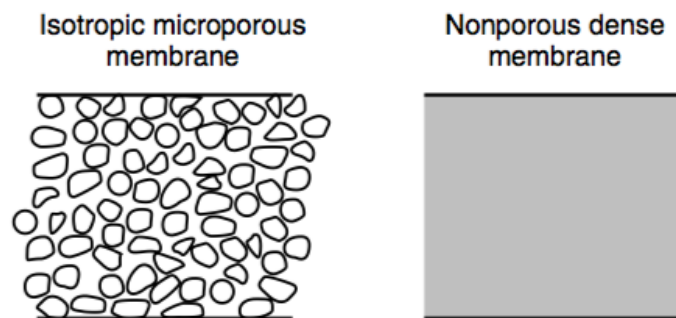
Advances in membrane technology are able to cater for these shortfalls of the conventional treatment processes. MF and UF polymeric or ceramic membranes best remove oil contaminants from produced water (Table 2.2). Various industrially proven pilot trails show however that UF membranes and not MF membranes are more effective, giving high oil removal efficiencies, lower energy costs, demanding less platform space and leaving lower environmental footprints (Bernardo and Drioli, 2010). A pilot plant in the North Seas oil field, aimed at treating produced water, successfully removed 96% of hydrocarbons, 54% of aromatics and 95% of heavy metals from produced water, to meet the required environmental standards (Bernardo and Drioli, 2010). The UF membrane used had a molecular weight cut off (MWCO) of 100 000 - 200 000 Da and reduced hydrocarbon concentrations to less than 2 mg/l. NACTO, one of the first producers of cellulose acetate membranes for natural gas sweetening, also made UF membranes that reduced the hydrocarbon content in treated produced water to less than 2 mg/l, after some pre-treatment processes (Bernardo and Drioli, 2010). For gaseous EOR processes, polyimide and perfluoropolymer membranes have better filtration performances than the conventional cellulose acetate membranes. The former has faster flows, ranging between 220 and 100 000 Nm^3/hr (Baker and Lokhandwala, 2008; Kentish, 2011). Though more expensive, polyimide and perfluoropolymer also have better CO_2/CH_4 selectivity ratio and are much stronger. Ceramic UF membranes are generally better than polymeric UF membrane because they have better chemical and thermal stabilities, reducing the concentration of dispersed oils and suspended solids to less than 5 mg/l and 1 mg/l respectively (Salehi et al., 2014).

2.5 Membrane preparation

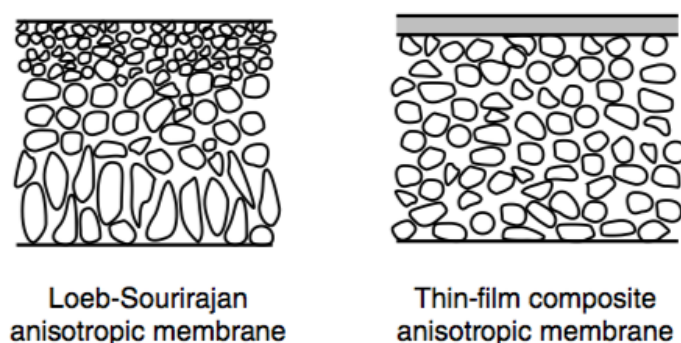
2.5.1 Types of membranes

Membrane filtration is the process of selectively separating a solute from a solvent using a semi-permeable film, across which a driving force has been applied (Kislik, 2010). Membranes can be classified as either isotropic (symmetric) or anisotropic (asymmetric) depending on its structure. Isotropic membranes are either microporous or non-porous and have a uniform composition and structure, while anisotropic membranes are made up of different structural layers with different permeability rates (Baker, 2000). Figure 2.1, adapted from Baker (2000) shows the structure of these two types of membranes.

An isotropic microporous membrane has randomly distributed and interconnecting pores while the non-porous isotropic membrane has a dense film over it, which covers its pores (Figure 2.1a). Therefore separation in an isotropic membrane is either *via* a pressure, concentration or an electric potential gradient. Transport through the non-porous or anisotropic membrane on the other hand is based on the solubility of the solute with the membrane material. Non-porous membranes are



(a) Isotropic membranes



(b) Anisotropic membrane

Figure 2.1: Isotropic and anisotropic membranes

commonly used for gas-separations. The surface layer of an anisotropic membrane controls the permeate rate while a subsurface layer which provides mechanical support (Figure 2.1b). Anisotropic membranes have higher fluxes than isotropic membranes and so are more common in industry (Baker, 2000).

Other classes of membranes include the ceramic, metallic and liquid membranes. These differ from isotropic and anisotropic membranes because they are not necessarily made of organic-polymers but have similar uses. Ceramic membranes are microporous and made from inorganic materials that possess better thermal, chemical and mechanical properties than most polymeric membranes (Salehi et al., 2014). Metallic membranes typically made of palladium and are common in gas separation processes (Itoh et al., 2014). Liquid membranes use liquid films to separate two phases. The separation is usually by a mobile carrier, which transports the solute across a concentration gradient by forming a mobile complexation agent (Kislik, 2010).

2.5.2 Preparation techniques

Membrane preparation is based on the type of membrane. Common techniques for isotropic membranes include track-etching, template leaching, solution casting to name a few (Choi et al., 2006a;

Apel, 2001; Sa-nguanruksa et al., 2004; Mackenzie, 2000; Baker, 2000).

Track-etching

Track-etching is a complex 2-step process that involves the use of a nuclear reactor or a radiation source to break the polymer chains of a thin film. This forms tracks open to chemical attacks which helps form the membrane pores. The advantage of this technique is that the pore sizes, shape and densities can be carefully controlled to be uniform and perpendicular to the membrane surface or engineered to the right specifications. Thus this technique is also called pore-piercing technique (Apel, 2001; Sa-nguanruksa et al., 2004).

Template leaching

The template leaching method is used to prepare microporous membranes. By adding and removing leachable components to the polymer mixture, membranes can be formed accordingly. This technique is good for making non-porous membranes (Sa-nguanruksa et al., 2004).

Solution casting

In the solution casting method, the polymer solution is cast onto a support using a casting blade set to a fixed thickness. The solvent is then allowed to evaporate. The solvent is replaced with water in the atmosphere to form the membrane. This technique is mainly used for lab scale production of membranes. It is important that the temperature, airflow and concentration of the casting solution be carefully regulated. If not properly controlled, an undesirable skin of dried polymer could form on the membrane surface (Mackenzie, 2000).

Anisotropic membranes have higher fluxes and are better suited in industry than isotropic membranes (Baker, 2000). The phase separation method, developed by Sidney Loeb and Srinivasa Sourirajan (sometimes called the Loeb-Sourirajan method), is the technique widely used in preparing anisotropic membranes (Suk et al., 2010). Other less common techniques include the interfacial polymerization method and the coating method (Morgan, 2002; Lee et al., 2011; Madaeni et al., 2013a).

Interfacial polymerization

Developed by Cadotte, this method for making anisotropic membranes involves a condensation reaction between an amine and an acid (Morgan, 2002).

Coating method

The coating method is similar to the PI method and involves the casting of a coat onto a support. This support can be a normal PI membrane. The curing takes place under a temperature control to enhance cross-linking (Madaeni et al., 2013a).

These methods are not as developed as the PI method. This research therefore focused on the PI method for the preparation of anisotropic membrane.

Phase inversion method

In the PI technique, a casting solution is prepared using a polymer and a solvent. This one phase polymer solution is converted into two separate phases by precipitating the casting solution. The two phases include a solid polymer rich phase and a liquid polymer poor phase. Precipitation is commonly done using a non-solvent bath. The non-solvent bath is usually de-ionized water because other organic based solvents like methanol precipitate the casting solution too slowly, pose various safety risks or result in denser membranes (Baker, 2000). The precipitation process can also be done by cooling, by solvent evaporation at room temperature or by absorption of water vapor, like in the solution casting method.

Other important factors that affect the quality of the membrane produced by the PI method include the choice of polymer (and its concentration), the choice of solvent, and the membrane modifiers used. A vast range of polymers can be used in preparing membranes. Ren and Wang (2008) give a comprehensive list of these polymers. The type of polymer used generally depends on the intended use of the membrane. Polyimide membranes for example, are commonly used for gas separation purposes while polyamide membranes are commonly used for RO processes. Table 2.2 summarizes the membrane processes and the polymers commonly used to produce them. The polymer used must have the physical, chemical and mechanical properties to be effective in its use. Polysulfone (PSf) is commonly used for UF membranes. PSf is a synthetic polymeric thermoplastic that has good chemical, physical and mechanical qualities commonly used to make asymmetric membranes (Blanco et al., 2006a). It has a high glass transition temperature of about 195°C, can withstand both harsh acidic and basic conditions and thus can be easily cleaned by chemical processes and high UF pressures. The chemical structure of PSf is illustrated in Figure 2.2. Another good alternative to PSf is polyether sulfone (PES), with similar characteristics except

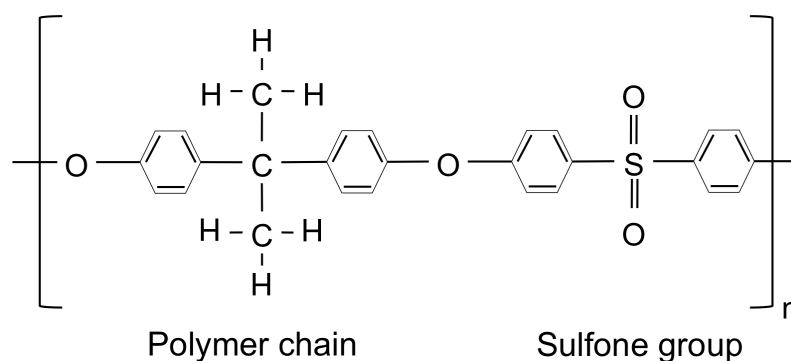


Figure 2.2: Structure of a PSf repeating unit

a higher glass transition temperature of 230°C. PES is therefore more thermally stable than PSf (Richardson et al., 2002).

Modifiers are often added to membranes to enhance the properties of the membrane. Scott et al. (1992) and more recently Gao et al. (2014) used cellulose acetate and cellulose-graft-myristyl respectively as modifying additives in a PSf membrane to enhance hydrophilicity and reduce the pollution effect of the membrane. Maphutha et al. (2013) and Wu et al. (2008) also used polyvinyl alcohol (PVA) as a membrane modifier to enhance solute retention, flux recovery and to improve the antifouling properties of the membrane. Some researchers also report casting on a polyester NWF while others do not use this support (Choi et al., 2006a; Gohil and Ray, 2009). Nano-materials like alumina particles, silica, metal oxides *etc.* have also been used for their ability to enhance the permeability and strength of membranes (Sen et al., 2014; Méndez et al., 2013). CNTs are also very popular membrane modifiers because of their extraordinary qualities and their interaction with the solvent (Gohil and Ray, 2009; Maphutha et al., 2013; Phao et al., 2013; Choi et al., 2006a; Ren and Wang, 2008).

Ham et al. (2005) investigated the dispersion of CNTs in various solvents using the Hansen solubility parameters. These parameters are expressed in Equation 2.1, where δ_d is the dispersive component, δ_h is the hydrogen bonding component, δ_p is the polar component and δ_t is the total solubility parameter.

$$\delta_t^2 = \delta_p^2 + \delta_d^2 + \delta_h^2 \quad (2.1)$$

They found that the dispersion of nanotubes in various solvents was independent of δ_t . However, solvents with a high polar or hydrogen-bonding component precipitated quickly because of the hydrophobic nature of nanotubes. The Hansen components for solvents commonly used in the preparation of polymeric membranes are compared in Table 2.3.

Table 2.3: Polarity and hydrogen bonding components for various solvents

Solvents	δ_d	δ_p	δ_h	δ_t
Chloroform	17.8	3.1	5.7	19.0
1-Methyl-2-pyrrolidinone (NMP)	18.0	12.3	7.2	22.9
Dimethylacetamide (DMAc)	16.8	11.5	10.2	22.7
Dimethyl sulfoxide (DMSO)	18.4	16.4	10.2	26.7
Dimethylformamide (DMF)	17.4	13.7	11.3	24.8
Water	15.6	16.0	42.3	47.8

The table shows that chloroform best disperses nanotubes because it has the lowest polarity and hydrogen bonding components of 3.1 and 5.7 respectively. NMP also makes a good solvent for the preparation of nano-composite membranes, while DMF does not disperse nanotubes as efficiently. Solvents with low δ_h are called aprotic solvents and unlike protic solvents, do not have hydrogen bonds in them, thus their good dispersion of nanotubes. Aprotic solvents are also capable of dissolving a wide range of polymers. Water (a protic solvents) is included in the table to show how CNTs precipitate quickly in water even when highly sonicated. Due o the good dispersion of nanotubes in NMP and DMAc, they are popular solvents used in the preparation of nano-composite

membranes (Sen et al., 2014; Lua and Shen, 2013; Méndez et al., 2013)

This research sought to fill the gap and investigate the use of CNT and NWF modified polymeric UF membranes in the treatment of produced water from the oil and gas industry. The membranes were modified with CNTs and a NWF. Numerous studies have been done on the use of CNT modified membranes in desalination water treatment processes (Sonune and Ghate, 2004; Su et al., 2012; Norouzbahari et al., 2009). Very little work has however been done on the combined effects of CNTs with NWF for waste water treatment in the oil and gas industry (Chakrabarty et al., 2010; Arockiasamy et al., 2013; Celik et al., 2011; Maphutha et al., 2013). The experimental methodology was developed from the discussion above. Acid treated CNTs were dispersed in NMP and blended with PSf to determine its effect on the filtration performance. It was expected that the physical properties of PSf membranes would be reinforced with the qualities of functionalized CNTs. It was also expected that the modified membranes would reduce the concentration of a synthetically made produced water from 1000 mg/l to 50 mg/l or less. This application should prove very useful on oil and gas service providers who operate in deep or ultra-deep offshore platforms. This would enable the treatment of large quantities of wastewater to meet environmental standards before disposal or recycling.

References

- Alvarado, D., Gottschlich, D., 2005a. Membrane matrimony. *Hydrocarbon Engineering* 10 (9), 104–108.
- Apel, P., Jun. 2001. Track etching technique in membrane technology. *Radiation Measurements* 34 (1–6), 559–566.
- Arockiasamy, D. L., Alam, J., Alhoshan, M., Mar. 2013. Carbon nanotubes-blended poly(phenylene sulfone) membranes for ultrafiltration applications. *Applied Water Science* 3 (1), 93–103.
- Arora, N., Sharma, N. N., Nov. 2014. Arc discharge synthesis of carbon nanotubes: Comprehensive review. *Diamond and Related Materials* 50, 135–150.
- Baker, R. W., 2000. *Membrane technology and applications*. McGraw-Hill, New York.
- Baker, R. W., Lokhandwala, K., Apr. 2008. Natural gas processing with membranes: An overview. *Industrial and Engineering Chemistry Research* 47 (7), 2109–2121.
- Baudot, C., Tan, C. M., Kong, J. C., Nov. 2010. FTIR spectroscopy as a tool for nano-material characterization. *Infrared Physics & Technology* 53 (6), 434–438.
- Bernardo, P., Drioli, E., 2010. 4.08 - membrane technology: Latest applications in the refinery and petrochemical field. In: Drioli, E., Giorno, L. (Eds.), *Comprehensive Membrane Science and Engineering*. Elsevier, Oxford, pp. 211–239.
- Blanco, J.-F., Sublet, J., Nguyen, Q. T., Schaetzel, P., Oct. 2006a. Formation and morphology studies of different polysulfones-based membranes made by wet phase inversion process. *Journal of Membrane Science* 283 (1–2), 27–37.
- Celik, E., Park, H., Choi, H., Choi, H., Jan. 2011. Carbon nanotube blended polyethersulfone membranes for fouling control in water treatment. *Water Research* 45 (1), 274–282.
- Chakrabarty, B., Ghoshal, A. K., Purkait, M. K., Dec. 2010. Cross-flow ultrafiltration of stable oil-in-water emulsion using polysulfone membranes. *Chemical Engineering Journal* 165 (2), 447–456.
- Choi, J.-H., Jegal, J., Kim, W.-N., Nov. 2006a. Fabrication and characterization of multi-walled carbon nanotubes/polymer blend membranes. *Journal of Membrane Science* 284 (1–2), 406–415.
- de Figueredo, K. S. L., Martínez-Huitle, C. A., Teixeira, A. B. R., de Pinho, A. L. S., Vivacqua, C. A., da Silva, D. R., Apr. 2014. Study of produced water using hydrochemistry and multivariate statistics in different production zones of mature fields in the potiguar basin – brazil. *Journal of Petroleum Science and Engineering* 116, 109–114.

- Dehghani, A., Bridjanian, H., Farshi, A., 2012. Selection separation method for hydrogen and light hydrocarbons gases from waste-gas streams of a petroleum refinery. *Petroleum Science and Technology* 30 (21), 2196–2207.
- Ebrahimi, M., Willershausen, D., Ashaghi, K. S., Engel, L., Placido, L., Mund, P., Bolduan, P., Czermak, P., Jan. 2010. Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment. *Desalination* 250 (3), 991–996.
- Endo, M., Strano, M. S., Ajayan, P. M., Jan. 2008. Potential applications of carbon nanotubes. In: Jorio, A., Dresselhaus, G., Dresselhaus, M. S. (Eds.), *Carbon Nanotubes*. No. 111 in *Topics in Applied Physics*. Springer Berlin Heidelberg, pp. 13–62.
- Fahim, M. A., Al-Sahhaf, T. A., Elkilani, A., 2009. *Fundamentals of petroleum refining*. Elsevier.
- Faiz, R., Li, K., May 2012a. Olefin/paraffin separation using membrane based facilitated transport/chemical absorption techniques. *Chemical Engineering Science* 73, 261–284.
- Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., Abidin, Z. Z., Oct. 2009. Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials* 170 (2–3), 530–551.
- Fane, A. G. T., Wang, R., Jia, Y., Jan. 2008. Membrane technology: Past, present and future. In: Wang, L. K., Chen, J. P., Hung, Y.-T., Shammas, N. K. (Eds.), *Membrane and Desalination Technologies*. No. 13 in *Handbook of Environmental Engineering*. Humana Press, pp. 1–45.
- Ferreira, F. C., Han, S., Boam, A., Zhang, S., Livingston, A. G., Sep. 2002. Membrane aromatic recovery system (MARS): lab bench to industrial pilot scale. *Desalination* 148 (1–3), 267–273.
- Fournier, R. L., 2011. *Basic transport phenomena in biomedical engineering*. CRC Press.
- Gao, Y., Li, B., Zhong, L., Zhang, L., Ding, Z., Sep. 2014. Effect of nano-amphiphilic cellulose as a modifier to PSf composite membranes. *Vacuum* 107, 199–203.
- Ghiazza, M., Vietti, G., Fenoglio, I., 2014. 8 - carbon nanotubes: properties, applications, and toxicity. In: Njuguna, J., Pielichowski, K., Zhu, H. (Eds.), *Health and Environmental Safety of Nanomaterials*. Woodhead Publishing, pp. 147–174.
- Gohil, J. M., Ray, P., Oct. 2009. Polyvinyl alcohol as the barrier layer in thin film composite nanofiltration membranes: Preparation, characterization, and performance evaluation. *Journal of Colloid and Interface Science* 338 (1), 121–127.
- Gould, R. M., White, L. S., Wildemuth, C. R., Apr. 2001. Membrane separation in solvent lube dewaxing. *Environmental Progress* 20 (1), 12–16.
- Green, D. W., Willhite, G. P., 1998. *Enhanced Oil Recovery*. Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers.

- Ham, H. T., Choi, Y. S., Chung, I. J., Jun. 2005. An explanation of dispersion states of single-walled carbon nanotubes in solvents and aqueous surfactant solutions using solubility parameters. *Journal of Colloid and Interface Science* 286 (1), 216–223.
- Hernadi, K., Fonseca, A., Nagy, J. B., Bemaerts, D., Fudala, A., Lucas, A. A., Nov. 1996. Catalytic synthesis of carbon nanotubes using zeolite support. *Zeolites* 17 (5–6), 416–423.
- Hou, P.-X., Liu, C., Cheng, H.-M., Dec. 2008. Purification of carbon nanotubes. *Carbon* 46 (15), 2003–2025.
- Iijima, S., Nov. 1991. Helical microtubules of graphitic carbon. *Nature* 354 (6348), 56–58.
- Itoh, N., Suga, E., Sato, T., Jan. 2014. Composite palladium membrane prepared by introducing metallic glue and its high durability below the critical temperature. *Separation and Purification Technology* 121, 46–53.
- Jones, L., Jan. 1992. Method of recovering oil using continuous steam flood from a single vertical wellbore. US Patent 5,080,172.
- Kentish, S. E., 2011. 11 - polymeric membranes for natural gas processing. In: Basile, A., Nunes, S. P. (Eds.), *Advanced Membrane Science and Technology for Sustainable Energy and Environmental Applications*. Woodhead Publishing Series in Energy. Woodhead Publishing, pp. 339–360.
- Kislik, V. S., 2010. Introduction, general description, definitions, and classification. overview. In: Kislik, V. S. (Ed.), *Liquid Membranes*. Elsevier, Amsterdam, pp. 1–15.
- Kołtuniewicz, A. B., Apr. 2006. The history and state of arts in membrane technologies. VIII Spring Membrane School.
- Kong, Y., Shi, D., Yu, H., Wang, Y., Yang, J., Zhang, Y., May 2006. Separation performance of polyimide nanofiltration membranes for solvent recovery from dewaxed lube oil filtrates. *Desalination* 191 (1–3), 254–261.
- Kumar, M., Ando, Y., Jun. 2010. Chemical vapor deposition of carbon nanotubes: A review on growth mechanism and mass production. *Journal of Nanoscience and Nanotechnology* 10 (6), 3739–3758.
- Lacerda, L., Bianco, A., Prato, M., Kostarelos, K., Dec. 2006. Carbon nanotubes as nanomedicines: From toxicology to pharmacology. *Advanced Drug Delivery Reviews* 58 (14), 1460–1470.
- Lee, K. P., Arnot, T. C., Mattia, D., Mar. 2011. A review of reverse osmosis membrane materials for desalination—development to date and future potential. *Journal of Membrane Science* 370 (1–2), 1–22.
- Liu, C., 2014. Advances in membrane technologies for drinking water purification. In: Ahuja, S. (Ed.), *Comprehensive Water Quality and Purification*. Elsevier, Waltham, pp. 75–97.

- Lua, A. C., Shen, Y., Feb. 2013. Preparation and characterization of asymmetric membranes based on nonsolvent/NMP/p84 for gas separation. *Journal of Membrane Science* 429, 155–167.
- Mackenzie, K. J., 2000. Film and sheeting materials. In: *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc.
- Madaeni, S., Badieh, M. M. S., Vatanpour, V., Sep. 2013a. Effect of coating method on gas separation by PDMS/PES membrane. *Polymer Engineering & Science* 53 (9), 1878–1885.
- Maphutha, S., Moothi, K., Meyyappan, M., Iyuke, S. E., Mar. 2013. A carbon nanotube-infused polysulfone membrane with polyvinyl alcohol layer for treating oil-containing waste water. *Nature* 3.
- Méndez, M. L., Romero, A. I., Rajal, V. B., Castro, E. F., Calvo, J. I., Palacio, L., Hernández, A., May 2013. Properties of polyethersulfone ultrafiltration membranes modified with polyethylene glycols. *Polymer Engineering & Science*, 1211–1221.
- Mhlanga, S. D., Mondal, K. C., Carter, R., Witcomb, M. J., Coville, N. J., 2009. The effect of synthesis parameters on the catalytic synthesis of MWCNTs using Fe-Co/CaCO₃ catalysts. *South African Journal of Chemistry* 62 (67).
- Morgan, P. W., 2002. Interfacial polymerization. In: *Encyclopedia of Polymer Science and Technology*. John Wiley & Sons, Inc.
- Motchelaho, M. A. M., Xiong, H., Moyo, M., Jewell, L. L., Coville, N. J., Feb. 2011. Effect of acid treatment on the surface of multiwalled carbon nanotubes prepared from Fe-Co supported on CaCO₃: Correlation with Fischer-Tropsch catalyst activity. *Journal of Molecular Catalysis A: Chemical* 335 (1–2), 189–198.
- Mubarak, N. M., Abdullah, E. C., Jayakumar, N. S., Sahu, J. N., Jul. 2014. An overview on methods for the production of carbon nanotubes. *Journal of Industrial and Engineering Chemistry* 20 (4), 1186–1197.
- Mukhopadhyay, K., Koshio, A., Sugai, T., Tanaka, N., Shinohara, H., Konya, Z., Nagy, J. B., Apr. 1999. Bulk production of quasi-aligned carbon nanotube bundles by the catalytic chemical vapour deposition (CCVD) method. *Chemical Physics Letters* 303 (1–2), 117–124.
- Nikolaev, P., Bronikowski, M. J., Bradley, R., Rohmund, F., Colbert, D. T., Smith, K., Smalley, R. E., 1999. Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chemical Physics Letters* 313 (1–2), 91 – 97.
- Norouzbahari, S., Roostaazad, R., Hesampour, M., Mar. 2009. Crude oil desalter effluent treatment by a hybrid UF/RO membrane separation process. *Desalination* 238 (1–3), 174–182.

- Osorio, A. G., Silveira, I. C. L., Bueno, V. L., Bergmann, C. P., Dec. 2008. H₂SO₄/HNO₃/HCl—functionalization and its effect on dispersion of carbon nanotubes in aqueous media. *Applied Surface Science* 255, 2485–2489.
- Pattinson, S. W., Windle, A. H., Koziol, K. K. K., Feb. 2013. Facile processing of zeolite based catalyst support for carbon nanotube synthesis. *Materials Letters* 93, 404–407.
- Peinemann, K.-V., Nunes, S. P., Giorno, L., 2011. *Membrane Technology: Volume 3: Membranes for Food Applications*. John Wiley & Sons.
- Phao, N., Nxumalo, E. N., Mamba, B. B., Mhlanga, S. D., 2013. A nitrogen-doped carbon nanotube enhanced polyethersulfone membrane system for water treatment. *Physics and Chemistry of the Earth, Parts A/B/C* 66, 148–156.
- Ren, J., Wang, R., Jan. 2008. Preparation of polymeric membranes. In: Wang, L. K., Chen, J. P., Hung, Y.-T., Shamas, N. K. (Eds.), *Membrane and Desalination Technologies*. No. 13 in *Handbook of Environmental Engineering*. Humana Press, pp. 47–100.
- Richardson, J., Harker, J., Backhurst, J., 2002. *Coulson and richardson's chemical engineering volume 2 - particle technology and separation processes* (5th edition).
- Romeo-Zerón, L. (Ed.), May 2012. *Introduction to enhanced oil recovery (EOR) processes and bioremediation of oil-contaminated sites*. InTech, Rijeka, Croatia.
- Sa-nguanruksa, J., Rujiravanit, R., Supaphol, P., Tokura, S., Feb. 2004. Porous polyethylene membranes by template-leaching technique: preparation and characterization. *Polymer Testing* 23 (1), 91–99.
- Salehi, E., Madaeni, S. S., Shamsabadi, A. A., Laki, S., Apr. 2014. Applicability of ceramic membrane filters in pretreatment of coke-contaminated petrochemical wastewater: Economic feasibility study. *Ceramics International* 40 (3), 4805–4810.
- Satter, A., Iqbal, G. M., Buchwalter, J. L., 2008. *Practical Enhanced Reservoir Engineering: Assisted with Simulation Software*. PennWell Books.
- Scott, K., McConvey, I., Adhamy, A., Sep. 1992. Application of crossflow microfiltration to emulsion separation in extraction processes. *Journal of Membrane Science* 72 (3), 245–257.
- Sen, D., Ghosh, A. K., Mazumder, S., Bindal, R. C., Tewari, P. K., Feb. 2014. Novel polysulfone–spray-dried silica composite membrane for water purification: Preparation, characterization and performance evaluation. *Separation and Purification Technology* 123, 79–86.
- Sharma, P., Ahuja, P., Oct. 2008. Recent advances in carbon nanotube-based electronics. *Materials Research Bulletin* 43 (10), 2517–2526.

- Sirkar, K. K., Nov. 2000. Application of membrane technologies in the pharmaceutical industry. *Current opinion in drug discovery & development* 3 (6), 714–722.
- Sonune, A., Ghate, R., Aug. 2004. Developments in wastewater treatment methods. *Desalination* 167, 55–63.
- Su, B., Dou, M., Gao, X., Shang, Y., Gao, C., Jul. 2012. Study on seawater nanofiltration softening technology for offshore oilfield water and polymer flooding. *Desalination* 297, 30–37.
- Suk, D. E., Matsuura, T., Park, H. B., Lee, Y. M., Oct. 2010. Development of novel surface modified phase inversion membranes having hydrophobic surface-modifying macromolecule (nSMM) for vacuum membrane distillation. *Desalination* 261 (3), 300–312.
- Tan, L.-L., Chai, S.-P., Mohamed, A. R., May 2012. Growth of carbon nanotubes on si/SiO₂ wafer etched by hydrofluoric acid under different etching durations. *Applied Surface Science* 258 (15), 5774–5777.
- Tetana, Z. N., Mhlanga, S. D., Bepete, G., Krause, R. W. M., Coville, N. J., 2012. The synthesis of nitrogen-doped multiwalled carbon nanotubes using an Fe-Co/CaCO₃ catalyst. *South African Journal of Chemistry* 65, 39–49.
- Triantafyllidis, K. S., Karakoulia, S. A., Gournis, D., Delimitis, A., Nalbandian, L., Maccallini, E., Rudolf, P., Apr. 2008. Formation of carbon nanotubes on iron/cobalt oxides supported on zeolite-y: Effect of zeolite textural properties and particle morphology. *Microporous and Mesoporous Materials* 110 (1), 128–140.
- Van Dyke, K., 1997. *Fundamentals of Petroleum*, 4th Edition. The University of Texas at Austin.
- Veil, J. A., 2006. Comparison of two international approaches to controlling risk from produced water discharges. In: 70th PERF meeting, Paris, France.
- Washim Uddin, M., Hägg, M.-B., Dec. 2012. Natural gas sweetening—the effect on CO₂–CH₄ separation after exposing a facilitated transport membrane to hydrogen sulfide and higher hydrocarbons. *Journal of Membrane Science* 423–424, 143–149.
- Wu, C., Li, A., Li, L., Zhang, L., Wang, H., Qi, X., Zhang, Q., May 2008. Treatment of oily water by a poly(vinyl alcohol) ultrafiltration membrane. *Desalination* 225 (1–3), 312–321.
- Yah, C. S., Simate, G. S., Moothi, K., Maphutha, K. S., Iyuke, S. E., Nov. 2011. Synthesis of large carbon nanotubes from ferrocene: The chemical vapour deposition technique. *Trends in Applied Sciences Research* 6 (11), 1270–1279.

Chapter 3

Experimental procedures & analytical techniques

3.1 Materials

Crude oil from NATREF Laboratorium in Sasolburg, South Africa was used in the production of synthetic oil water mixture. This procedure is presented in Appendix A. All chemicals were analytical grade chemicals from Sigma-Aldrich, unless otherwise stated. PSf beads (mol wt. 35 000 Da), 1-Methyl-2-pyrrolidinone (NMP, $\geq 99\%$), powdery NaY zeolite catalyst, calcium carbonate (CaCO_3), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 98\%$), cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $98 + \%$) and 55% nitric acid (HNO_3 of 55% concentration) were all bought from Sigma-Aldrich. Technical grade nitrogen and acetylene gas were bought from Afrox, South Africa. The chemistry department of the University of Witwatersrand, South Africa donated hydrofluoric acid (HF) of 50% concentration. Sojitz Corp, Japan also donated polyester NWF.

3.2 Preparation of Fe/Co catalyst supported on zeolite and CaCO_3

The wet impregnation method was used to prepare a 10% concentration Fe/Co catalyst (5% each), supported on zeolite and CaCO_3 as described by Phao et al. (2013). Iron (III) nitrate nonahydrate and cobalt (II) nitrate hexahydrate were used as the metal sources while zeolite and CaCO_3 were used as the supports. A 3.62 g of iron nitrate and 2.46 g of cobalt nitrate were measured and added to 30 ml of distilled water. Detailed calculations are presented in Appendix B. The mixture was stirred until a homogeneous solution was obtained. This was then added drop wise to 10 g of the support and slowly stirred for 30 min (Figure 3.1). The solution was further stirred for another 30 min and dried at 60°C for 8 h. The resulting precursor was calcined at 400°C for an hour to ensure the complete removal of all nitrates. The products were characterized using the FEI Nova Nanolab 600 scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and the

X-ray diffraction analysis (XRD).

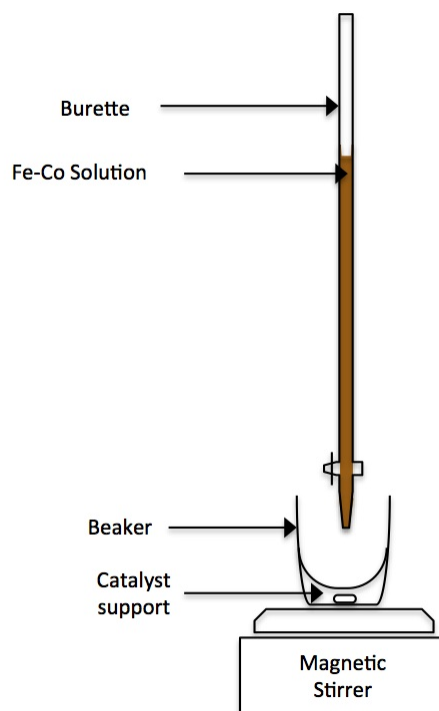


Figure 3.1: Set up for preparing catalyst using the wet impregnation method

3.2.1 CNT production

The CVD method described by Mhlanga et al. (2009) was used in the production of CNTs, with acetylene as the carbon source and the produced metallic alloy as the catalyst. The set up is illustrated in Figure 3.2a. Nitrogen was used as the inert gas to purge the system of any foreign material and reduce the chances of impurities in the CNTs. For the CNT synthesis, 1 g of the catalyst is measured onto a quartz boat and placed in the center of the horizontal furnace. The furnace was set to 700 °C and inert nitrogen gas passed through the quartz tube at 180 ml/min for a while. After purging, acetylene gas (along with nitrogen gas) was allowed through the system at a rate of 90 ml/min for 1 h to initiate the CNT growth. Nitrogen gas flowed through the system during cooling.

3.2.2 Functionalizing and washing of CNTs

The procedure described by Mhlanga et al. (2009) was again used in functionalizing the CNTs. The as grown CNTs were immersed in 100 ml of 55 % HNO₃. This was then refluxed at 110 °C for 4 h. The mixture was allowed to cool and poured into a 5000 ml beaker of distilled water for the functionalized CNTs (fCNTs) settle. The fCNTs were thoroughly washed with distilled water until a neutral pH was attained. The fCNTs were dried at 120 °C prior to characterization.

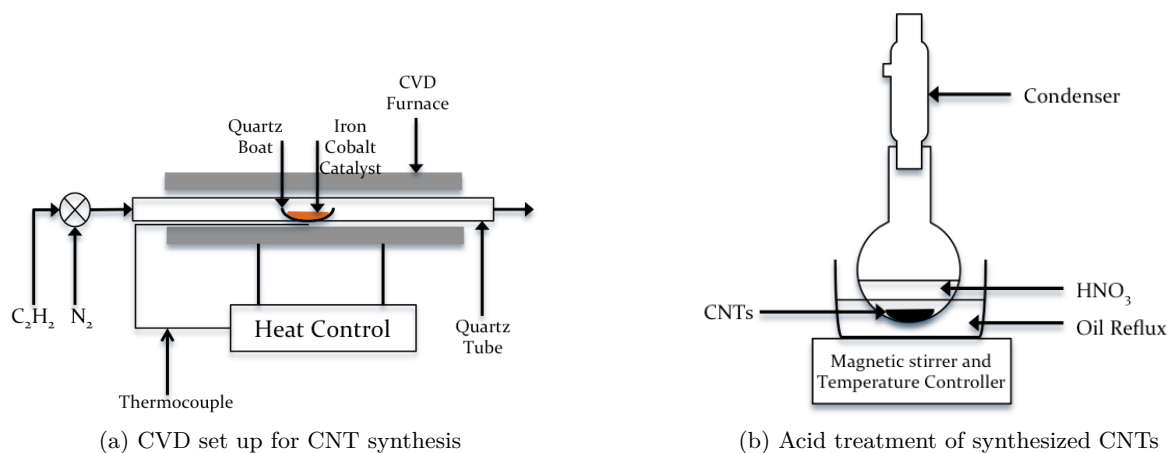


Figure 3.2: CNT synthesis and functionalization setup

3.2.3 CNT and fCNT characterization

The FEI Tecnai Spirit G2 transmission electron microscope (TEM) was used to confirm the existence of CNTs and the Raman spectroscopy and Fourier transform infrared radiation (FTIR) used to confirm the presence of functional groups in the CNTs walls.

Raman spectroscopy was one of the standard nondestructive characterization techniques used for carbon based materials, specifically for crystalline, nano-crystalline and amorphous carbons (Ferrari and Robertson, 2000). The Raman plots for nanotubes have two characteristic peaks: one at a frequency of 1350 cm^{-1} and the other at 1580 cm^{-1} . The G band at 1580 cm^{-1} confirms the presence of graphene sheets in the carbon material while the D band at 1350 cm^{-1} is a result of disorder present in the graphene structure. The degree of disorder is determined by the D and G intensity ratios ($I_{D/G}$), which represents the proportion of sp^3 carbon and in turn the amount of structural defects in the nanotubes (Flahaut et al., 2005).

The Bruker TENSOR 27 FTIR spectrometer was used for this analysis. These nondestructive analytical techniques helped supported each other by verifying and identifying the functional groups present in the walls of the CNTs. When CNTs are introduced to infrared radiation of the FTIR, there is a difference in charge due to the stretching and bending of carbon atoms. The difference in charge then induces an electric dipole, which is read as signals on the FTIR spectra. The extent of this induced dipole determines the presence of functional groups (Osorio et al., 2008). Ideally, as grown CNTs are symmetrical and thus generally generate weak signals. Functionalization disrupts this symmetry and in turn increases the charge difference.

An EDS analysis and thermogravimetric analysis (TGA) analysis were used to investigate the purity, composition and thermal properties of the CNTs and fCNTs. The TA SDTQ 600 was used to perform the TGA on the synthesized nanotubes. Unlike the other techniques, this analytical technique is a destructive technique and quantitatively determines composition, quality (specifically the amount of metallic impurities) and thermal stability of the CNTs under specific atmospheres. A

5 mg sample of the nanotubes was burnt off in air and the weight loss recorded with the temperature change in the TGA to determine the temperature profile.

ImageJ image processing software was used to analyze the size distribution of the membranes.

3.2.4 Purification of functionalized CNTs

The fCNTs synthesized on zeolite-supported catalysts (fCNT-z) were etched in hydrofluoric acid as recommended by Hernadi et al. (1996). A 50 ml solution of HF was measured and poured in a plastic cap and used to soak the fCNTs for 8 h under constant stirring. The resulting etched fCNTs were then characterized using an SEM, EDS, TEM and TGA.

The first part of this research was focused on the production and characterization of CNTs, investigating the effects of the various catalyst support on the its properties. Figure 3.3 summarizes the steps taken to achieve this.

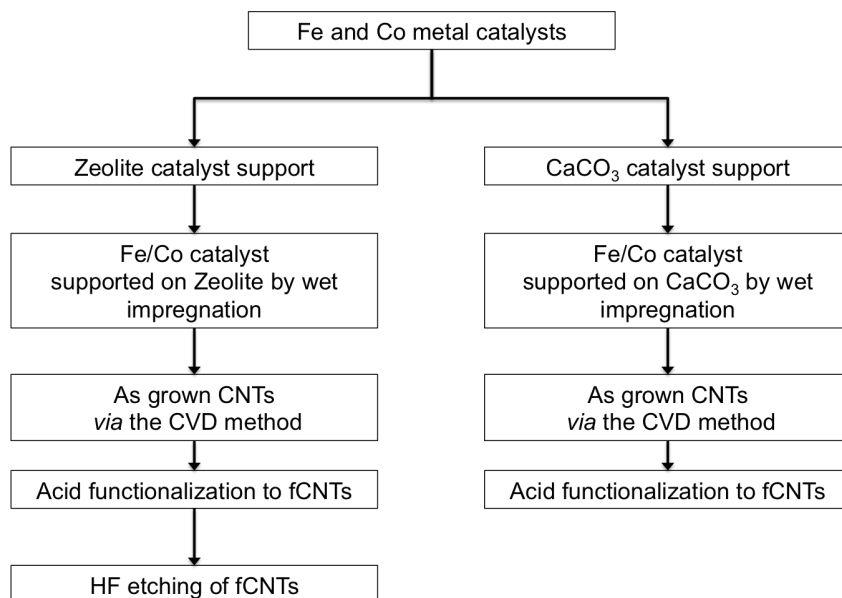


Figure 3.3: CNT process flow diagram

3.3 Membrane preparation, characterization and evaluation

Two techniques were employed in the preparation of the polymeric membranes: the PI and immersion method and the solution casting method using a CAM-T0 table top tape caster (Section 2.5.2). The procedures described by Maphutha et al. (2013) and Phao et al. (2013) were slightly changed and adapted for this research. A 20 % w/w casting solution was prepared using PSf as the polymer and NMP as the solvent. The PSf beads were dissolved in the solvent by magnetic stirring for 24 h, until a homogenous solution was obtained (Gohil and Ray, 2009). For the fCNT/PSf blended membranes, a 0.04wt% concentration of fCNTs was dispersed in the solvent and mixed

via ultrasonication until a homogenous solution was obtained. The PSf beads were only added after a homogeneous solution was obtained. Phao et al. (2013) found this CNT concentration to be optimal, yielding the best fluxes. The NMP was used to top up the solution to its initial level to ensure that a 20% w/w solution was maintained. In order to improve the surface quality of the produced membranes, bubbles were removed from the casting solution by sonicating for a further 10 min. The solution was then cast using a casting blade set to $250\mu\text{m}$. The casting solution was cast on a glass plate, with the polyester NWF firmly supported onto the glass. The cast solution was then immersed into a bath of distilled water for the phase separation step. The membrane was further washed with distilled water and stored in another water bath for 24 h to ensure the complete liquid-liquid transfer of the liquid and solvent.

For the solution casting method, the polyester NWF was firmly supported on the rolling tape of the machine and the roller speed and chamber temperature set to 60°C . The cast solution was left to dry in the heated chamber with regulated airflow for 24 h before characterization. Figure 3.4 illustrates the PI and solution casting methods.

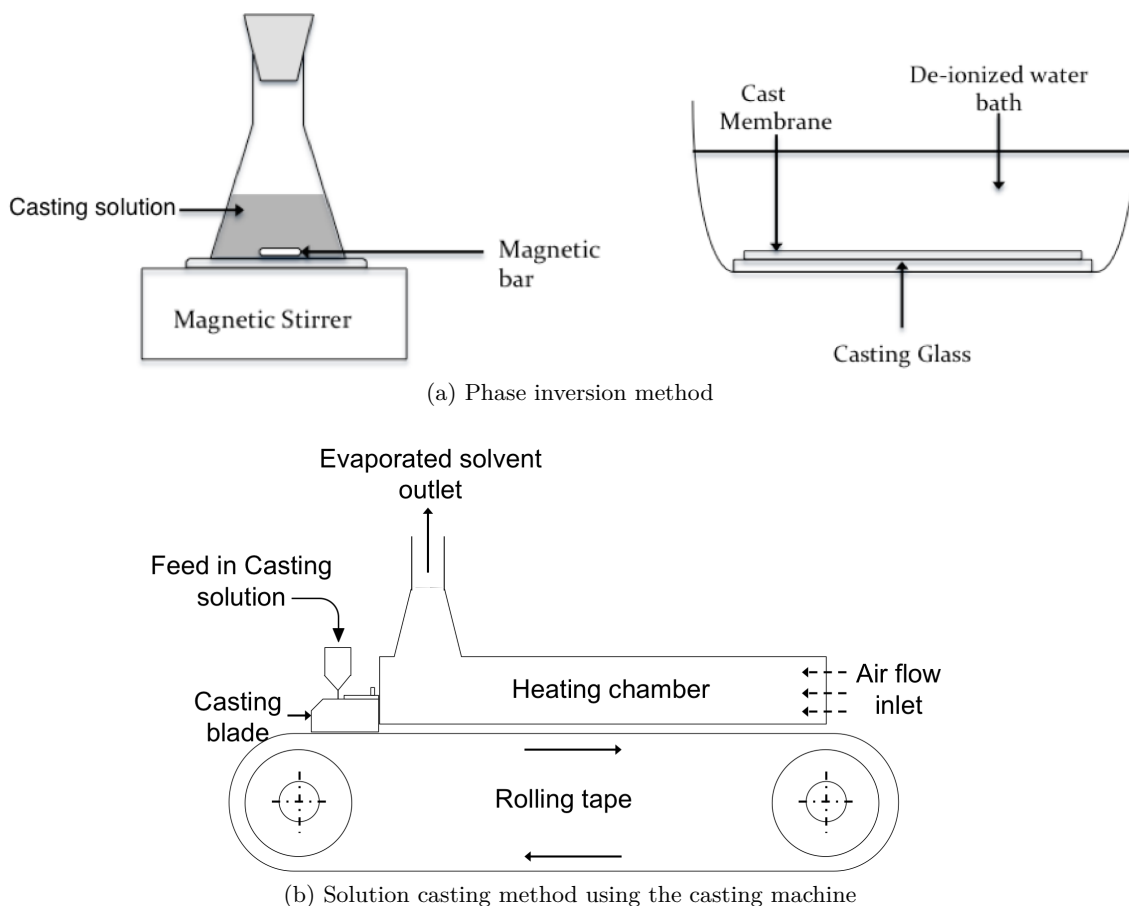


Figure 3.4: Membrane preparation methods

3.3.1 Membrane characterization

An SEM was used to evaluate the surface and cross sectional morphologies of the membranes. The membranes were freeze-voided before analyzing the cross sectional area. An FTIR analysis was also performed on all synthesized membranes to confirm the polymerization and the presence of functional groups in the membrane.

To determine the pore distribution on the membrane surface and roughness of the top surface of the membrane, the contact mode (or tapping mode) Veeco Di3100 atomic force microscope (AFM) was used. A laser beam was deflected off the back of a cantilever and the deviation signals were read and illustrated as the topographic images (Khayet et al., 2004). The pore distribution was qualitatively analyzed and surface roughness presented. The surface roughness of a membrane is directly related to the gas permeability of the membrane Khulbe and Matsuura (2000). In the 3D images, the nodules (or peaks) represent the bright spots, while the pores (or valleys) represent the dark spots.

The thermal properties of the membranes were analyzed using the TGA/DTG. The sessile drop experiment was performed using a goniometer to determine the contact angles of the membrane. Strips of the membrane were cut and pasted onto a two-sided tape and attached to a flat stage facing a camera. A syringe, filled with distilled water was used to deliver drops onto the surface of the membrane. The averages of the contact angles from the drops were measured and reported.

Finally the mechanical properties of the membranes were characterized using a TX.XT Plus texture analyzer. A 35×15 mm strip of membrane was stretched by the long side and the force for every distance stretched recorded. The stress and strains applied on the membranes were computed using Equations 3.1 and 3.2 respectively;

$$\sigma = \frac{F}{A_L} \quad (3.1)$$

$$\epsilon = \frac{dL}{L_o} \times 100 \quad (3.2)$$

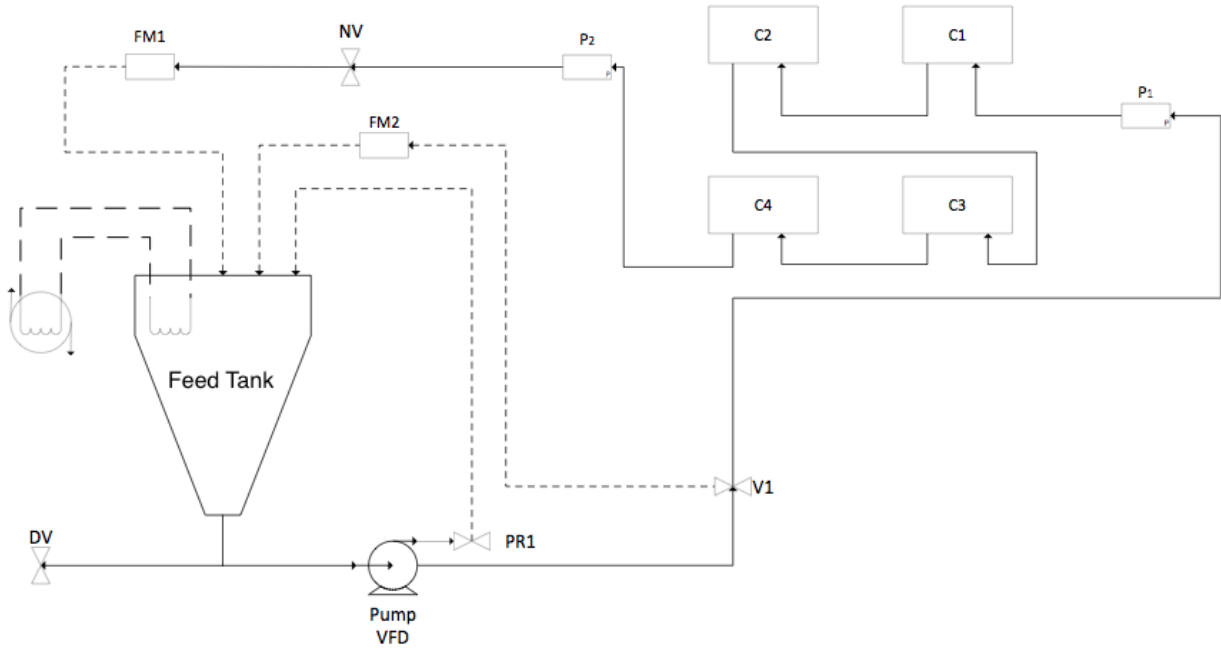
where σ is the stress measured in kPa, F is the force in N, A_L is the area across which the load is exerted and is a constant of 525 mm² ($5.25 \times 10^{-4} \text{ m}^2$), ϵ is the strain relationship in %, dL is the elongation of the membrane and L_o is the original length of the membrane (35 mm).

Both relationships are used to calculate the modulus of elasticity of the membrane or the Young's modulus (E) given as

$$E = \frac{\sigma}{\epsilon} \quad (3.3)$$

3.3.2 Membrane performance evaluation

A SterlitechTM membrane test cell system was used for the filtration tests (Figure 3.5). The system can test 4 membranes simultaneously. This made it easier to repeat the experiment and reduce the standard deviation. To compact the membranes, distilled water was passed through each membrane



Displayed text	Description
P1	Inlet pressure sensor in psi/bar
P2	Outlet pressure sensor in psi/bar
VFD	Variable frequency drive
PR1	Pressure relief valve in 150 psi
DV	Tank drain valve
V1	Bypass needle valve
NV	Control valve
FM 1& 2	Flow sensor 1 and 2
C1, C2, C3 & C4	Membrane cells

Figure 3.5: SterlitechTM membrane test cell system used for filtration tests

at 100 psi (689.475 kPa) for a minimum of 4 h. Compacting ensured that the permeate fluxes were stabilized before recording, to allow for a true representation of the fluxes. Pure water fluxes were calculated at four different pressures for each membrane: 25, 35, 45 and 55 psi (or 172.37, 241.32, 310.26 and 379.21 kPa). Chakrabarty et al. (2010) used similar cross flow UF pressures in separation oil water mixtures. The prepared synthetic produced water was passed through the membranes and the permeate fluxes determined at the same pressures. The fluxes were calculated using Equation 3.4

$$J_p = \frac{V}{A \times \Delta t} \quad (3.4)$$

where J_p is the permeate flux (for both distilled water and produced water fluxes) obtained and is measured in $(L/m^2.hr)$, V is the volume of the collected permeate in liters, A is the effective membrane area (which is a constant of $0.0042 m^2$ for this system) and Δt is running time during which permeate was collected in hours.

The same experiment was conducted at a constant pressure of 45 psi for 2 h to determine the flux variation with time. The volume after every 15 min was measured using measuring cylinders. The collected volumes were used to calculate the relative flux (J_r), which is given by Equation 3.5;

$$J_r = \frac{J_t}{J_o} \quad (3.5)$$

where J_t is the flux after every 15 min and J_o is the initial flux. The flux decline (FD_t) was then calculated using Equation 3.6;

$$FD_t = \left(1 - \frac{J_t}{J_o}\right) \times 100 \quad (3.6)$$

The efficiencies of the membranes were determined by calculating the percentage oil rejection (R) using Equation 3.7;

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3.7)$$

where C_f in mg/l is the concentration of the prepared synthetic produced oil (1000 mg/l) and C_p is that of the oil in the permeate. The permeate concentrations were measured using a UV-Vis photo-spectrometer with wavelength ranging from 200nm to 800nm. The calibration curve used to determine the concentrations of the oil permeates was obtained from literature and it is the curve mostly used for crude oil-water mixtures (Chakrabarty et al., 2010).

If all the modifications considered above are taken into consideration, 12 different membranes. They include

1. Bare PSf membrane made *via* the PI method
2. Bare PSF membrane made *via* the SC method
3. fCNT/PSf membrane made *via* the PI method (fCNT grown from on Fe/Co on $CaCO_3$)
4. fCNT/PSf membrane made *via* the SC method (fCNT grown from on Fe/Co on $CaCO_3$)
5. fCNT/PSf membrane made *via* the PI method (fCNT grown from on Fe/Co on zeolite)
6. fCNT/PSf membrane made *via* the SC method (fCNT grown from on Fe/Co on zeolite)
7. Bare PSf membrane made *via* the PI method on an NWF support
8. Bare PSF membrane made *via* the SC method on an NWF support

9. fCNT/PSf membrane made *via* the PI method on an NWF support (fCNT grown from on Fe/Co on CaCO_3)
10. fCNT/PSf membrane made *via* the SC method on an NWF support (fCNT grown from on Fe/Co on CaCO_3)
11. fCNT/PSf membrane made *via* the PI method on an NWF support (fCNT grown from on Fe/Co on zeolite)
12. fCNT/PSf membrane made *via* the SC method on an NWF support (fCNT grown from on Fe/Co on zeolite)

Not all these variations were however studied primarily due to limited budget and time constraints. The fCNT grown from on Fe/Co on zeolite supports were not used in membrane production because of their low yield and high level impurities. Membranes made from the SC method were also not evaluated during the filtration tests because their very dense nature did not allow any permeates to be collected at the operating pressures

References

- Chakrabarty, B., Ghoshal, A. K., Purkait, M. K., Dec. 2010. Cross-flow ultrafiltration of stable oil-in-water emulsion using polysulfone membranes. *Chemical Engineering Journal* 165 (2), 447–456.
- Ferrari, A. C., Robertson, J., May 2000. Interpretation of raman spectra of disordered and amorphous carbon. *Physical Review B* 61 (20), 14095–14107.
- Flahaut, E., Laurent, C., Peigney, A., 2005. Catalytic CVD synthesis of double and triple-walled carbon nanotubes by the control of the catalyst preparation. *Carbon* 43 (2), 375–383.
- Gohil, J. M., Ray, P., Oct. 2009. Polyvinyl alcohol as the barrier layer in thin film composite nanofiltration membranes: Preparation, characterization, and performance evaluation. *Journal of Colloid and Interface Science* 338 (1), 121–127.
- Hernadi, K., Fonseca, A., Nagy, J. B., Bemaerts, D., Fudala, A., Lucas, A. A., Nov. 1996. Catalytic synthesis of carbon nanotubes using zeolite support. *Zeolites* 17 (5–6), 416–423.
- Khayet, M., Khulbe, K. C., Matsuura, T., Jul. 2004. Characterization of membranes for membrane distillation by atomic force microscopy and estimation of their water vapor transfer coefficients in vacuum membrane distillation process. *Journal of Membrane Science* 238 (1–2), 199–211.
- Khulbe, K. C., Matsuura, T., Mar. 2000. Characterization of synthetic membranes by raman spectroscopy, electron spin resonance, and atomic force microscopy; a review. *Polymer* 41 (5), 1917–1935.
- Maphutha, S., Moothi, K., Meyyappan, M., Iyuke, S. E., Mar. 2013. A carbon nanotube-infused polysulfone membrane with polyvinyl alcohol layer for treating oil-containing waste water. *Nature* 3.
- Mhlanga, S. D., Mondal, K. C., Carter, R., Witcomb, M. J., Coville, N. J., 2009. The effect of synthesis parameters on the catalytic synthesis of MWCNTs using Fe-Co/CaCO₃ catalysts. *South African Journal of Chemistry* 62 (67).
- Osorio, A. G., Silveira, I. C. L., Bueno, V. L., Bergmann, C. P., Dec. 2008. H₂SO₄/HNO₃/HCl—functionalization and its effect on dispersion of carbon nanotubes in aqueous media. *Applied Surface Science* 255, 2485–2489.
- Phao, N., Nxumalo, E. N., Mamba, B. B., Mhlanga, S. D., 2013. A nitrogen-doped carbon nanotube enhanced polyethersulfone membrane system for water treatment. *Physics and Chemistry of the Earth, Parts A/B/C* 66, 148–156.

Chapter 4

Results and discussions

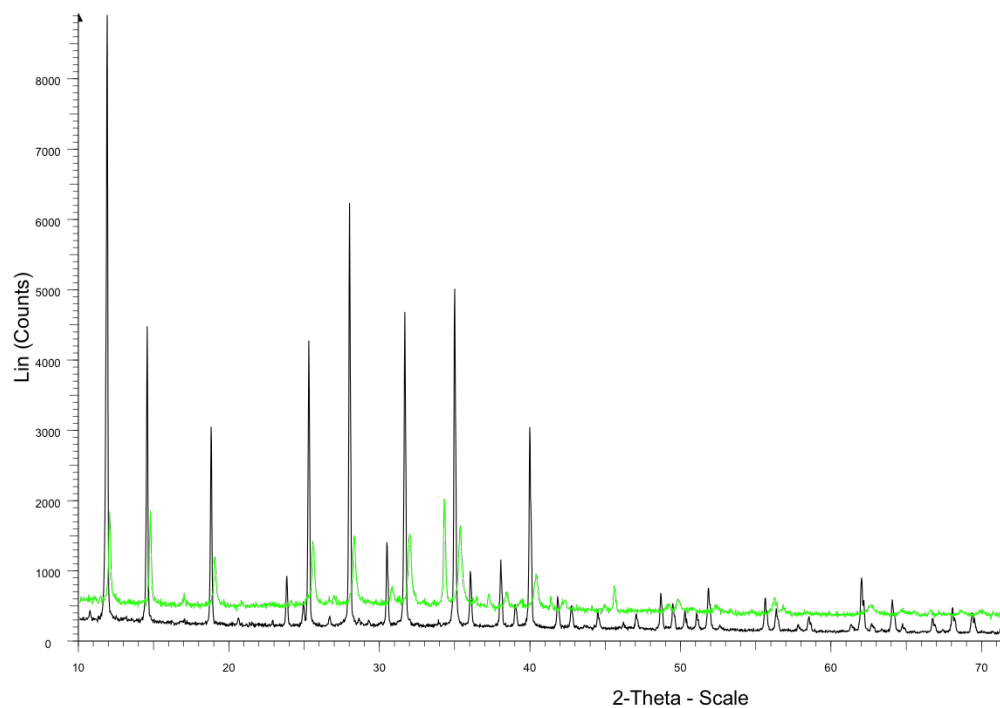
4.1 Introduction

This chapter presents the qualitative and quantitative results obtained from this research. The characterization techniques performed on the CNTs are first presented. The physical, chemical and mechanical properties of the membranes were then analyzed according to three different criteria: the effect of the membrane preparation technique, the effect of CNT addition and the effect of the NWF support. The performance of the membranes are also reported. The effects of pressure and time on the permeate flux and flux decline due to fouling were investigated and reported. The oil rejections of each membrane are also discussed in this chapter. Conclusions and recommendations presented in the next chapter are drawn from the experimental results presented here.

4.2 Characterization of the Fe/Co catalysts

The spectra presented in Figure 4.1 confirm the crystalline structures of the zeolite (the red spectrum in Figure 4.1a) and CaCO_3 to be cubic and rhombic respectively (the black spectrum in Figure 4.1b). The spectra for just zeolite shows the peaks that correspond to sodium, aluminate and silicate, with sodium being the cation adsorbed onto the alumina silicate structure. This spectra corresponds to zeolite with a chemical formula of $\text{Na}(\text{AlO}_2)(\text{SiO}_2)$. Similarly Figure 4.1b confirms the chemical equation of the CaCO_3 support. After impregnation, two different phases are formed for the zeolite support; a cubic phase of cobalt sodium aluminate silicate ($\text{Co}_4\text{Na}_4\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$) phase, and an orthorhombic phase made of Sekaninaite ($\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$). The detection limits for the Fe and Co metals is too low in the CaCO_3 support and thus not too evident in Figure 4.1b. The shift in the spectrum further verifies the success of the wet impregnation method.

These results are confirmed with an SEM and EDS analysis in Figures 4.2 and 4.3. The SEM images confirm the cubic and rhombic structures of the zeolite and CaCO_3 supports respectively (Figures 4.2a and 4.2c). The crystalline structures are still evident after impregnation with a few defects (Figures 4.2b and 4.2d). The EDS also shows that the Fe and Co metals got imbedded into the micropores of the supports (Figures 4.3).



(a) XRD spectrum for zeolite and Fe/Co on zeolite

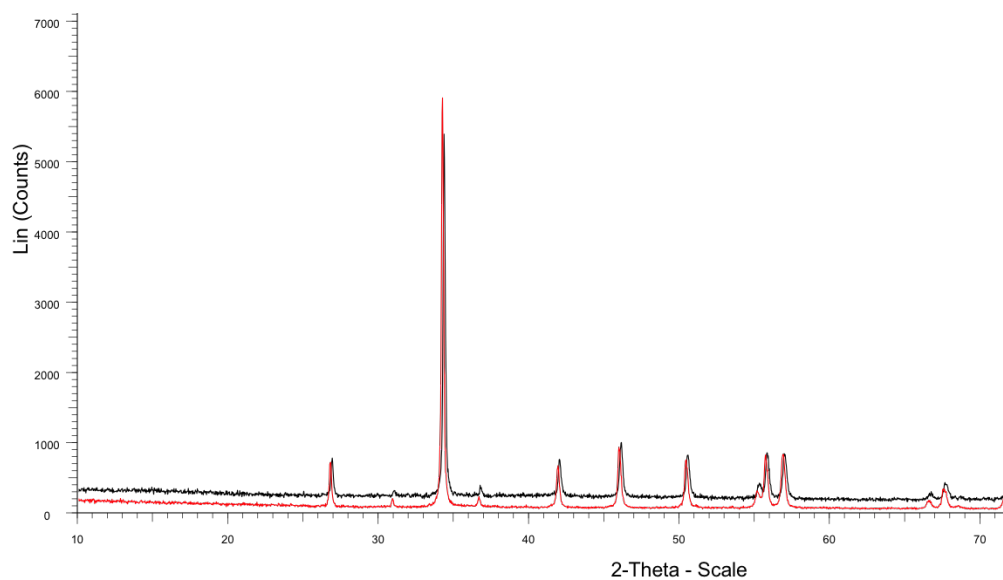
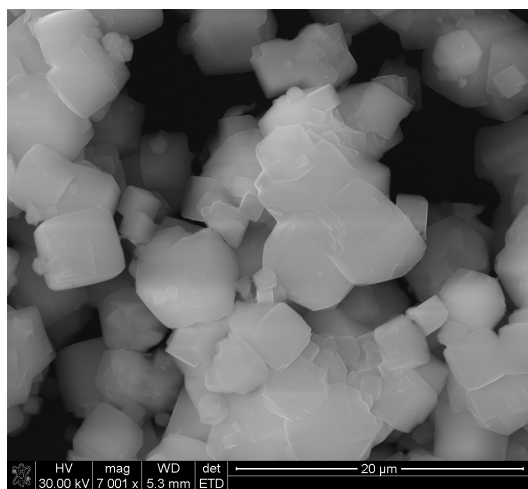
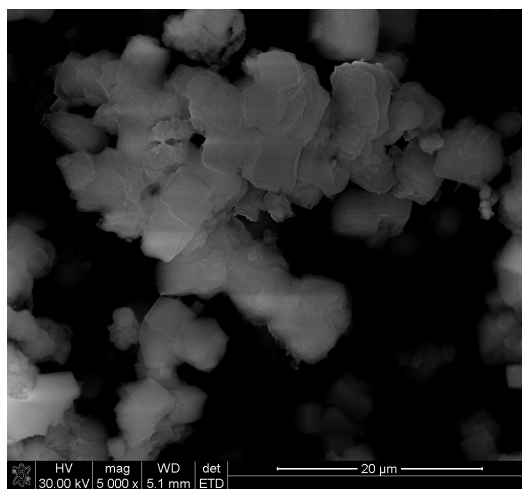
(b) XRD spectrum for CaCO_3 and Fe/Co on CaCO_3

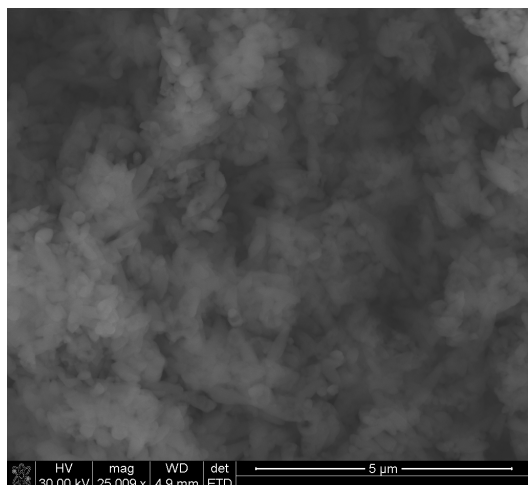
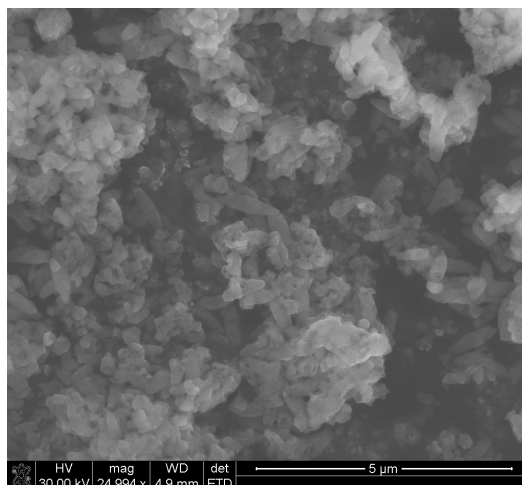
Figure 4.1: XRD spectrum for catalysts

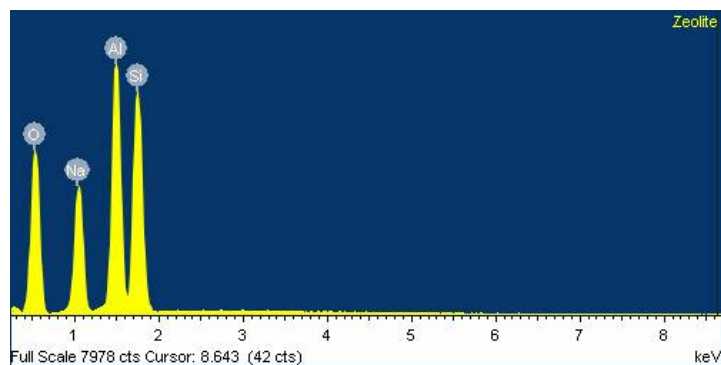


(a) SEM image for Zeolite

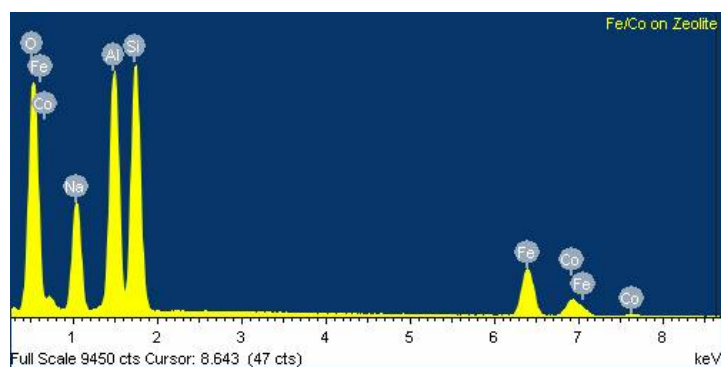


(b) SEM image for Fe-Co catalyst supported on Zeolite

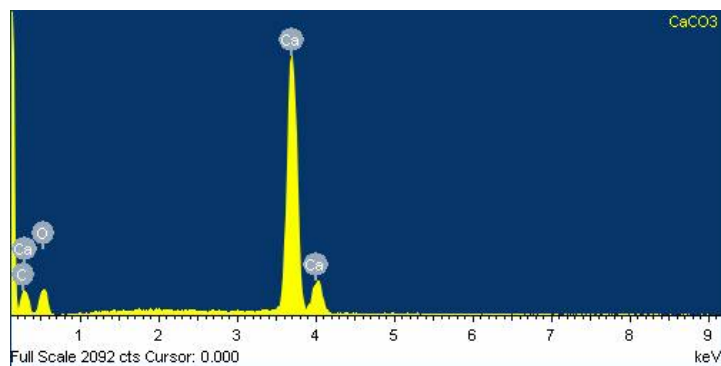
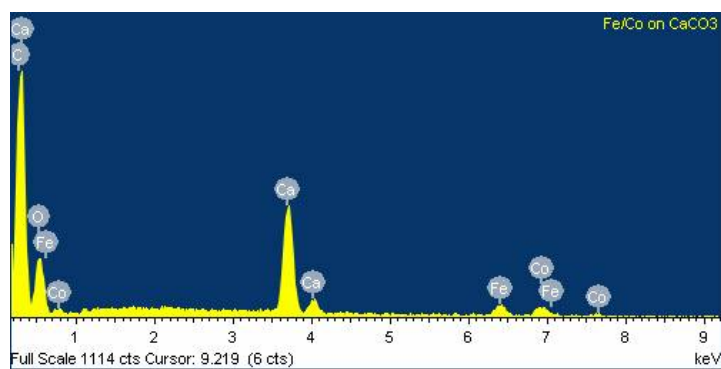
(c) SEM for pure CaCO₃(d) SEM image for Fe/Co on CaCO₃Figure 4.2: SEM images metal catalysts on a zeolite and CaCO₃ supports



(a) EDS analysis for pure zeolite



(b) EDS analysis for Fe/Co catalyst on Zeolite support

(c) EDS for pure CaCO_3 (d) EDS for Fe/Co catalysts on CaCO_3 supportFigure 4.3: EDS analysis for Fe/Co catalyst on zeolite and CaCO_3 supports

The results presented above for characterizing the catalysts validated the success of the wet impregnation method. These catalysts were then used to prepare CNTs.

4.3 CNT yields

On average, CNTs produced from CaCO_3 support had a larger yield than that produced from the zeolite support. About 4 runs were performed for each catalyst support. For every gram of CaCO_3 supported catalysts (CNT-c), an average of $2.30 \text{ g} \pm 0.31$ of raw CNTs was produced while an average of $1.17 \text{ g} \pm 1.12$ of CNTs was produced for every gram of zeolite supported catalyst (CNT-z) used. All the operating conditions such as the gas flow rates and reaction temperatures were kept constant. It was expected that CNT-z have a higher yield of CNTs with smaller diameters due to zeolite's larger surface area and better metal-support interaction (Kumar and Ando, 2010). The deviation is attributed to the poor quality CNTs produced by this catalyst as shown in the characterization below. The conditions used here did not provide the perfect conditions to fully allow the CNTs to grow from the metal catalyst embedded in the zeolite pores.

Large amounts of CNTs were also lost during functionalization, washing, filtration and drying and CNT agglomeration lost during the experimental procedures. It is therefore useful to have a higher yield to allow for these losses during further treatment processes.

4.4 Characterization of CNTs

4.4.1 TEM analysis

The TEM images for both the raw and as grown CNTs are presented in Figure 4.4. The images confirm the formation of tubular multi-walled structures. The as grown CNTs in Figures 4.4a and 4.4c are from CNT-z and CNT-c respectively. The dark spots show are impurities in the synthesized CNTs. These impurities are either metallic, amorphous carbon, or other nano-particles (Hou et al., 2008). The dark spots are not as evident in the fCNTs in Figures 4.4b and 4.4d. The smaller image of higher magnification in Figure 4.4a shows zeolite catalyst at the tip of the tube, confirming the growth mechanism of the CNTs as the tip growth mechanism.

From these morphological images, the outer diameter distributions for the grown CNTs were analyzed using ImageJ image processing software. Figure 4.5 shows the diameter distribution in both the as grown nanotubes and the cleaned nanotubes for both supports. The diameters were reduced after functionalization of the CNT-c. However the reverse effect was observed for the CNT-z. The HNO_3 used for functionalization interacted with the impurities and the outer walls of the CNTs. In the case of the CNT-c this reduced the outer diameters (Phao et al., 2013). For the CNT-z however, the acid removed any remaining metallic or zeolitic catalysts, amorphous carbons, or nano-particles with small diameters leaving just CNTs with larger diameters. The figure also shows that CNT-z and fCNT-z both have a smaller size distribution ranging from 10nm to 50nm, compared to CNT-c and fCNT-c, which have a larger size distribution ranging from 20nm to 80nm.

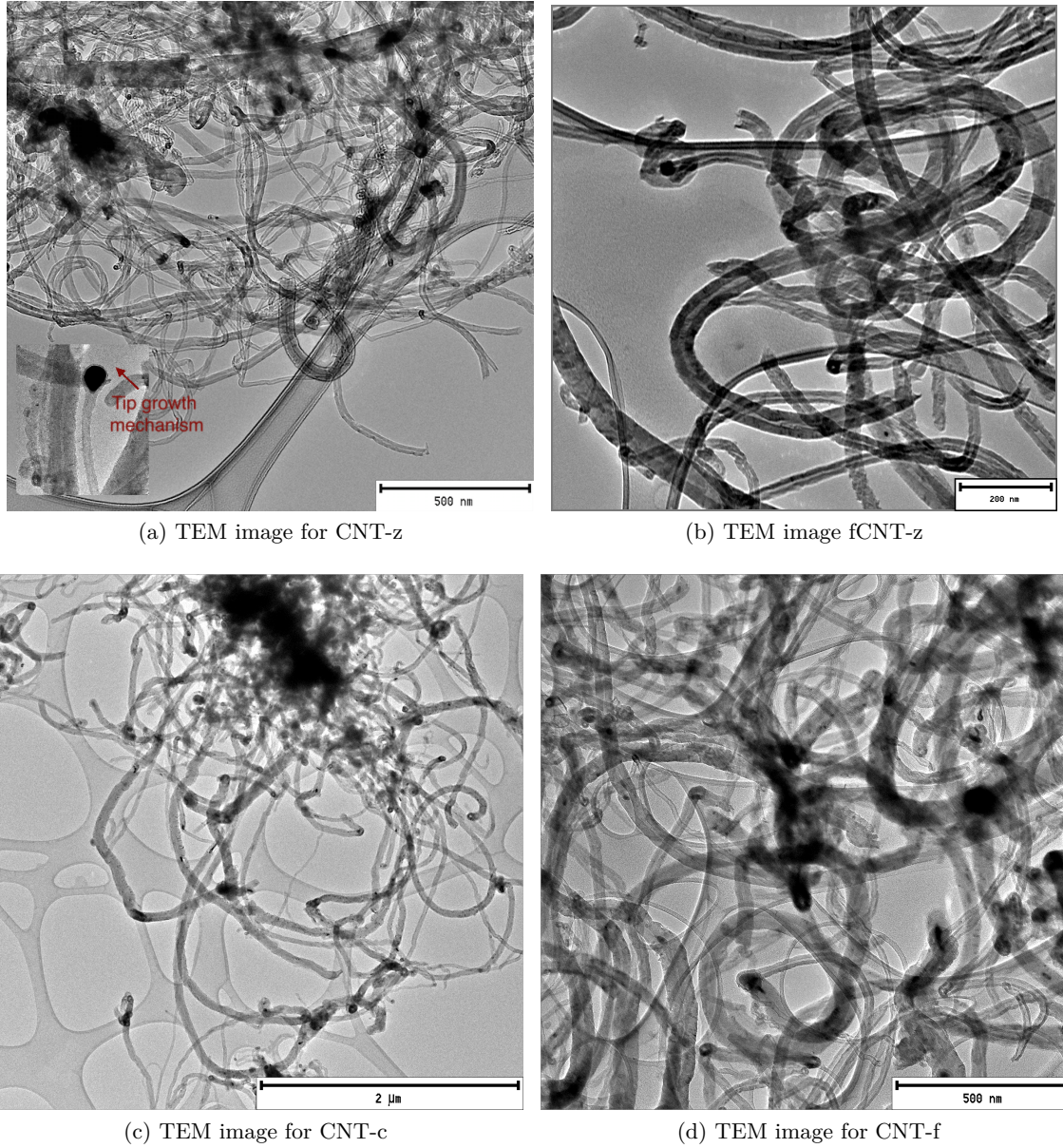


Figure 4.4: TEM images for synthesized CNTs

This is attributed to the difference on pore sizes of the CaCO_3 and zeolite crystals, where the metallic catalysts are imbedded (Hernadi et al., 1996; Pattinson et al., 2013). The pore size for a typical Y zeolite is $7.4\text{\AA}$ compared to that of C_{60} which is $10.0\text{\AA}$.

4.4.2 Raman spectroscopy

Figure 4.6 presents the Raman spectra for the as grown CNTs and fCNTs. The plot clearly shows the characteristic D and G bands present in CNTs, confirming that the synthesized material was carbon based with some defects in it. The increase in intensity ratios $I_{D/G}$ for CNT-c and fCNT-c

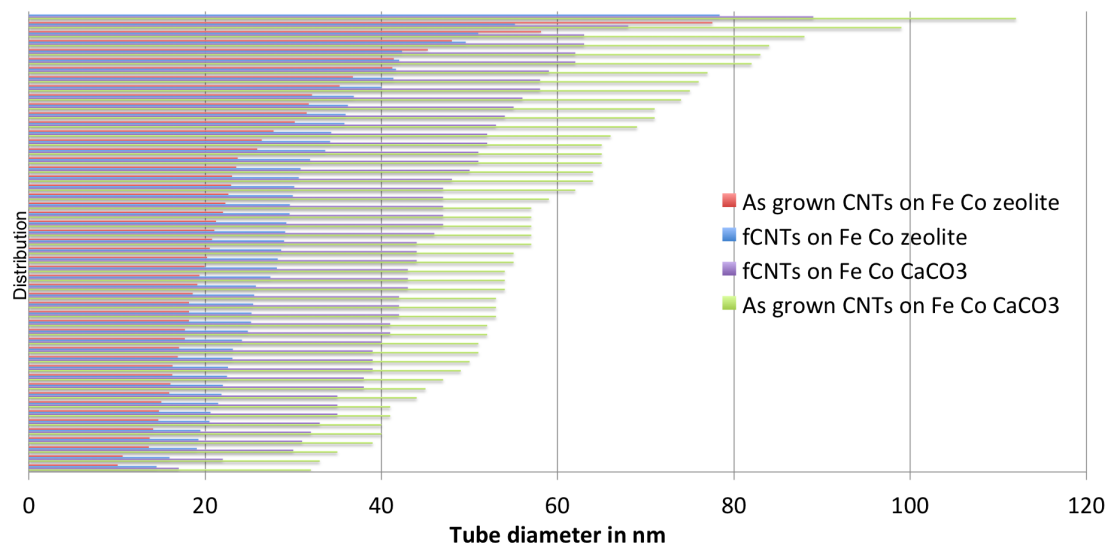


Figure 4.5: CNT diameter distribution

(from 0.899 to 0.940 for CNT-c and fCNT-c respectively) shows that the disorder in the graphene structures increased after functionalization. The $I_{D/G}$ ratio for CNT-z and fCNT-z however decreased from 0.950 to 0.929 for CNT-z and fCNT-z respectively, indicating a decrease in the disorder. This disparity can be attributed to presences of alumina-silicate impurities in CNT-zs.

All the plots have peaks forming at the same shifts. This indicates that they are the same material i.e. the acid treatment did not significantly affect the synthesized CNTs. The spectrum also distinguishes between the CNTs grown from the zeolite support and that from CaCO_3 support. The $I_{D/G}$ is higher for the CNT-z and fCNT-z than for CNT-c and fCNT-c. This indicates a lesser degree of graphization and disorder in the latter CNTs.

4.4.3 FTIR

Figure 4.7 shows the FTIR spectra for the synthesized CNTs. There are 2 peaks indicated on the plot that indicates the proper synthesis and functionalization of CNTs: the $C = C$ at 1600 cm^{-1} and the $C - O$ peak at 1030 cm^{-1} , which indicates the presence of carboxylic groups from acid treatments (Vatanpour et al., 2011). There are slight peaks in the plot for fCNTs-c between 2900 cm^{-1} and 3400 cm^{-1} which would prove the presence of $C - H$ and $C - O$ bonds. These peaks are however not too defined thus are not conclusive enough to conclude the presence of these bonds.

Results from the FTIR agree with the results from the Raman spectroscopy to confirm that the CNTs were functionalized.

4.4.4 TGA and DTG

Figure 4.8 shows the temperature profiles of the CNTs. From the plot, CNTs start decomposing at 500°C . The CNT-cs are the most thermally stable CNTs, decomposing later than all the other

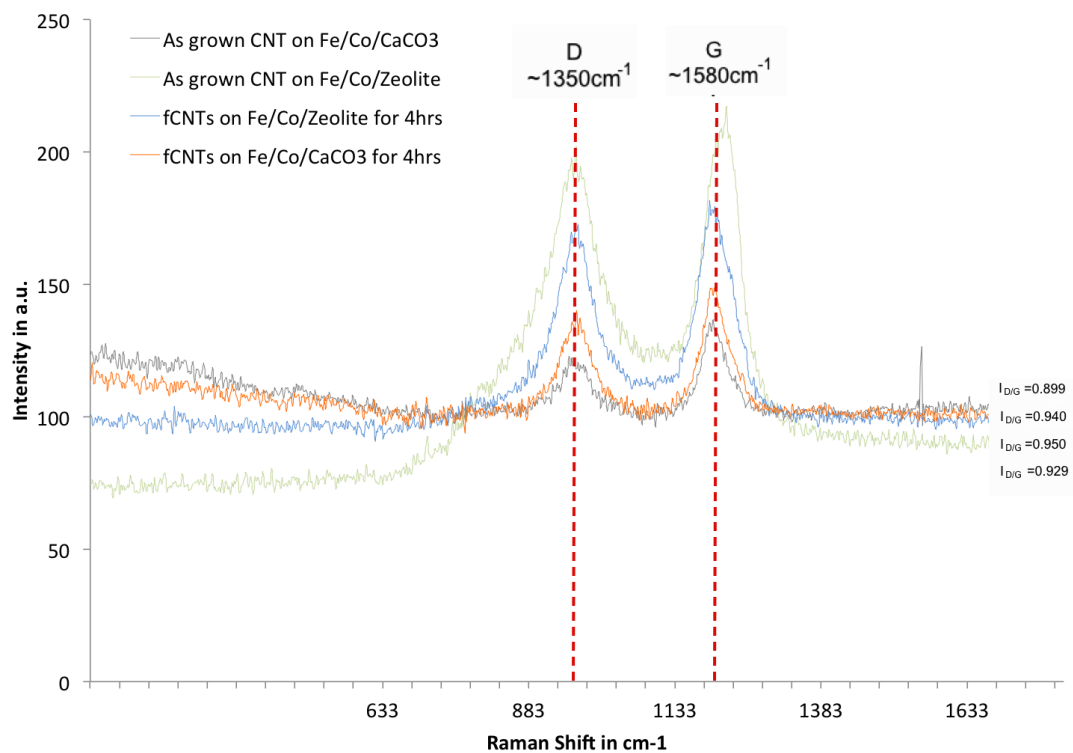


Figure 4.6: Raman spectra for synthesized nanotubes

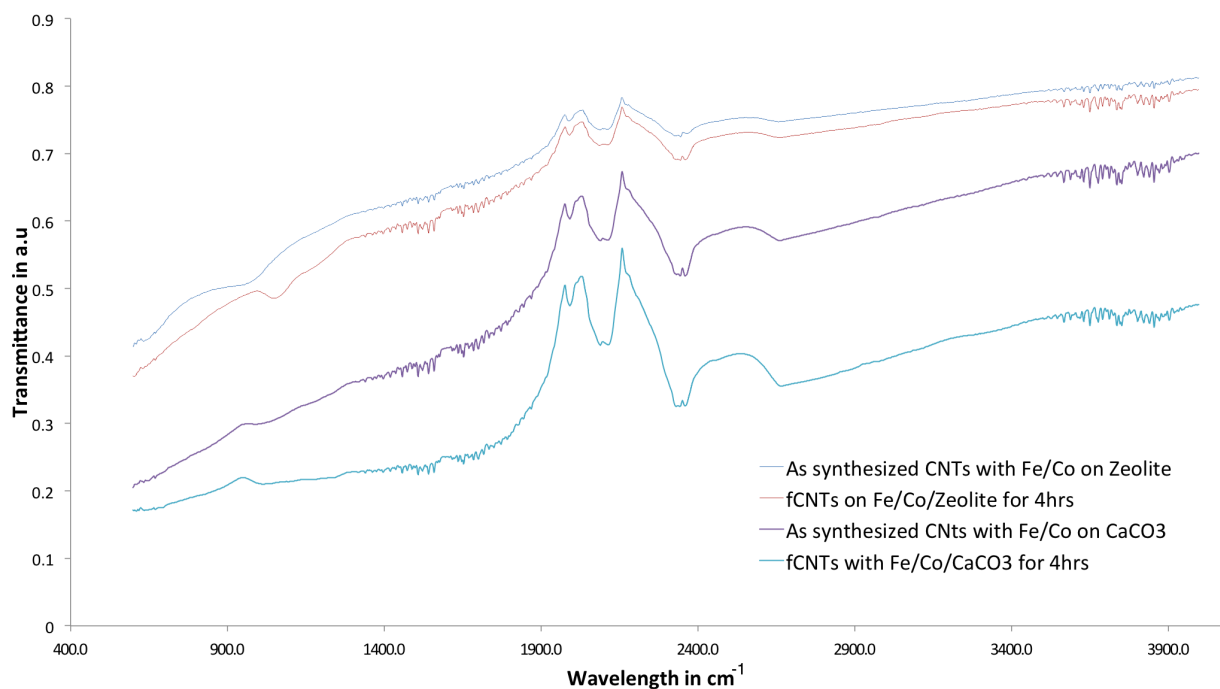


Figure 4.7: FTIR spectra for synthesized nanotubes

CNTs. This can be attributed to the impurities prevalent in the CNT-zs (Mhlanga et al., 2009). The plot also shows that fCNTs decompose before the as grown CNTs. This is the case for both the CNT-c and CNT-z. This is because the presence of functional groups in the fCNTs distorts the graphene structure making it easier to decompose (Flahaut et al., 2005). These results generally agree with that from literature and also with the Raman spectroscopy and FTIR results.

The TGA profiles also help distinguish the effect of the support on the grown CNTs better. CNT-c and fCNT-c lose 90% and 97% of its weight respectively after decomposition. CNTs-z and fCNT-z on the other hand lose just 40% and 63% of their weights respectively. This indicates that CNTs grown from CaCO_3 supported catalysts are of a higher purity than those grown from zeolite-supported catalysts. The metals in both catalysts are converted to oxides which are removed during CNT production and functionalization. For the CNT-c and fCNT-c, the CaCO_3 support is converted to CaO (lime), which in turn is burnt off at CO or CO_2 during the combustion reaction (Motchelaho et al., 2011). Zeolite on the other hand has a much stronger structure and required further characterization to determine the weight of the remaining materials.

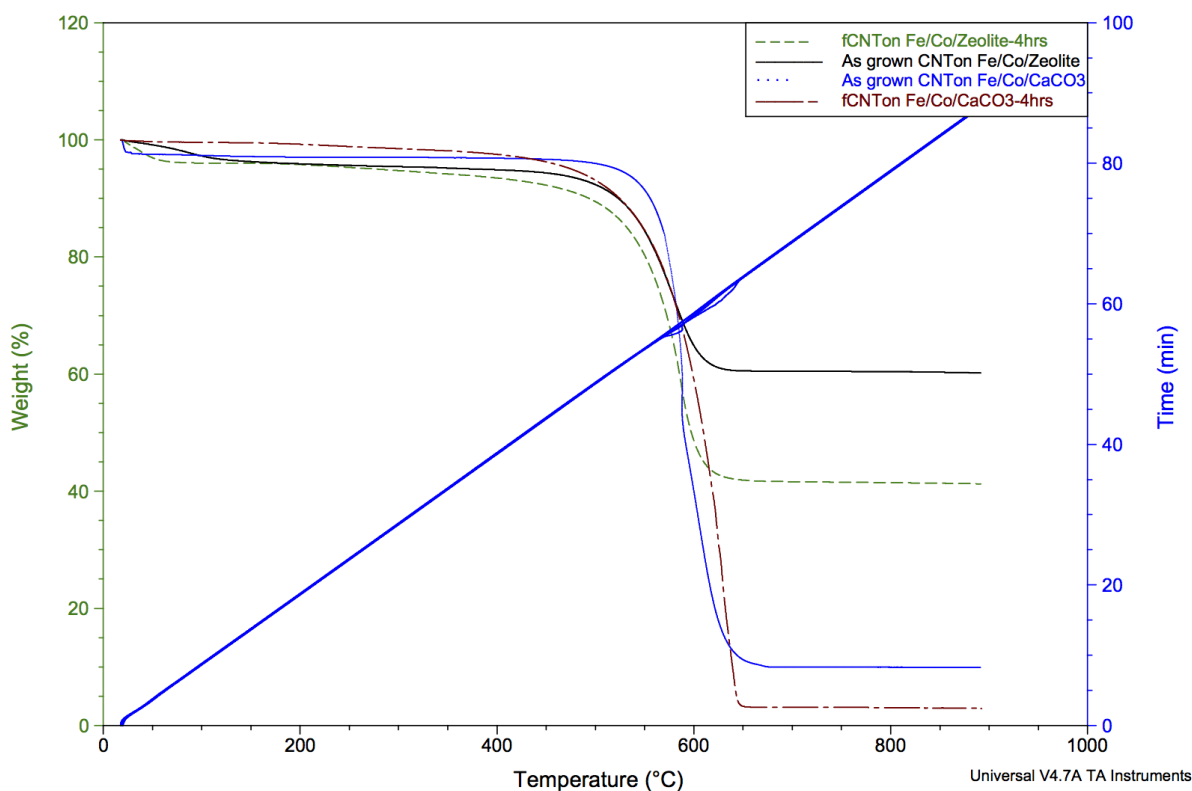


Figure 4.8: TGA profile for synthesized nanotubes

Derivate weight loss analysis (DTG) presented in Figure 4.9 gives the decomposition temperatures of the various components providing an indication of the purity of the nanotubes. The figure shows two decomposition peaks for CNT-c and fCNT-c support while CNT-z and fCNT-z have single peaks. Motchelaho et al. (2011) reports similar plots for CNTs grown on CaCO_3 supported

catalyst, attributing the peaks to the existence of SWCNTs and MWCNTs. Results presented in Figure 4.5 show that CNTs-c and fCNT-c have a larger range of outer diameters and thus the double peaks. CNT-z and fCNT-zs on the other hand have a small range of outer diameters and thus the single peaks. The increase in peak size after acid treatment also confirms the presence of functional groups in the CNTs walls (Tetana et al., 2012).

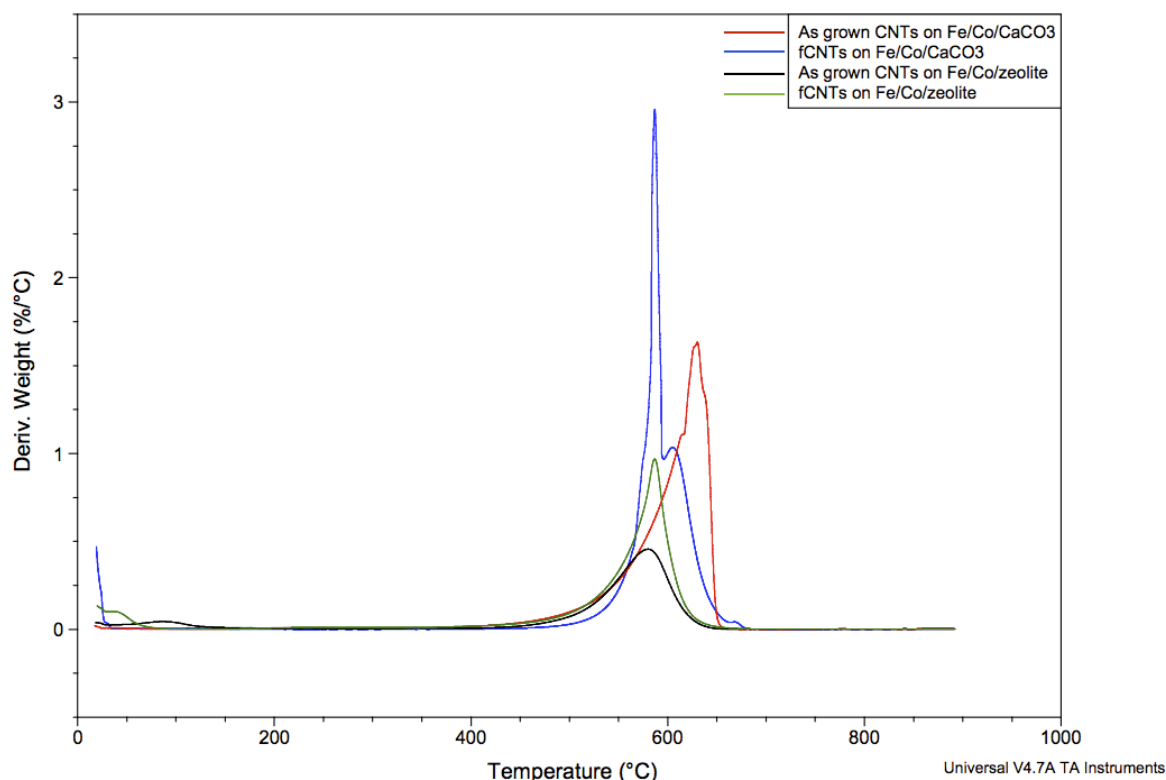


Figure 4.9: DTG Analysis for synthesized nanotubes

4.5 Further characterization of CNTs from zeolite supported catalyst

An SEM and EDS analysis was performed on CNT-z and fCNT-z to determine the composition of the impurities. The impurities are more evident in a low magnification SEM image (Figure 4.10) than they are in the TEM images (Figure 4.4b). An EDS analysis presented in Figure 4.11 shows the removal of all the catalytic impurities after the acid treatment except for SiO_2 remaining after the acid treatment. This means that SiO_2 accounts for the 37% weight left in the after the

nanotubes are burnt off (Figure 4.8). SiO_2 has a very high thermal stability and only decomposes at high temperatures (Ha et al., 2012) In order to remove the impurities from CNTs, Hernadi et al.

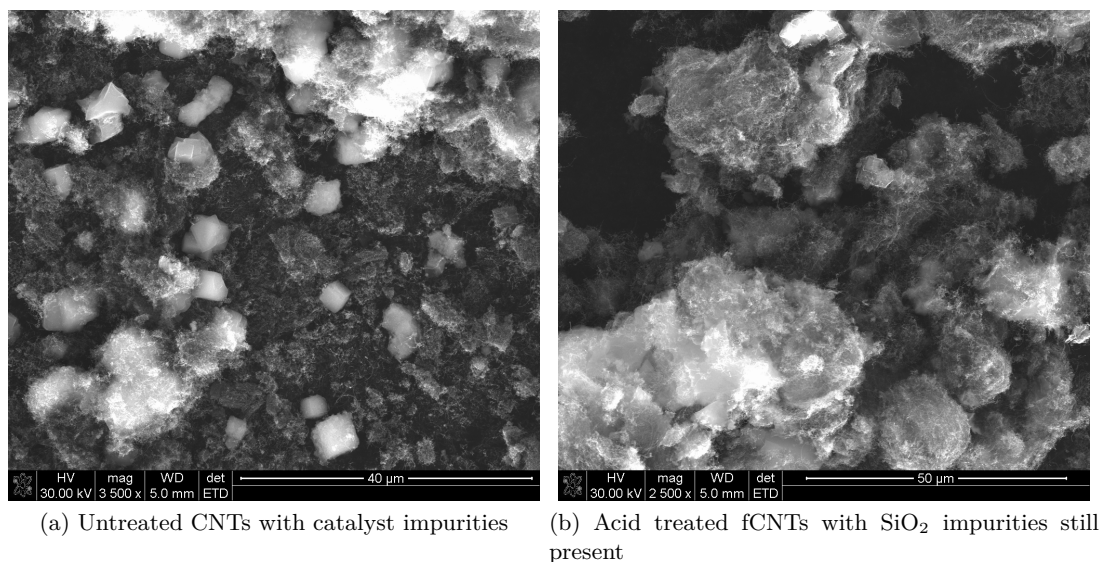


Figure 4.10: SEM analysis of CNTs grown from zeolite-supported catalyst

(1996) proposed HF treatment. A 50% HF solution is used to dissolve the silicates leaving just nanotubes. Figure 4.12 shows the TEM and SEM images for the HF etching fCNTs. It shows a significant decrease in the presence of SiO_2 . From the TEM images, it is seen that the HF treatment did not destroy the walls of the nanotubes. TGA and EDS analysis shown in Figures 4.13 and 4.14 also substantiate the complete removal of impurities from the etched zeolite. The TGA profile in Figure 4.13 shows the decomposition of carbon at 527°C , until 100% of the weight is burnt off. This in turn results in the cleanest fCNT; even more clean than fCNT-c in Figure 4.8, which loses 97% of its weight.

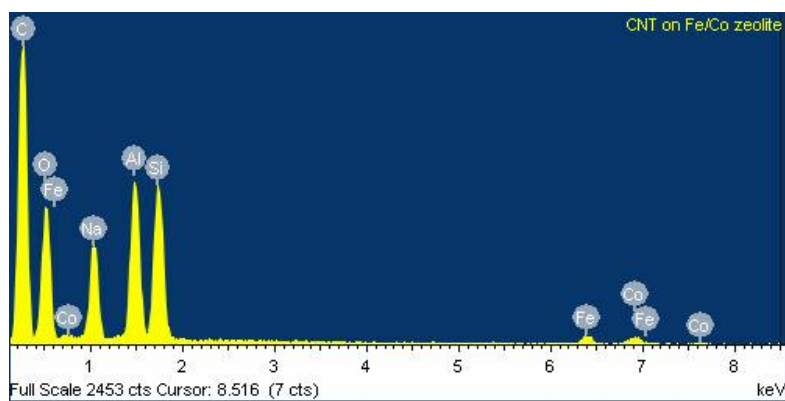
4.6 Membrane characterization

The properties of the synthesized membranes are presented here.

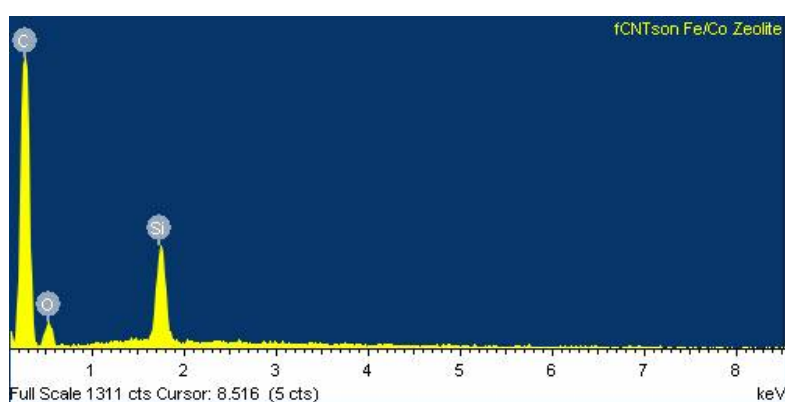
4.6.1 Effect of membrane preparation technique

Membranes prepared using both the PI technique and the solution casting method were characterized and the differences in their properties presented.

There is a clear distinction in the physical appearance of the membranes. PI turns the membranes opaque when immersed in the water (Figure 4.15a). Solution casting (SC) on the other hand produces clear membranes after drying in the heated chamber (Figure 4.15b).



(a) Untreated CNTs with catalyst impurities



(b) Acid treated fCNTs with silicate impurities

Figure 4.11: EDS analysis of CNTs grown from zeolite supported catalyst

SEM

Figure 4.16 shows the top and cross sectional SEM images of the membranes. Figures 4.16a and 4.16c shows very distinct differences between the membranes from the different techniques. Figure 4.16a shows the surface microporous structures of the bare PSf membrane from the PI method. These microporous structures are not observed in the PSf membrane made by the SC method. These top surface images are similar to those reported in literature (Maphutha et al., 2013; Phao et al., 2013). The cross sectional morphologies, confirm that types of membranes synthesized. The PI method makes membranes with a very thin top surface layer (approximately 130nm thick) and very visible sub surface voids while the SC method makes membranes with a very dense and thick to layer (about $23\mu\text{m}$ thick) with no clear sub-surface void. Comparing the SEM images 4.16 to that in Figure 2.1, it can be concluded that the PI method make microporous anisotropic membranes while the SC method produces non-porous isotropic membranes (Figure 2.1). The subsurface voids in the cross sectional image in Figure 4.16b is an indication of the permeability of the membrane. The average void size of the membranes made by PI is $0.659\mu\text{m}$. The sizes of these voids confirm the synthesis of micro-filtration PSf membranes (Table 2.2). These images are also consistent with

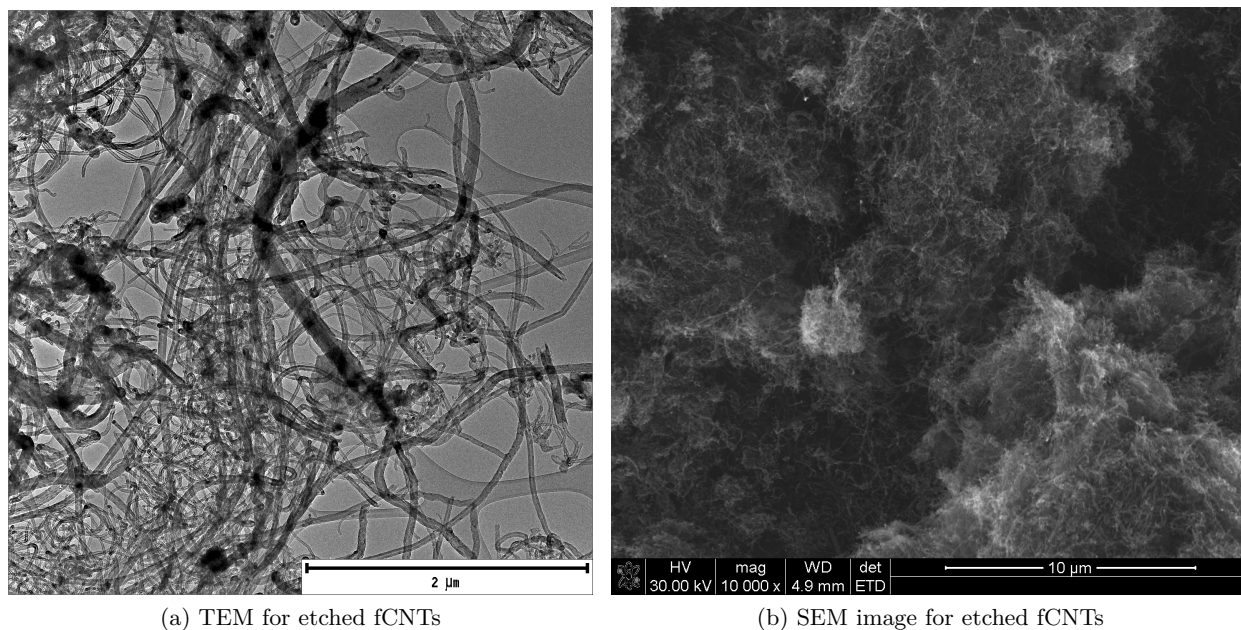


Figure 4.12: Morphology analysis of etched fCNT from zeolite-supported catalyst

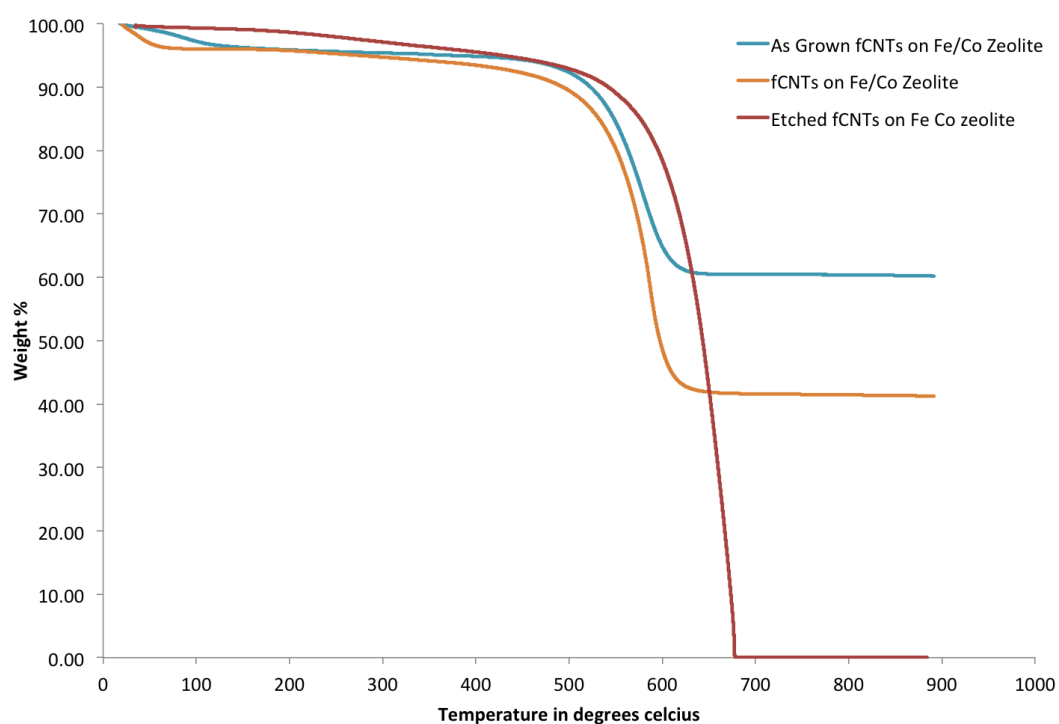


Figure 4.13: TGA comparing etched fCNTs on Fe/Co zeolite to non-etched CNTs

that from literature (Ghaemi et al., 2012; Pagidi et al., 2014).

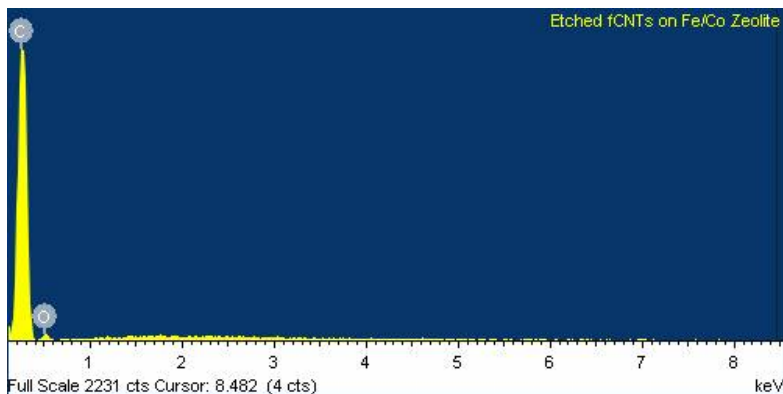


Figure 4.14: EDS for etched fCNTs

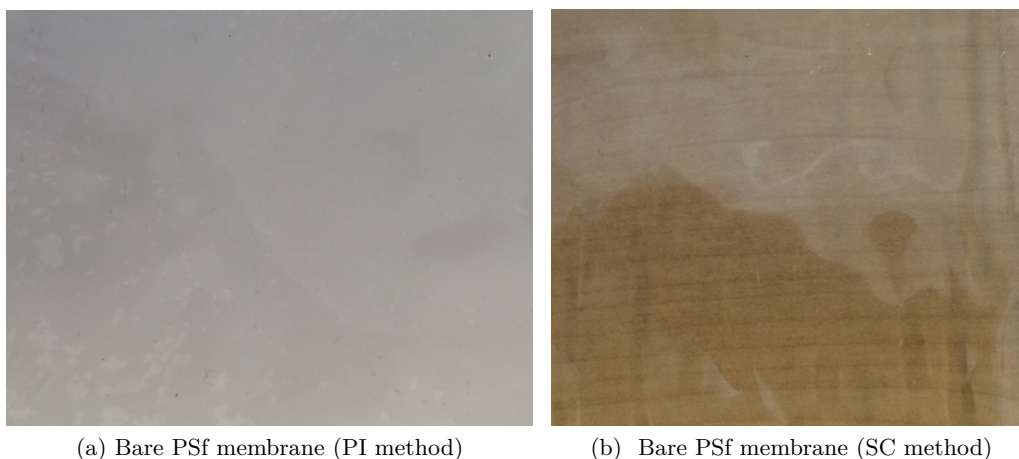


Figure 4.15: Difference in physical appearance of the PI and SC methods

AFM and contact angles

Figure 4.17 presents the AFM images for the PI and SC membranes. The image shows that the PI method (Figure 4.17a) produces membranes with a larger pore distribution than the SC membranes (Figure 4.17b). The mean roughness (R_a) of the membranes is 62.837nm and 13.296nm for the PI and SC membranes respectively. As expected, this makes the PI membrane more permeable than the SC membrane.

A sessile drop experiment was performed to determine the water contact angles of the membranes. These values gave an indication of how hydrophilic the membranes were. Results from the contact angle agree with the R_a measurements. The contact angles for the membranes were 79.832° and 88.210° for the the PI and SC methods respectively. The PI method made membranes with high permeabilities which soaks up water better than the non-porous isotropic SC membranes and thus the lower contact angles in the former. Table 4.1 summarizes the R_a and contact angles for the two membranes.

The difference in the roughness, the permeability rates and the contact angles could be due

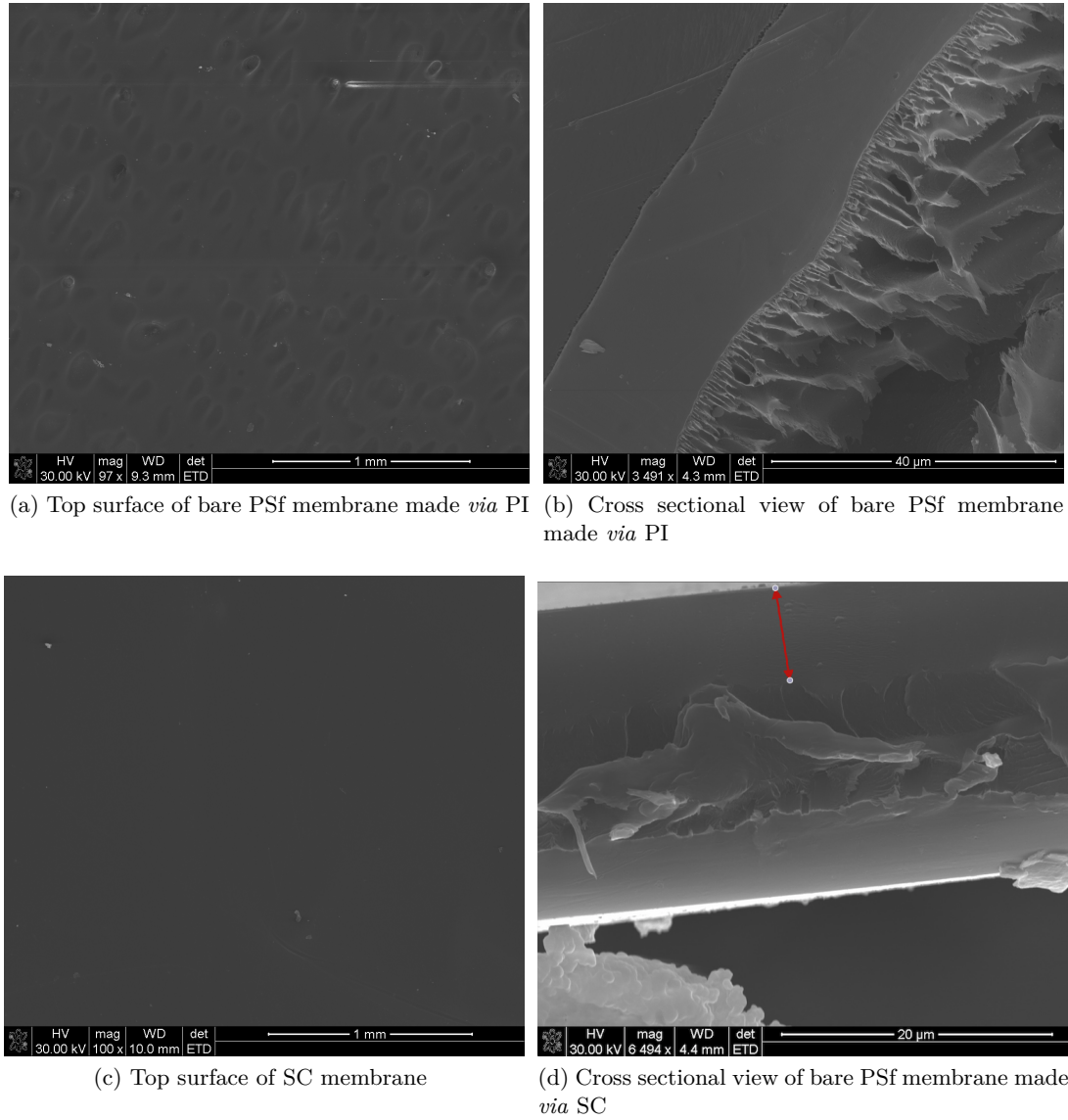


Figure 4.16: Top and cross-sectional SEM images of bare PSf membranes made *via* both PI and CS method membranes showing top surface and cross section

Table 4.1: Summary of contact angle and roughness results for the different techniques

	Contact angles	Roughness (R_a)
Bare PSf Membrane <i>via</i> PI	79.83 °	62.39 nm
Bare PSf SC membrane	88.21 °	13.40 nm

to the solvent evaporation process used in the two techniques. PI introduces pores more quickly during the water immersion process than drying in air in the solution casting method (Baker and Lokhandwala, 2008). The SC method relies on the water content in the atmosphere and thus has a slower liquid-liquid exchange compared to the PI method, which happens almost instantaneously

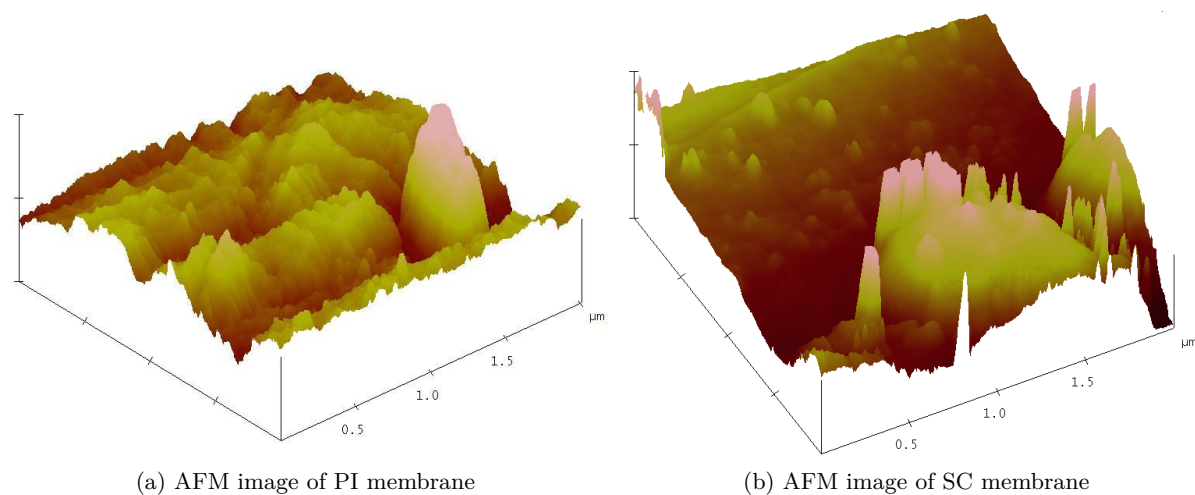


Figure 4.17: AFM images of PI and SC membranes

Mackenzie (2000).

FTIR

FTIR results confirm the atomic or bond structures of the two membranes. Figure 4.18 shows the spectrum for both membranes and the characteristic peaks for membranes. The characteristic

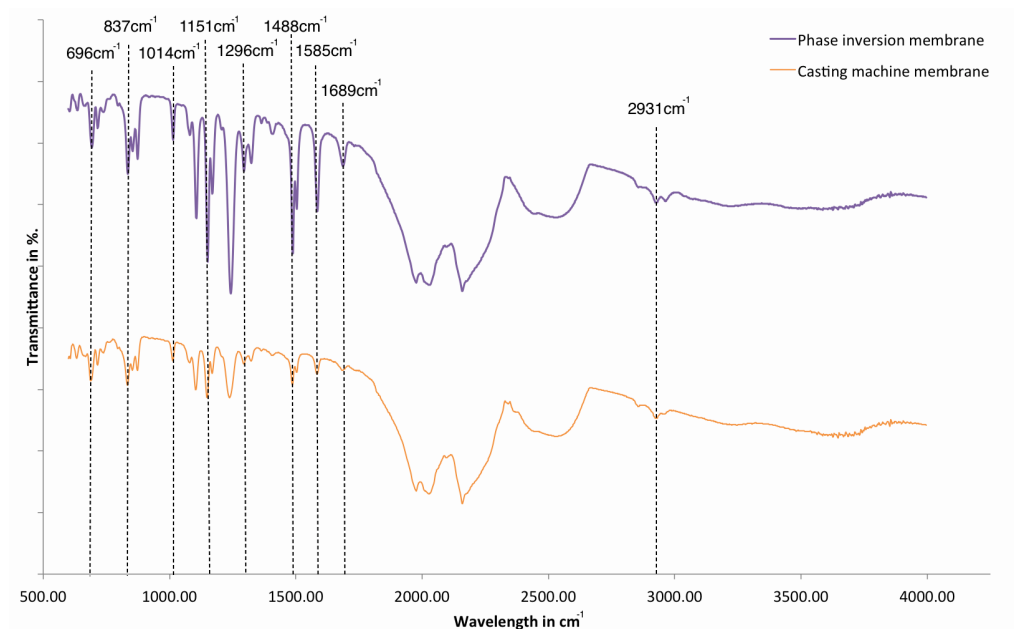


Figure 4.18: FTIR spectrum for bare PSf membranes for both the PI and SC methods

peaks of PSf membranes with no additives are summarized in Table 4.2 (adapted from Ghaemi et al. (2012)).

Table 4.2: Summary of characteristic peaks for PSf membranes

Wavelength in cm^{-1}	Bonds	
691	C-H	Aromatic out of plane
840	S-O-C	In PSf structure
1120 to 1150	R-SO ₂ -R	Symmetric stretching of sulfonated group
1220 to 1300	R-SO ₂ -R	Asymmetric stretching of sulfonated group
1015	C- O - C	Symmetric stretching of diphenyl ether group
1480 to 1600	C ₆ H ₆	Benzene structure
2940	C-H	Methyl group in isopropylene unit

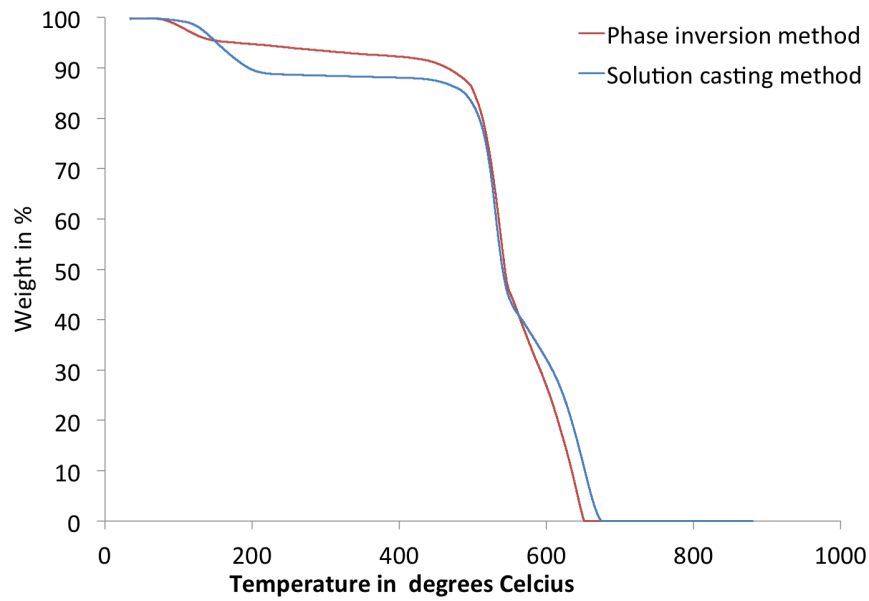
The FTIR spectrum for the PI membrane possesses these entire characteristic peaks, consistent with results presented in literature (Ghaemi et al., 2012; Choi et al., 2006a; Gao et al., 2014). The spectra for the bare PSf SC membrane also possess these peaks but at lower intensities due to the limited stretching and bending of bonds when introduced to the IR. This indicates a more structured SC membrane.

TGA

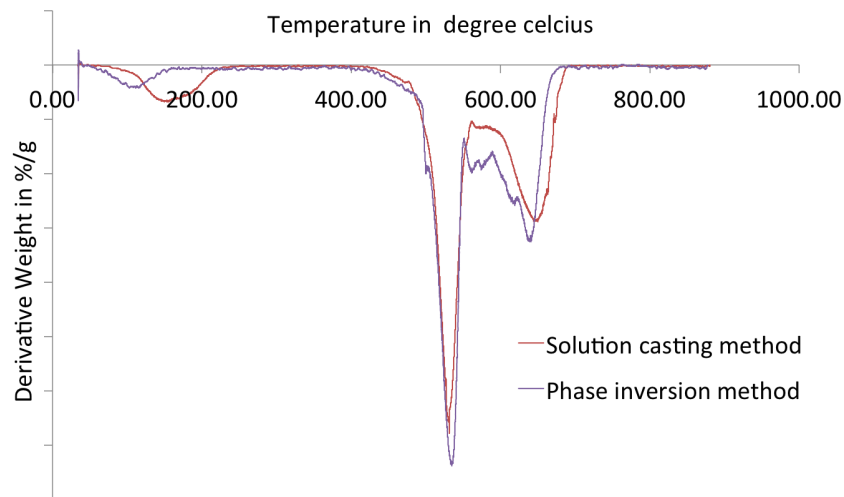
The membranes were burnt off under the same conditions the CNTs were exposed to; air at a flow rate of 20ml/min. The temperature profiles are presented in Figure 4.19. There are 3 major degradation points evident on the temperature profiles. The first peak between 100 °C and 200 °C was attributed to the solvent or water evaporating off the membrane. The second peak at 530 °C was due to the removal of the sulfone group from the PSf membrane and the third peak at 640 °C was attributed to the break down of the polymer chains (Figure 2.2) (Arockiasamy et al., 2013). The PI method produced membrane that more thermally stable at temperatures below 570°C, after which the SC membranes became more thermally stable. From the FTIR results in the previous section, the SC method produced membranes that were more structured, stretching and bending less under infrared. The thermal stability of this membrane at higher temperatures could be attributed to its structured nature. Another factor that could explain the thermal stability of the membrane produced *via* the SC method is the drying conditions the membrane was subjected to; a carefully temperature regulated chamber. This could have an influence in making the SC method produce membranes that are thermal stability at high temperatures compared to the PI method.

Tensile strength

Equations 3.1 and 3.2 were used in determining the tensile stress of the membranes. This gives an indication of the mechanical properties of each membrane and is important for the filtration process. It is the maximum stress under which the membrane can handle before it breaks. This is often called the ultimate tensile strength (UTS). Membranes with higher tensile stress are able



(a) TGA profile



(b) DTG profile

Figure 4.19: Temperature profile for PI and SC membranes

to withstand higher cross flow pressures and thus less susceptible to breaking during the filtration process. Membranes with a higher UTS are regarded as rigid.

The Young's modulus or the modulus of elasticity is also presented to give an indication of the stiffness of the membrane. It is expressed as a ratio of the stress and the strain (Equation 3.3).

The tensile strengths for the membranes were 13.55 and 61.34kPa respectively for the PI and SC methods respectively. The microstructures formed by the PI method, influenced the strength of the membrane by making it weaker. The dense structure of the SC membrane on the other

hand enhanced the strength of the membranes. It also had a significant effect on the rigidity of the membrane produced *via* the SC method, as shown in its higher Young's modulus. Table 4.3 summarizes the tensile strength and Young's modulus information for both techniques.

The tensile stresses expressed here are smaller than what the actual membranes were subjected to during the filtration tests. This is because the membrane samples used here were significantly smaller than those used in the filtration tests. The results however gave an accurate representation of the stresses the membranes can handle. Appendix C details how these values are obtained.

Table 4.3: Mechanical properties of the PI and SC techniques

	Tensile stress in kPa	Young's modulus in kPa
Bare PSf Membrane <i>via</i> PI	13.55	433.78
Bare PSf SC membrane	61.34	2000.00

4.6.2 Effect of CNT addition to the PSf membranes

A 0.04wt% CNT concentration was introduced into the membranes and its effect on the membranes' properties investigated. Phao et al. (2013) recommended this CNT concentration for the best permeate fluxes in PSf membranes. The fCNTs grown from the Fe/Co on CaCO_3 was used for this part of the project. This is because they have larger diameter sizes and therefore better interaction with the membrane than the fCNT-zs, which have smaller diameters. The fCNTs-c also had a higher yield and thus allowed more room for experimentation. Time constraints also did not permit for CNTs grown from the Fe/Co zeolite support to be blended with the PSf membranes for comparison. Figure 4.20 shows the difference between the CNT embedded membranes produced from the PI and SC techniques.

There is an even dispersion of CNTs on both membranes. The CNTs are however more evident in the SC membrane because of its transparent nature as shown in Figure 4.20b.

SEM

Figure 4.21 illustrates the top surface and cross sectional image of the bare PSf and fCNT/PSf membranes produced *via* the PI method.

The top surface of the fCNT/PSf membrane was similar that of the bare PSf membrane both evidently having surface pores. The voids in the cross section were slightly larger in the fCNT/PSf membranes with an average size of $1.587 \mu\text{m}$, compared to the $0.659 \mu\text{m}$ of the bare membranes. This is because the hydrophilic fCNTs increase the rate of liquid-liquid exchange between water and the NMP solvent (Choi et al., 2006a). These pore and void sizes are consistent with a microporous anisotropic membrane (Baker, 2000).

Similarly, the membranes produced *via* the SC method are presented in Figure 4.22, which shows the SEM images for the top surface and cross sectional view for both the bare and the CNT imbedded membranes.

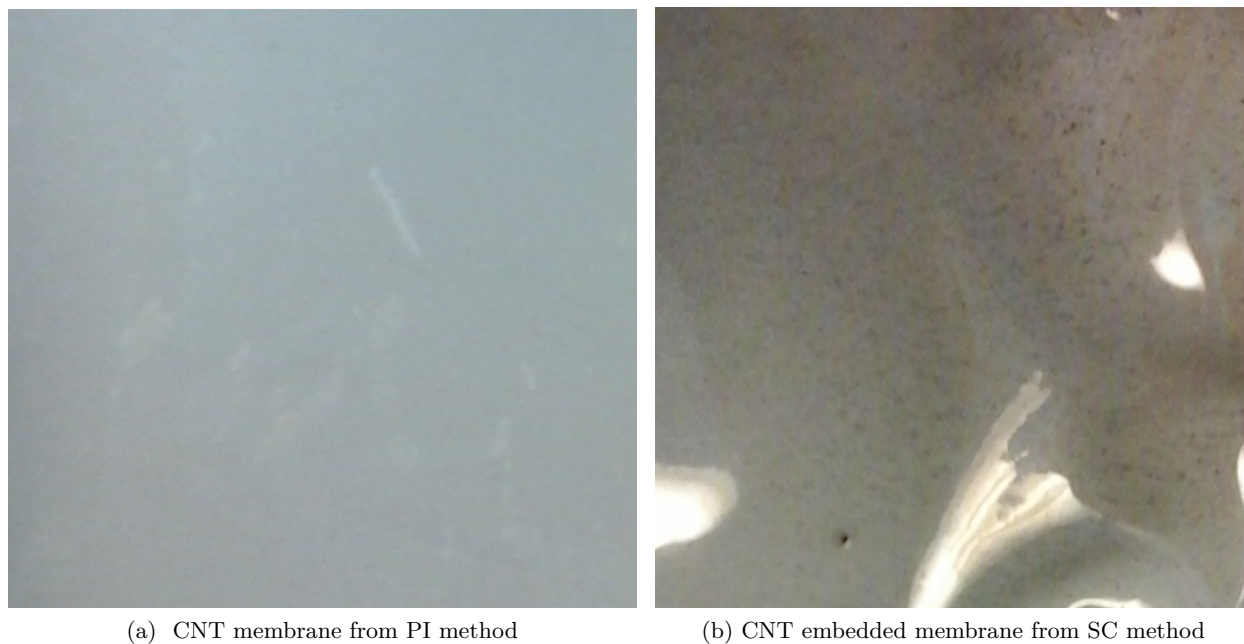


Figure 4.20: Difference in membrane's physical appearances

For the SC method, there is no difference between the top surface images of the bare and fCNT/PSf membranes. The surface roughness however increases with the addition of CNTs as observed in Figure 4.20 (and quantified in the AFM results). This in turn increases the permeability of the membrane.

AFM and contact angles

Figure 4.23 presents the AFM images for the bare and fCNT/PSf membranes for the PI method. Figure 4.23b has a higher distribution of dark and light spots (nodules and pores) for the same area. This is translated to an increase in the R_a from 62.387 nm to 328.33 nm. This agrees with what is expected i.e. the modification of the membrane with CNT should translate to an increase in the permeability of the membrane (Khulbe and Matsuura, 2000). The addition of CNTs to the PSf membrane adds irregularities to the membrane surface, affecting its original smooth nature.

The contact angles measured for the two membranes also agree with the expected decreasing trends: 79.832° and 72.158° for the bare PSf and fCNT/PSf membranes respectively.

Similar results are obtained for the SC method.. The R_a parameter increases from 13.396nm for the bare PSf membrane to 15.839nm for the fCNT/PSf membrane indicating an increase in the permeability of the membranes with the addition of CNTs. Analogously the contact angles decreased from 88.210° to 84.355° indicating an increase in hydrophilicity.

Table 4.4 summarizes the R_a and contact angles for the membranes. The increase in permeability with the addition of CNTs only holds for low concentrations of CNTs (Choi et al., 2006a). Higher CNT concentrations block the pores and hinder permeate flow. These results validate the

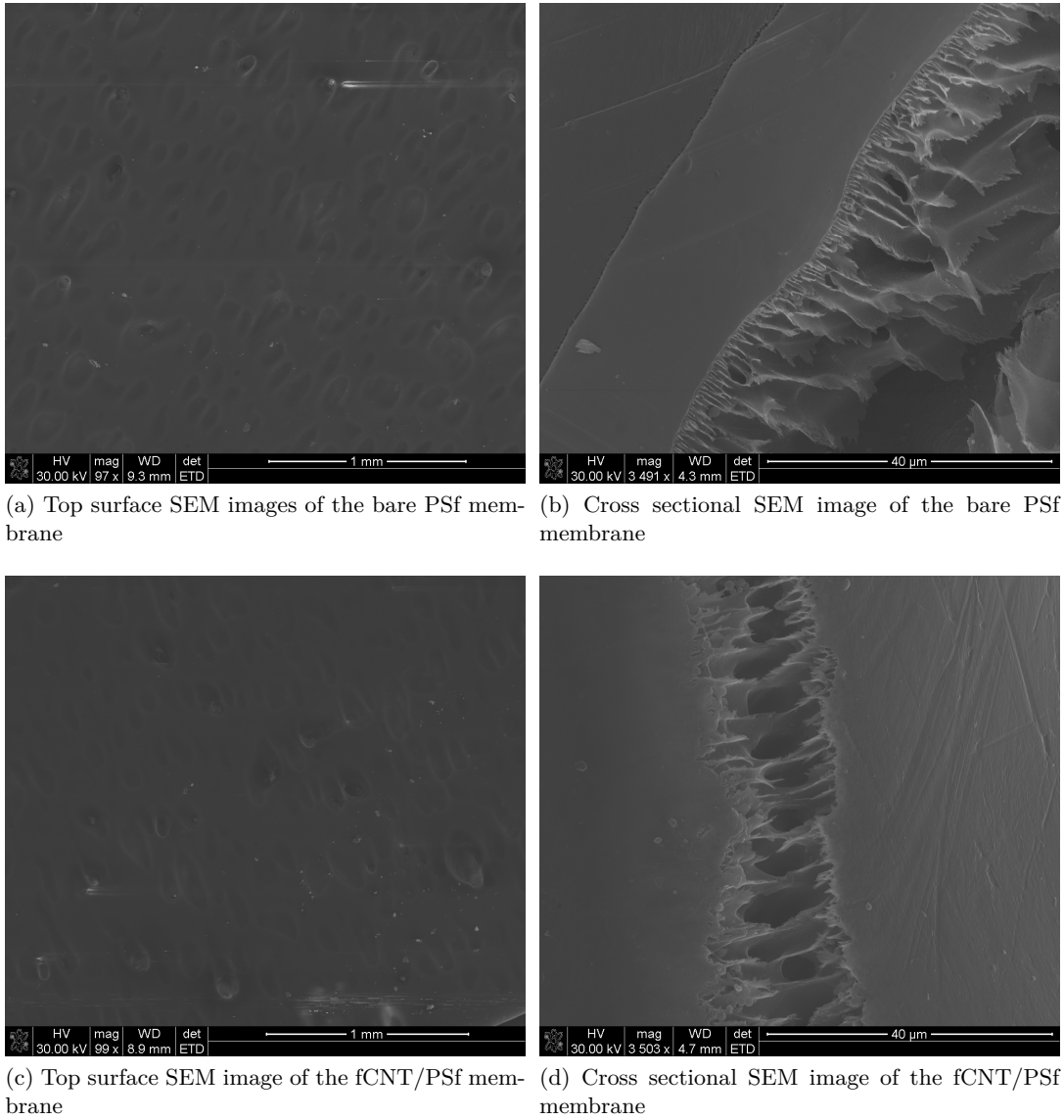


Figure 4.21: SEM images of bare PSf and fCNT/PSf membranes produced *via* PI method, showing the top surface and cross-sectional image

increase in pore sizes observed from the subsurface voids of the two membranes.

Table 4.4: Summary of contact angle and roughness results for CNT imbedded membranes

	Contact angles	Roughness (R_a)
Bare PSf Membrane <i>via</i> PI	79.83°	62.39nm
fCNT/PSf membrane <i>via</i> PI	72.16°	328.33nm
Bare PSf Membrane <i>via</i> SC	88.21°	13.40nm
fCNT/PSf membrane <i>via</i> SC	84.36°	15.84nm

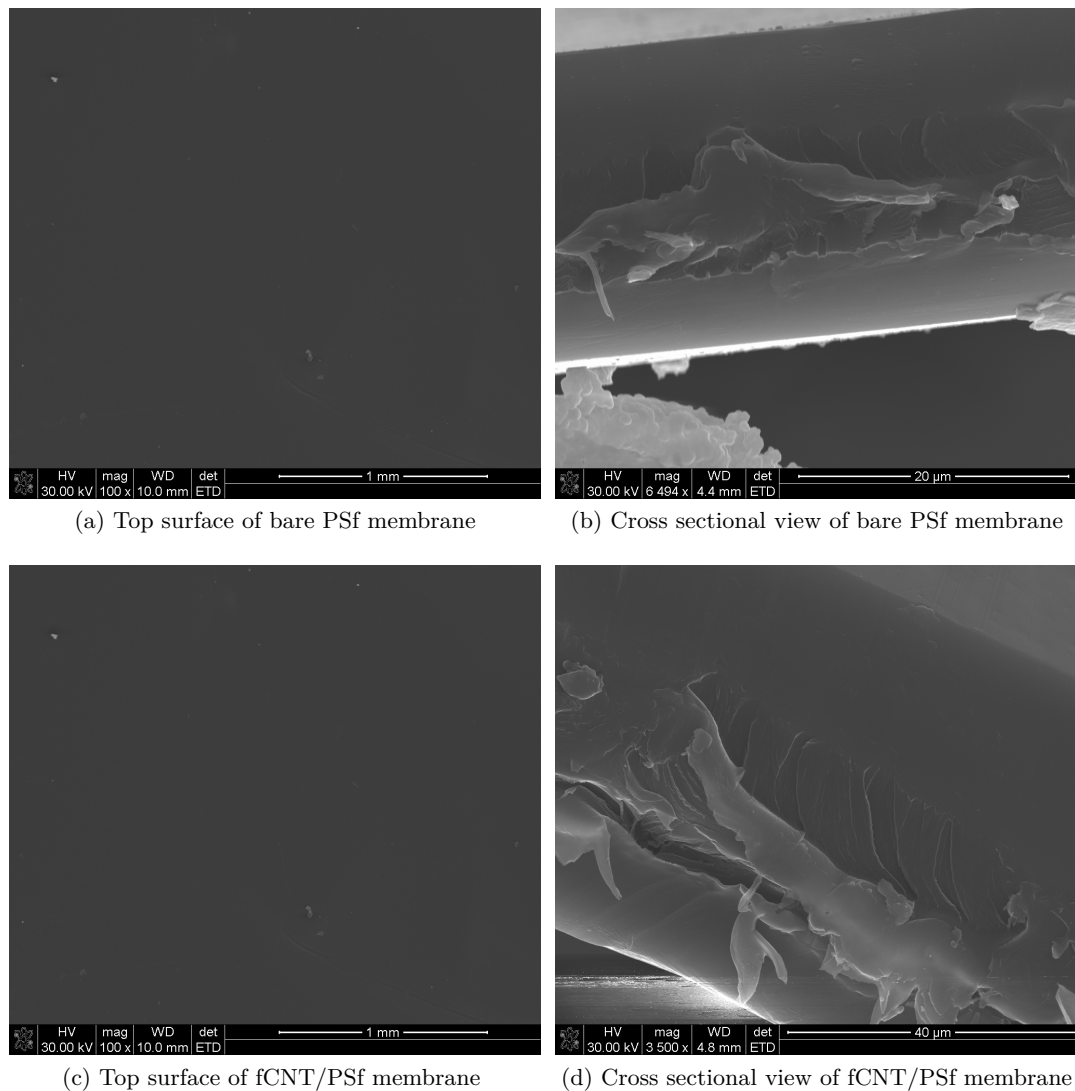


Figure 4.22: SEM images of bare and fCNT/PSf membranes produced *via* the SC method, showing the top surface and cross-sectional image

FTIR

Figure 4.25 shows the spectra for the bare PSf and fCNT/PSf membranes for the PI method. The spectra for both membranes have the characteristic peaks for a PSf membrane. The spectra for the fCNT/PSf membrane however contain an extra band from 3400 cm^{-1} to 3480 cm^{-1} , characteristic for hydrogen bonds formed between the OH bonds in the acid and the oxygen atom present in PSf (Gao et al., 2014). The presence of this band confirms the presences of the fCNTs interacting with the PSf structure and explains the increased pore sizes, permeabilities and hydrophilicity.

This band is not as pronounced in the membranes produced *via* the SC method presented in Figure 4.26.

The spectra for the fCNT/PSf membrane however are very similar to the bare PSf membrane.

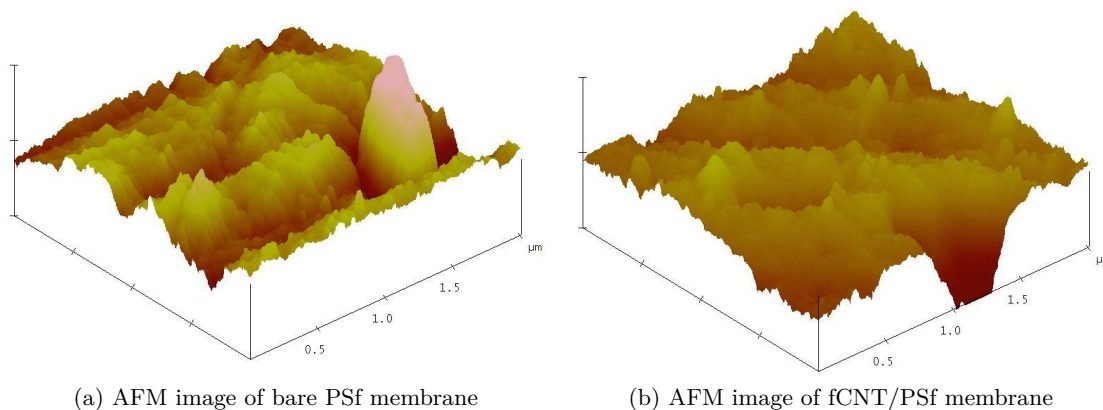


Figure 4.23: AFM image of bare PSf membrane and fCNT/PSf membrane from the PI method

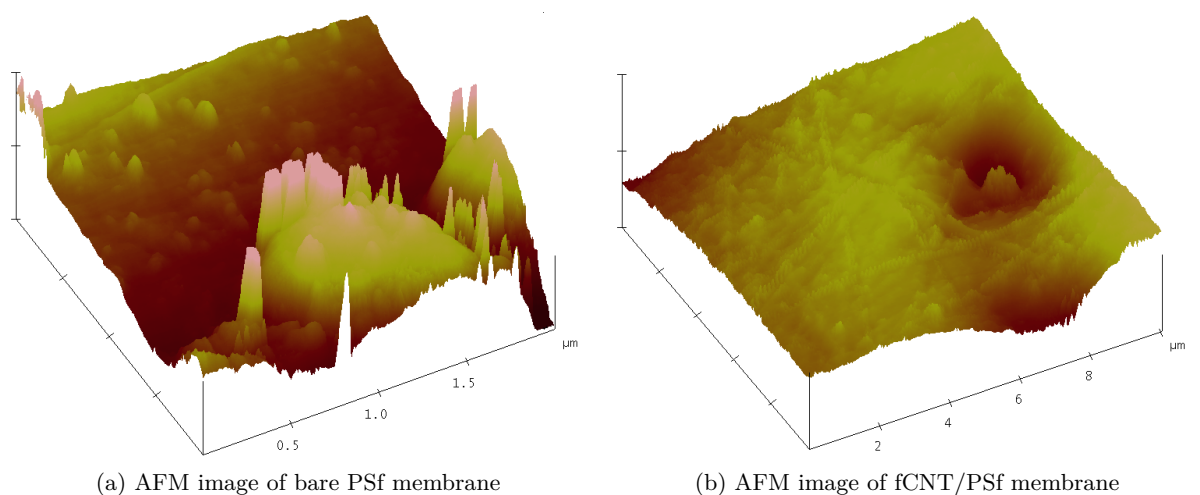


Figure 4.24: AFM images for the bare PSf and fCNT/PSf membranes produced *via* SC method

The hydrogen bond band (3400cm^{-1} to 3480cm^{-1}) is as profound as that in the fCNT/PSf membrane produced *via* PI in Figure 4.25. From Section 4.6.2 it is shown that the increase in surface roughness and decrease in contact angles is also not as profound for the two membranes.

TGA

The temperature profiles of the membranes are presented in Figure 4.27. The introduction of CNTs into the PSf membranes reduced the last thermal degradation temperature of the membranes. The fCNT/PSf membranes decomposed at a slightly lower temperature than the bare PSf membrane for both production methods. The introduction of CNTs into the membrane structure disturbed the symmetry of the membrane, making it more susceptible to thermal decay. This also indicates an interaction between the membrane matrix and the CNTs.

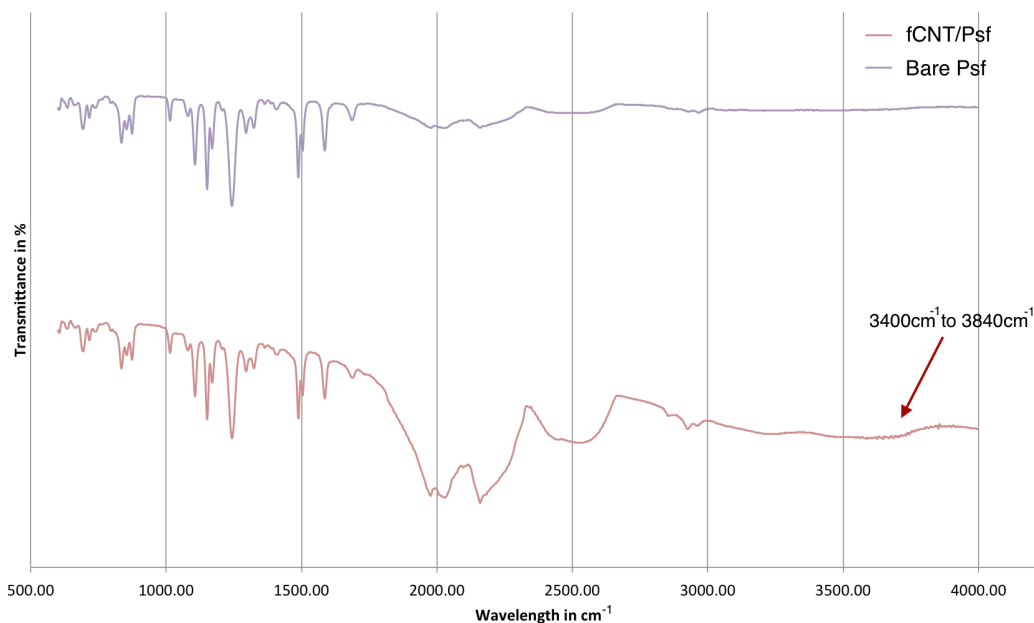


Figure 4.25: FTIR spectra for PSf and fCNT/PSf membranes produced *via* PI method

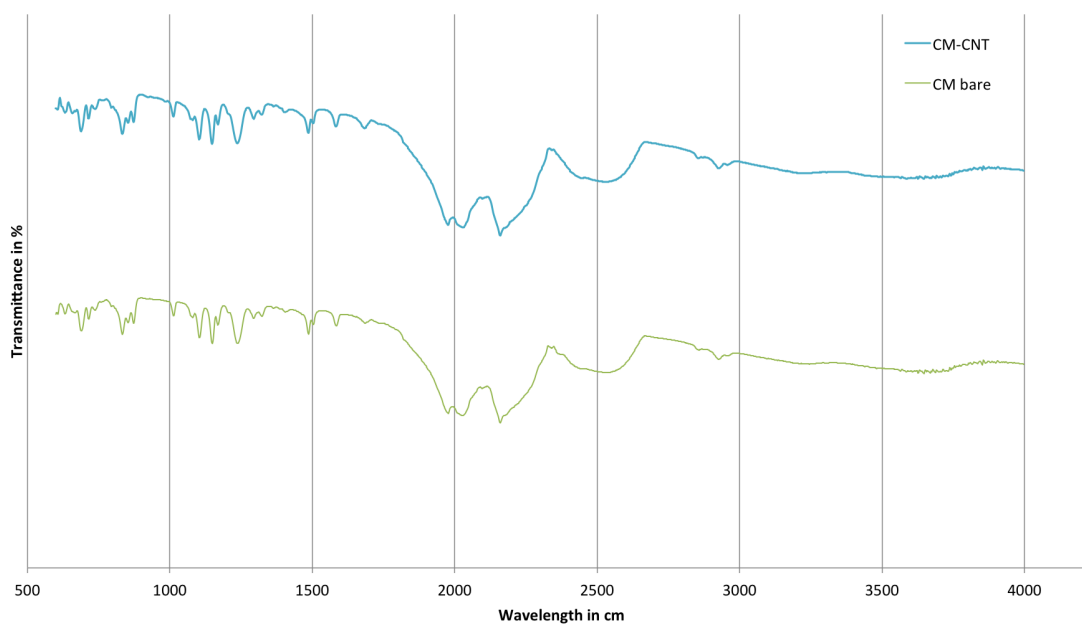


Figure 4.26: FTIR spectra for SC bare and SC CNT membranes

Tensile strength

Table 4.5 summarizes the tensile strength and Young's modulus information for the membranes imbedded with CNTs. The addition of CNT increased the tensile strength of the membranes for both the PI and SC methods. CNTs are known to have high tensile strengths (Ghiazza et al., 2014). This quality was transferred to the membrane when CNTs were imbedded. The CNTs

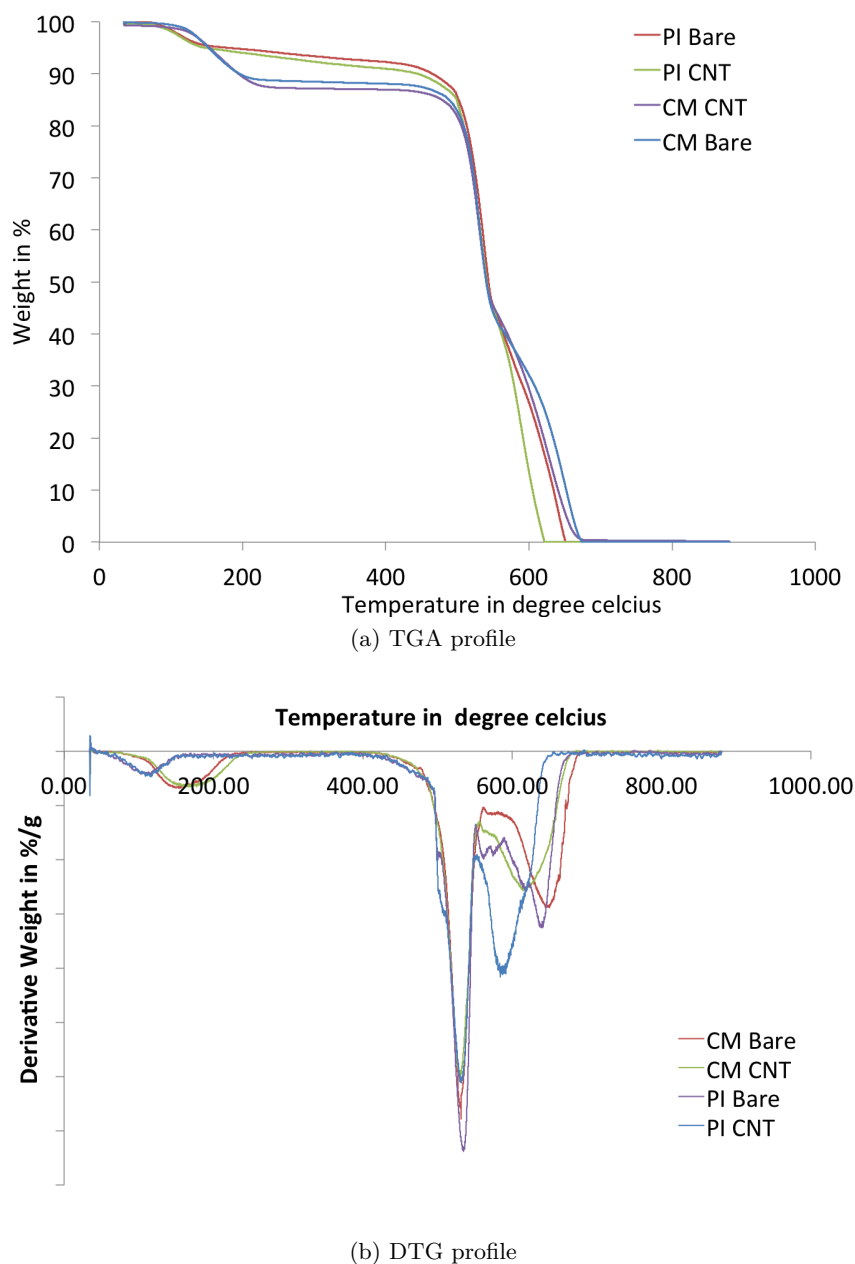


Figure 4.27: Temperature profile for bare and CNT imbedded membranes

however reduced the rigidity of the bare PSf membrane. This could be due to the interaction between the CNTs and the polymer structures of both membranes. The FTIR shows a significant interaction between the CNTs and the PSf membranes with the introduction of the OH bond. The reduced rigidity can be attributed to this interaction. The FTIR showed that the SC membranes did not interact with the CNTs as intensely and this could explain the constant Young's modulus after adding CNTs.

The tensile stresses shown here were lower than the actual conditions in which the membranes

were subjected to during the filtration tests. This was because the membrane samples used here were significantly smaller (force per 11 cm) than those used in the filtration tests (force per 35 mm). The results however give an accurate representation of the stresses that the membranes can handle.

Table 4.5: Effect of CNTs on the mechanical properties of the membrane

	Tensile stress in kPa	Young's modulus in kPa
Bare PSf Membrane <i>via</i> PI	13.55	433.78
fCNT/PSf membrane <i>via</i> PI	16.24	421.14
Bare PSf Membrane <i>via</i> SC	61.34	2000.00
fCNT/PSf membrane <i>via</i> SC	72.84	2000.00

4.6.3 Effect of a NWF support

The final parameter that was studied during the membrane preparation process was the support used. A 05TH-48 type polyester NWF was used as the fabric support. Figure 4.28 shows a high magnification SEM image of the NWF where the non-woven, intertwined fabric is evident. Table 4.6 summarizes the information about the fabric from the manufacturer.

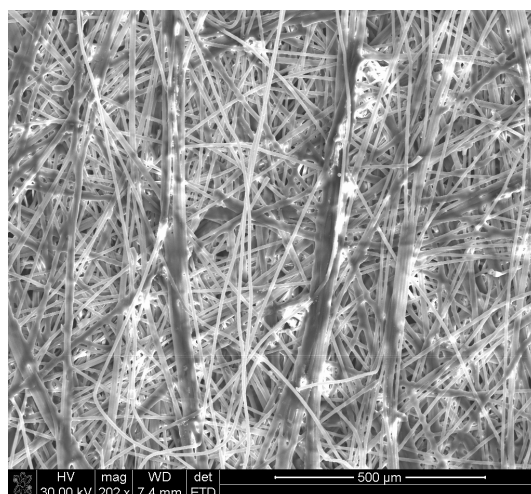


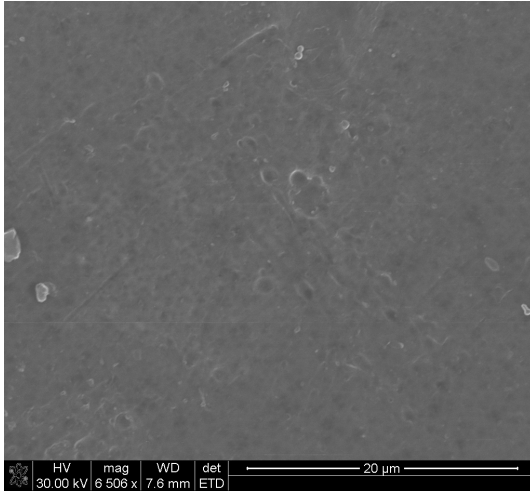
Figure 4.28: A high magnification SEM image of the polyester NWF used as a support in this study

SEM

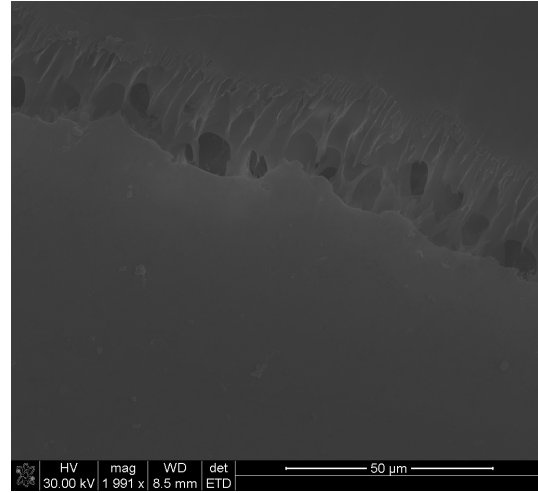
Figure 4.29 illustrates the top surface and cross sectional images of the membranes produced on the NWF. The microporous structures on the top surfaces (Figures 4.29a and 4.29c) were slightly different from those obtained with membranes without the fabric supports (Figures 4.21a and 4.21c). Table 4.7 summarizes the surface pores and cross sectional void sizes. The surface pores

Table 4.6: Summary of data of the polyester NWF used in this study

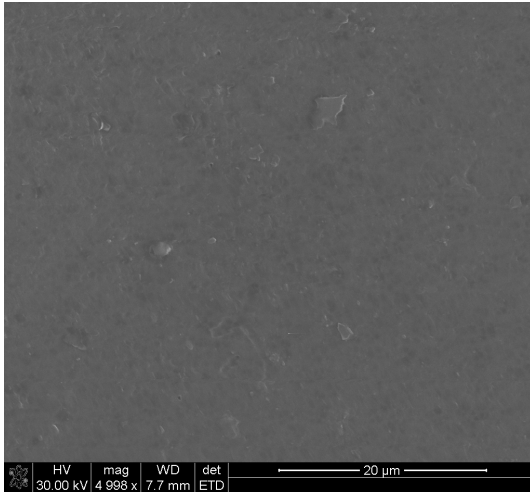
Properties	Value
Basic weight	46.80 g/m ²
Thickness	97.00 μ m
Air permeability	19.66 cc/SC ² .sec
Tensile strength	
- Machine direction	59.00 N/15mm
- Cross direction	31.00 N/15mm



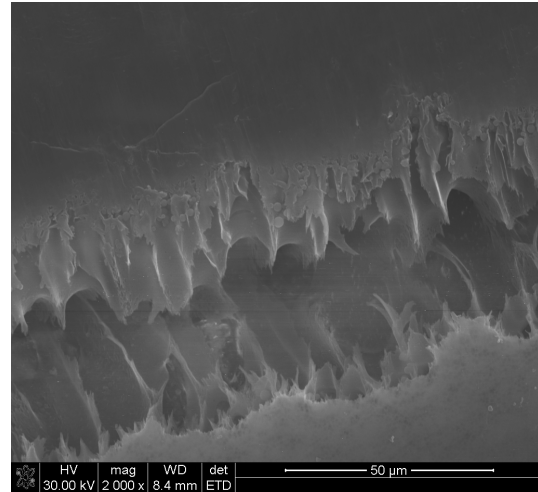
(a) Top surface of bare PSf membrane on an NWF



(b) Cross sectional view of bare PSf membrane on an NWF



(c) Top surface of fCNT/PSf membrane on an NWF



(d) Cross sectional view of fCNT/PSf membrane on an NWF

Figure 4.29: SEM images for bare PSf and fCNT/PSf membranes produced *via* PI method

are more dense and smaller in size: $1.192\ \mu\text{m}$ and $1.592\ \mu\text{m}$ for the bare PSf on the NWF and fCNT/PSf on the NWF respectively. The cross sectional voids in the Figures 4.29b and 4.29d were $1.73\ \mu\text{m}$ and $3.42\ \mu\text{m}$ respectively. Similar to the results presented in Section 4.6.2, the surface pores and cross sectional void sizes increased after CNTs were imbedded into the membrane. The membranes cast on fabric possessed smaller surface pore and larger cross sectional voids than those without the NWF. This was due to the interaction between the casting solution and the fabric, which seems to enhance the rate of the liquid-liquid exchange between the water and the NMP solvent and in turn increases the pore sizes of the membrane.

Table 4.7: Summary of the pore and void sizes synthesized membranes

	Top surface Pore size	Cross sectional void size
PI bare	0.164mm	$0.659\ \mu\text{m}$
PI CNT	0.191mm	$1.587\ \mu\text{m}$
PI bare on fabric	$1.192\ \mu\text{m}$	$1.727\ \mu\text{m}$
PI CNT on fabric	$1.598\ \mu\text{m}$	$3.417\ \mu\text{m}$
SC bare on fabric	-	$7.171\ \mu\text{m}$
SC CNT on fabric	-	$12.318\ \mu\text{m}$

Similarly Figure 4.30 compares the membranes cast on fabric support and prepared using the SC method. The fabric support is more evident in these images. Figure 4.30a shows the top surface of the bare PSf membrane on a fabric with a higher magnification image of how a slight defect reveals the NWF support. The top surfaces for both the bare and CNT imbedded membranes are plane without the microporous structures evident in the membranes by the PI method. The cross sectional images in Figures 4.30b and 4.30d show the interaction between the pore structures and the fabric. These membranes, unlike those without the fabric support seem to have some subsurface cross-sectional voids. These voids for the bare PSf and fCNT/PSf on fabric supports are $7.17\ \mu\text{m}$ and $12.31\ \mu\text{m}$ respectively. Table 4.7 summaries the pore and cross-sectional void sizes for all the synthesized membranes presented. The fabric seems to significantly enhance the liquid-liquid exchange in the SC membrane, attracting more atmospheric water vapor and forming subsurface voids.

AFM and contact angles

Figure 4.31 below presents the AFM for the PI membranes with the fabric support. For the PI method, the AFM analysis of the membranes on the NWF indicate that the introduction of fCNT increases the pore and nodule distribution on the membrane surface (Figure 4.31). The R_a for the bare PSf and fCNT/PSf membrane on the NWF are $92.911\ \text{nm}$ and $154.77\ \text{nm}$ respectively. The contact angles in turn decrease from 80.730° to 77.929° for the NWF supported bare PSf and fCNT/PSf membranes respectively. Comparing the membranes without the support with those with a support reveals that the introduction of the fabric support increased the surface roughness

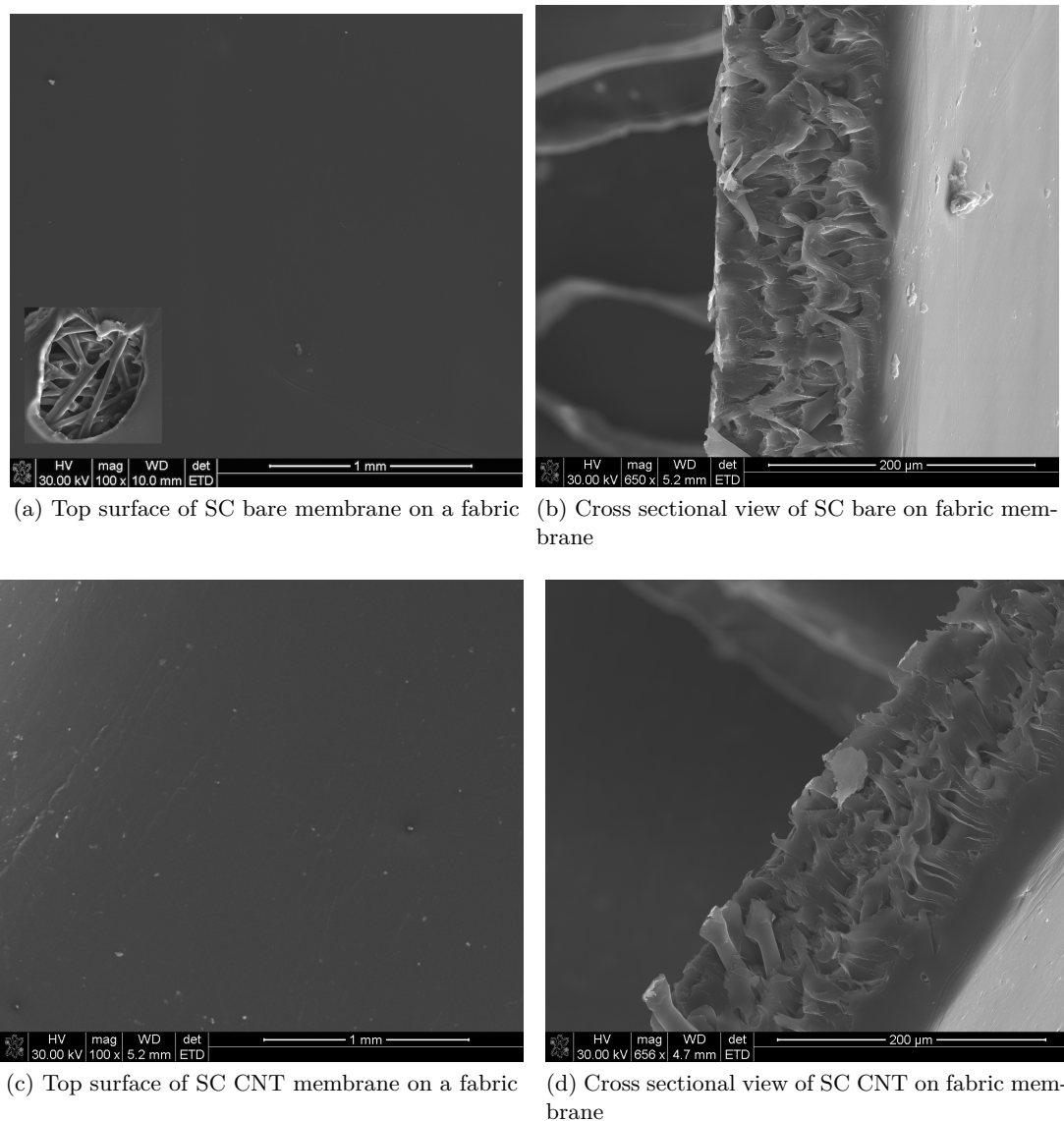


Figure 4.30: SEM images for SC bare and SC CNT on a fabric

and the contact angles of the membranes (Table 4.8). This makes them more permeable to gases but slightly less hydrophilic. Table 4.8 summarizes the AFM and contact angle results for all the synthesized membranes.

The membranes produced *via* the SC method do not completely conform to the existing trend. The R_a parameter for the bare PSf and the fCNT/PSf membranes on the NWF are 16.459nm and 56.064nm respectively. The contact angles are 74.993 and 60.692 respectively. Like the membranes produced *via* PI, the introduction of the fabric increases the membranes roughness but the contact angles are reduced with the introduction of the NWF. The introduction of the fabric brought about subsurface voids into the SV membranes (Figure 4.30d) and this is what makes the SC membranes on an NWF more hydrophilic. Table 4.8 summarizes the AFM and contact angle results for all the

synthesized membranes.

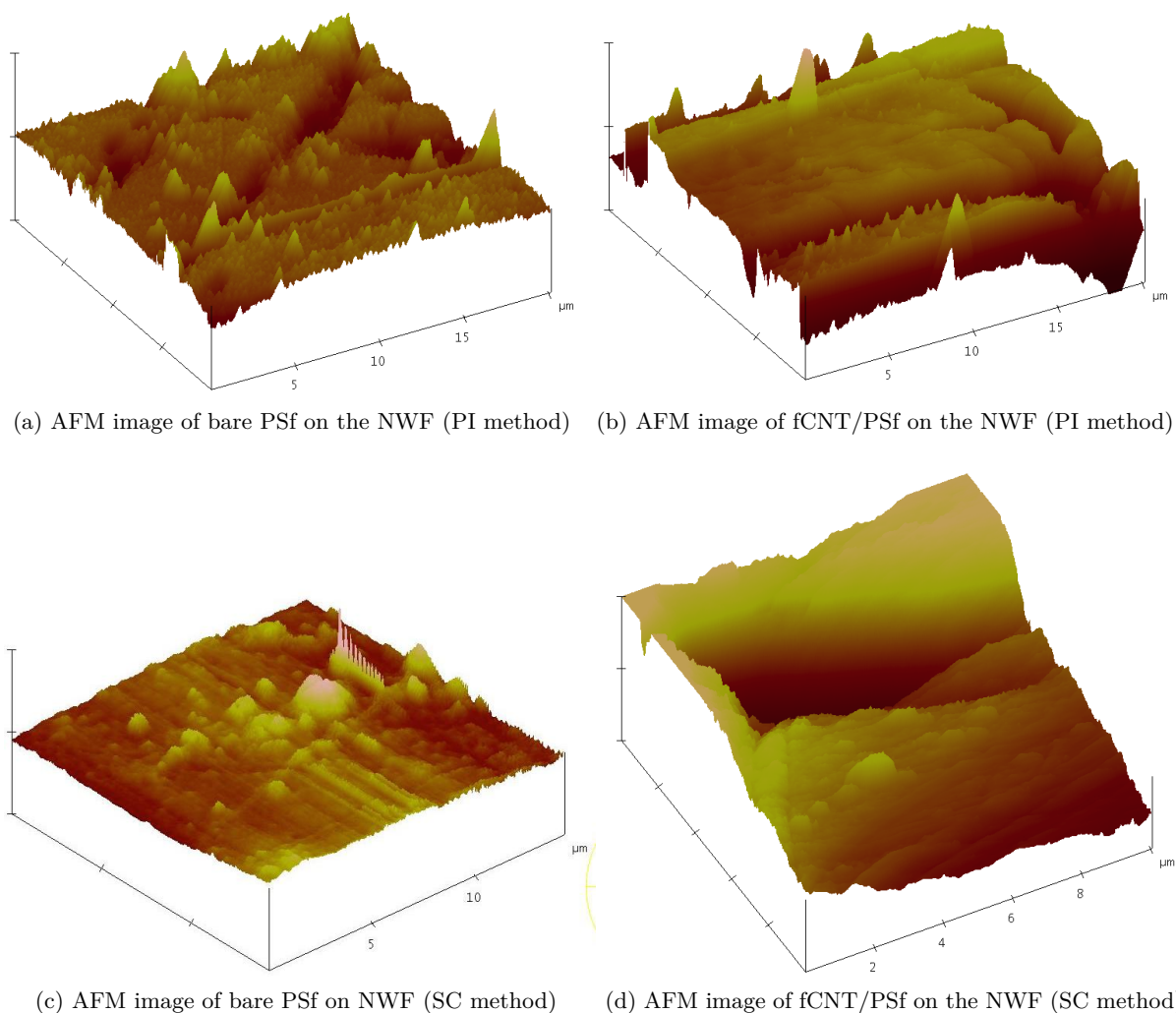


Figure 4.31: AFM images comparing the membranes supported on the NWF for both PI and SC methods

FTIR

The FTIR plots for the membranes produced by the PI method (Figure 4.32) shows that there is no significant change in the bond structure with the addition of the fabric support. One slight difference however is the reduction of the peak at 1095 cm^{-1} . This peak reduces and merges with the peak at 1109 cm^{-1} in the membranes supported on a fabric. This peak is associated with the stretching and bending of the sulfonated group. This could indicate some interaction between the polymer layer and the NWF support.

Figure 4.33 shows the FTIR spectra for the SC produced membranes. This spectra presents a clear distinction between the NWF supported membranes and those without. The intensities of

Table 4.8: Summary of contact angle and roughness results for fabric supported membranes

	Contact angles	Roughness (R_a)
PI Bare	79.83 °	62.39 nm
PI CNT	72.16 °	328.33 nm
SC Bare	88.21 °	13.40 nm
SC CNT	84.36 °	15.84 nm
PI bare fabric	80.73 °	92.91 nm
PI CNT fabric	77.93 °	154.77 nm
SC bare fabric	74.99 °	16.46 nm
SC CNT fabric	60.69 °	56.06 nm

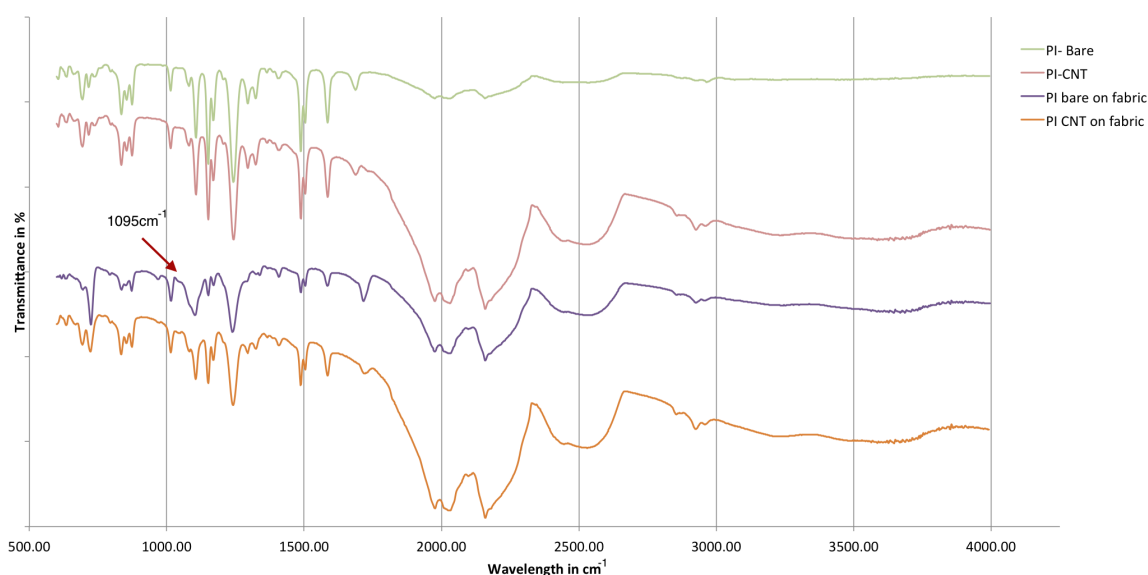


Figure 4.32: FTIR spectra comparing PI membranes with and without a fabric supported

the spectra significantly reduce with the introduction of the fabric, indicating less stretching and bending of the bonds.

TGA

Figure 4.34 presents the TGA and DTG profiles for the membranes cast on a fabric. All the characteristic peaks are evident in the TGA and DTG plot. The one difference between the membranes on a fabric and those without is the fact that the membranes on a fabric decompose earlier: at 150 °C, 450 °C and 570 for the membranes with a fabric support and 150 °C, 530 °C and 640 °C for the non-supported membranes at the three respective decomposition temperatures. There is an extra peak on the DTG curve (Figure 4.34b) at 415 °C, which can be attributed to the combustion of the polyester MWF.

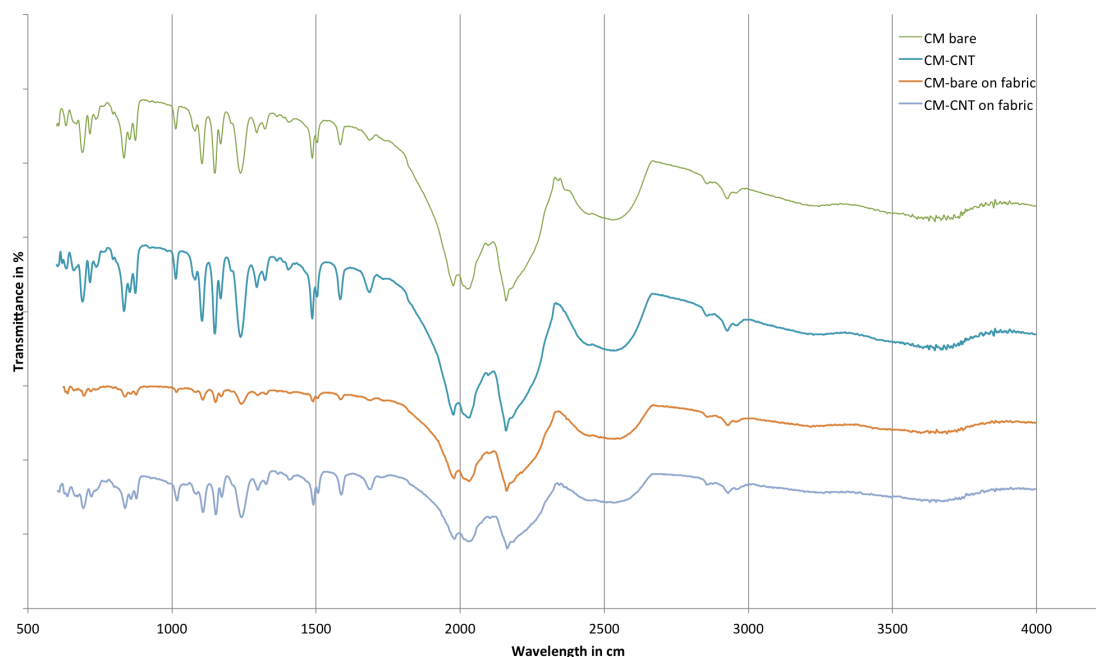


Figure 4.33: FTIR spectra comparing SC membranes with and without a fabric supported

Tensile strength

From the information presented in Table 4.6, it was expected that the fabric would strengthen the membrane. Table 4.9 shows a significant increase in the tensile strength and Young's moduli for the membrane cast on the NWF support. The membrane, supported by the NWF, inherits the properties of the fabric.

Table 4.9: Effects of the fabric on the mechanical strength of the membranes

	Tensile stress in kPa	Young's modulus in N/m ²
Bare PSf	13.55	433.78
fCNT/PSf	16.24	421.14
Bare PSf on the NWF	64.77	1000.00
fCNT/PSf on the NWF	75.92	913.57

All the other trends discussed above are seen: the addition of CNTs increased the tensile strength of the membrane but reduced its rigidity. The analysis was performed on just the PI membranes because the TX.XT Plus texture analyzer could not exert enough force to break the SC membranes.

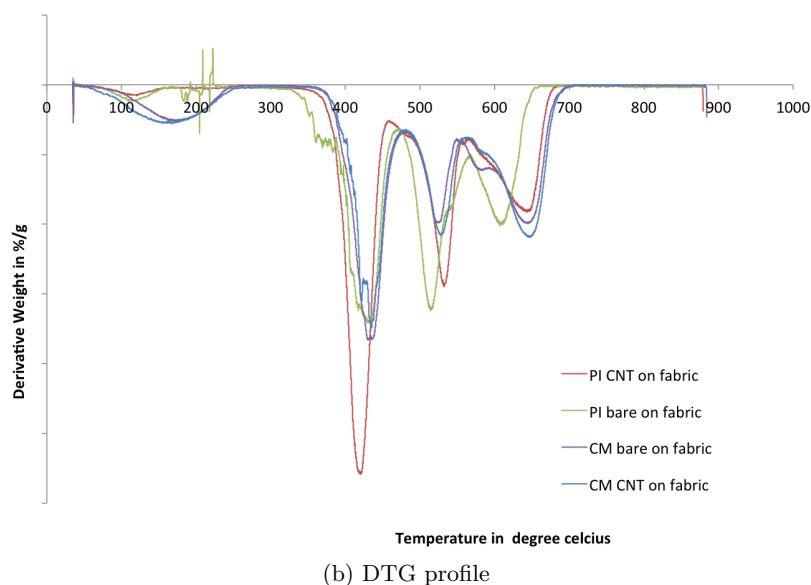
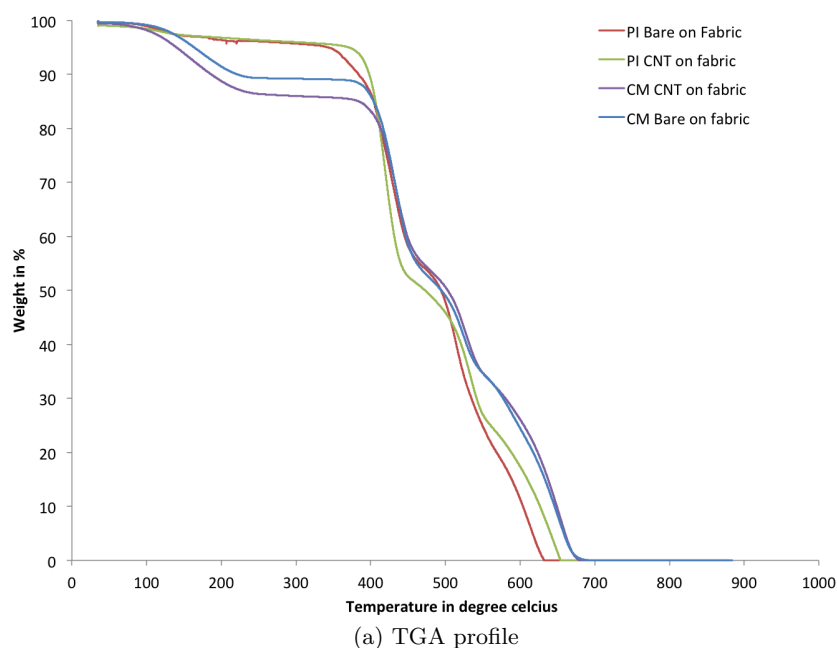


Figure 4.34: TGA and DTG profiles for membranes supported on a fabric

4.7 Filtration tests

The results obtained from the filtration tests for only the PI membranes are presented here. The SC membranes were not considered for further studies because the permeation rates were found to be too small and often nonexistent to carry out the experiment. This was attributed to the dense nature of these membranes. These membranes would therefore require higher pressures in order to achieve acceptable permeation rates and this could increase the costs associated with using these

membranes in industry (Baker, 2000)

After compacting the for at least 4 h, the pure water fluxes through the membranes were recorded at various pressures. The synthetic produced water was then passed through the membrane and the permeate fluxes were collected and recorded at the same pressures. These permeates were then characterized for oil rejections using the UV-Vis. The variation of flux with time was also recorded to study the effects of fouling on the membrane.

4.7.1 Permeate flux

It can be seen from Figure 4.35 that the fluxes increases with pressure for all the membranes. Increasing pressure increased the driving force applied across the membrane and in turn increased the flux. The membranes supported on the NWF had lower fluxes compared to those without. This suggests that the NWF provided additional resistance to the flow across the membrane. The NWF acts as an additional filter through which the permeates must go through. This in turn slows down the permeate rate in these membranes. The addition of CNTs to the membrane increased the fluxes across the membranes. This is due to the presence of the OH bonds present in the CNT modified membranes, which alters the contact angles and the roughness of the of the membranes (Table 4.8).

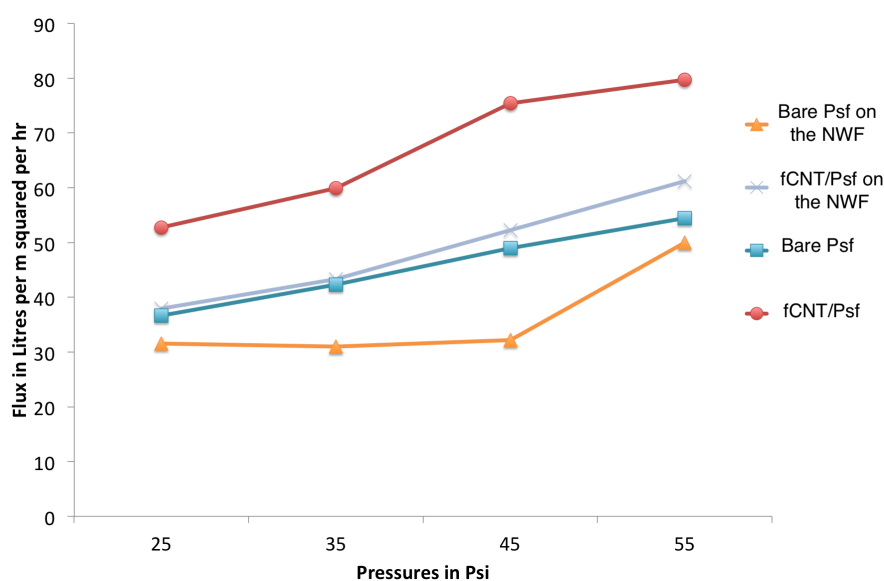


Figure 4.35: Pure water fluxes at various pressures

Similar results were obtained for the produced water fluxes (Figure 4.36). The increase in pressure resulted in an increase in flux. The expected fluxes, similar to that of the pure water flux are seen for the membranes on fabric. However for the membranes without the fabric support, the graphs shows that the bare PSf membrane had the highest permeate flux while the addition of

CNTs decreased the fluxes through the membrane. This was due to the interaction between the oil droplets and the CNTs.

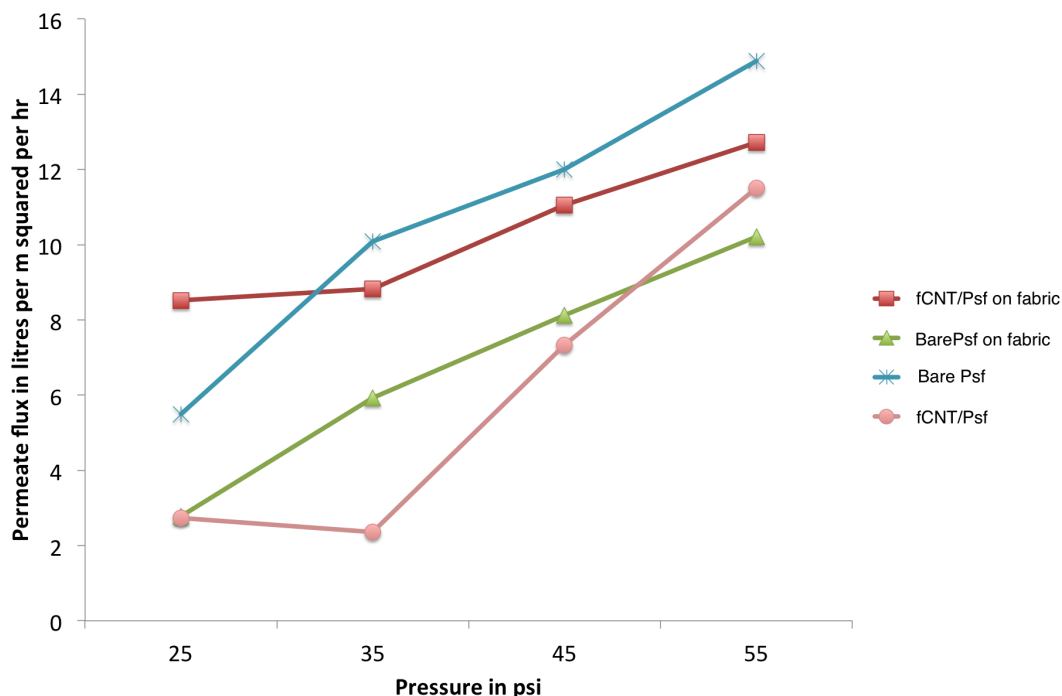


Figure 4.36: Permeate fluxes at various pressures; initial oil concentration 1000 mg/l

The increase in flux with pressure was non linear in all the cases studied. This was because the membranes offer a resistance to flow during the filtration process (Chakrabarty et al., 2008b). The effect of flow resistance is better understood by varying the time.

4.7.2 Flux decline

The variation of flux with time is presented in Figure 4.37. These experiments were conducted at a constant pressure of 45 psi. The plots show a similar trend of reduction in flux with time. This was attributed to two main phenomena; pore blockage and resistance due to concentration polarization (Chakrabarty et al., 2008b). Some oil particles get locked up in the pores of the membranes and hinder flow across the membranes. Oil droplets also collide with each other as they are being forced through the membrane. With time, larger droplets of oil are formed that can no longer pass through the pore structures of the membrane. This was caused by the decline in flux over time. The addition of CNTs helped control flux decline by controlling fouling of the membrane (Li et al., 2006).

The relative flux through the membranes with time is shown in Figure 4.38. The plots explain the contribution of pore blockage and the formation of a concentration polarization layer in decreasing permeate flux.

The plots show a sharp decline in the flux in the first half hour of the filtration process. In the

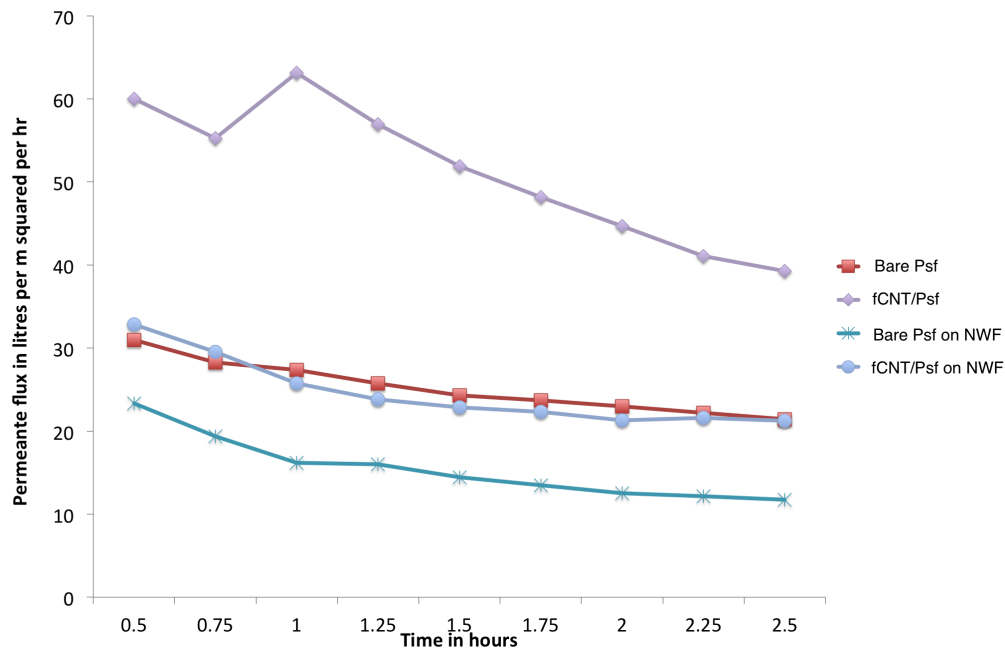
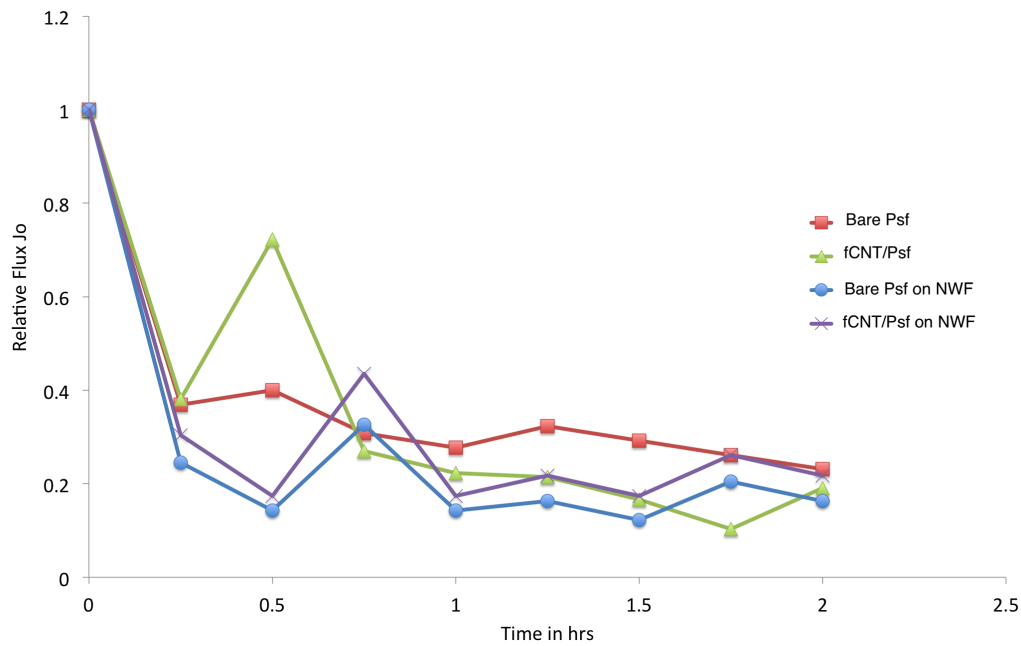


Figure 4.37: Flux variation with time at a constant pressure of 45 psi

Figure 4.38: Relative flux J_o at a constant pressure of 45 psi

last hour however, the fluxes remain relatively constant. Oil droplets quickly block up the pores of the membrane i.e. the flux decline observed within the first half hour is due to pore blockage while the flux decline during the remaining time is attributed to concentration polarization (Kołtuniewicz and Field, 1996; Chakrabarty et al., 2008b). The bare PSf on an NWF is shown to be most affected

by fouling while the bare PSf membrane without the NWF support is least affected by the flux decline. The plot also shows that CNTs improved the effects of pore blockage in all the membranes. The fluxes do not reduce as sharply in the membranes with CNTs as it does in those without CNTs. The addition of an NWF support however seems to make the membrane more susceptible to fouling *via* pore blockages. This can be attributed to the pore sizes presented in Table 4.7. The membranes with the NWF have smaller pores and so are easily blocked and this could have influenced flux decline more rapidly within the first half hour. The size of the oil particles could have contributed to this phenomenon. Sonicating produced water for a longer time would break the oil particles into smaller pieces and could increase the time taken for fouling *via* pore blockage.

Figure 4.39 compares the bare PSf and fouled bare PSf membranes where the oil build-up is evident. In Figure 4.39b, the dried oil marks are evident covering up the surface pores. This evidently reduces flux through the membrane.

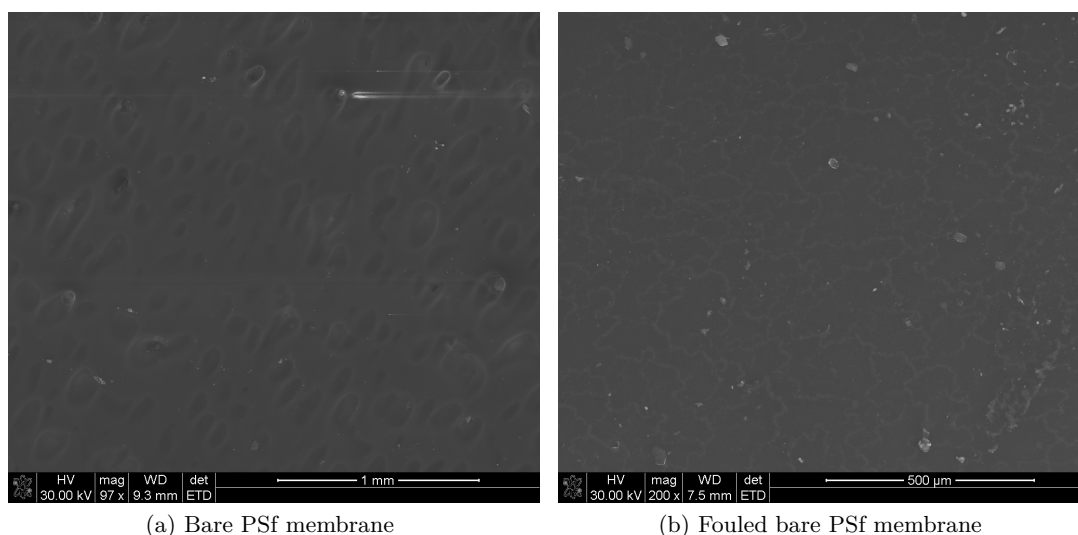


Figure 4.39: SEM image comparing the bare PSf membrane and fouled bare PSf membranes both produced *via* the PI method

Figure 4.40 shows the flux decline for the 4 types of membranes over the 2 h period. The graph shows that the bare PSf membrane on the NWF had the highest flux decline and this flux decline decreased with the addition of CNTs. This was expected because of the restriction to flow provided by the fabric. The plot also shows the point at which flux decline shoots up the most: between the second half hour for the bare PSf membrane and fCNT/PSf membrane on an NWF and between the third half hour for the fCNT/PSf membrane and the bare PSf on an NWF membrane. Flux decline stays the same for the last half hour in the fCNT/PSf on an NWF membrane and this could be due to build up of the oil layer on the membrane surface.

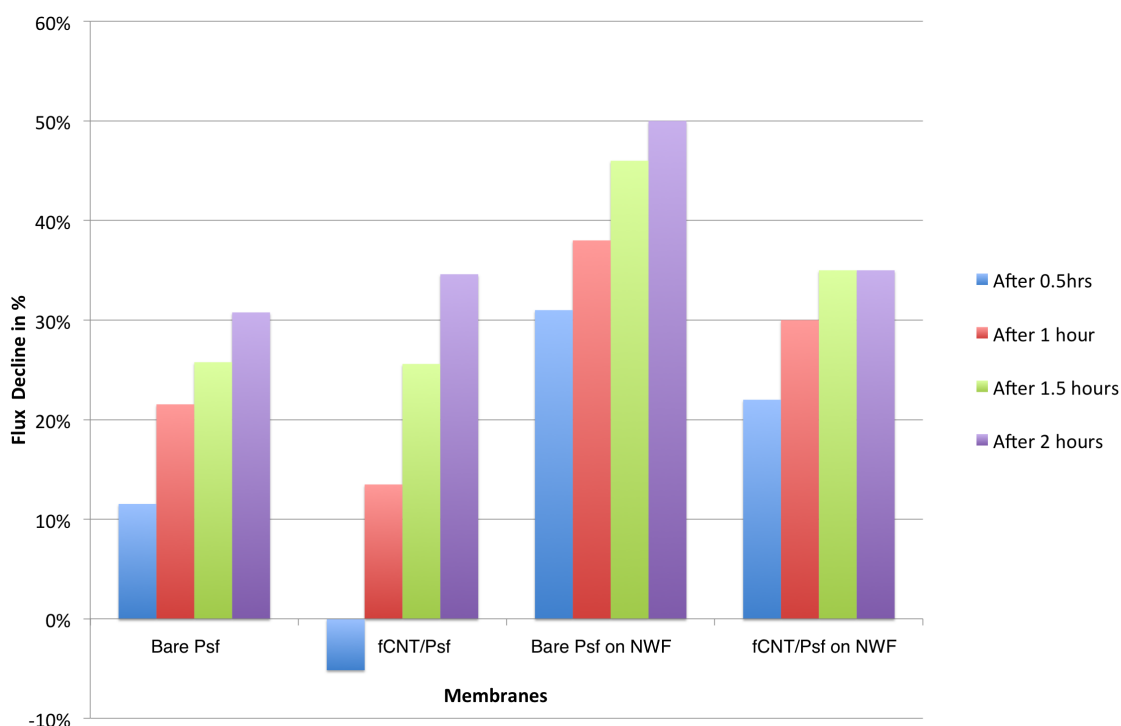


Figure 4.40: Flux decline of the membranes at a constant pressure of 45 psi

4.7.3 Oil rejections

Figure 4.41 shows the oil rejections from each membrane. The rejections ranged between 78 % and 90 %, with the fabric-supported membranes having higher rejections compared to the membranes without the fabric support. The oil rejections decreased with an increase in pressure. This could be explained by the fact that increasing cross membrane pressure forces the oil through the membrane pores and in turn reduces its rejection values. The membranes supported on a fabric required larger cross membrane pressures to overcome the extra resistance provided by the fabric and thus the higher oil rejections recorded. Also the addition of CNTs to the membranes increased the oil rejections. The interaction between the CNTs and the membrane allowed for more water and less oil to pass through the membrane.

The membranes yielded high oil rejections and the permeates were very clear. Figure 4.42 shows the membranes concentration of the permeates. The figure corroborates that in Figure 4.41 showing a drastic decline in the oil concentrations. The addition of fCNTs and an NWF support helped improved the purity of the permeate. The fCNT/PSf on and NWF membrane produced the cleanest permeates due to the combined effects of the CNTs and the extra filter the fabric provided.

Chakrabarty et al. (2008a) in their study, also separated crude oil/water mixtures (produced water) with a concentration 100 mg/l. They reported oil rejections between 80 % and 97 %. They also operated at pressures higher than what were used in this study (68.9, 103.9, 137.9

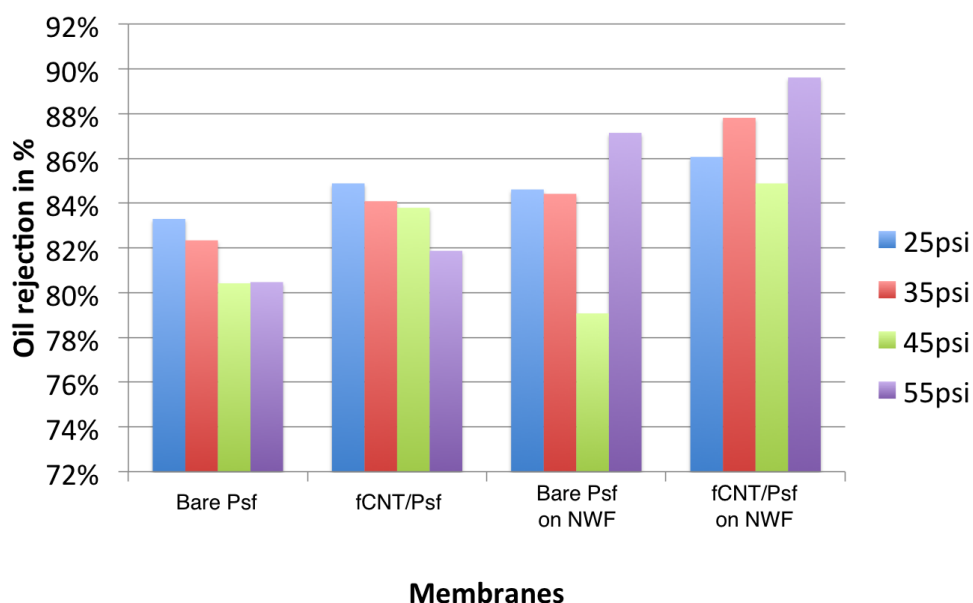


Figure 4.41: Oil rejections for the various pressures

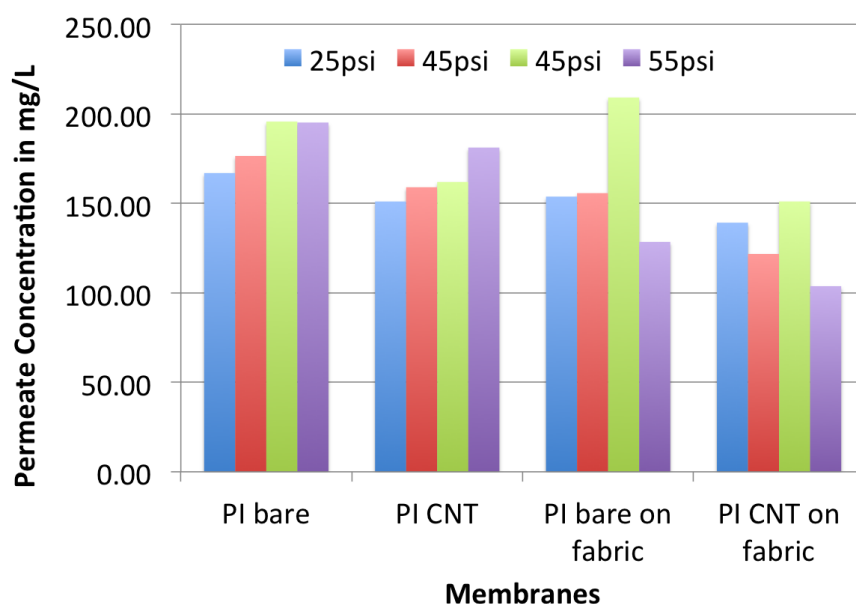


Figure 4.42: Comparing permeate concentrations to allowable discharge limits

and 172.4 kPa). Maphutha et al. (2013) also reported higher oil rejections 87.11% to 99.65% when separating oil-water emulsions using a fCNT/PSf membrane. Compared to literature, the oil rejections presented in this study are slightly lower. This could be due to the various additives used other studies which alters the structure of the membranes Chakrabarty et al. (2008a). The concentration of produced water used in this study is also significantly higher than that reported in other studies.

References

- Arockiasamy, D. L., Alam, J., Alhoshan, M., Mar. 2013. Carbon nanotubes-blended poly(phenylene sulfone) membranes for ultrafiltration applications. *Applied Water Science* 3 (1), 93–103.
- Baker, R. W., 2000. *Membrane technology and applications*. McGraw-Hill, New York.
- Baker, R. W., Lokhandwala, K., Apr. 2008. Natural gas processing with membranes: An overview. *Industrial and Engineering Chemistry Research* 47 (7), 2109–2121.
- Chakrabarty, B., Ghoshal, A. K., Purkait, M. K., Feb. 2008a. Effect of molecular weight of PEG on membrane morphology and transport properties. *Journal of Membrane Science* 309 (1–2), 209–221.
- Chakrabarty, B., Ghoshal, A. K., Purkait, M. K., Nov. 2008b. Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane. *Journal of Membrane Science* 325 (1), 427–437.
- Choi, J.-H., Jegal, J., Kim, W.-N., Nov. 2006a. Fabrication and characterization of multi-walled carbon nanotubes/polymer blend membranes. *Journal of Membrane Science* 284 (1–2), 406–415.
- Flahaut, E., Laurent, C., Peigney, A., 2005. Catalytic CVD synthesis of double and triple-walled carbon nanotubes by the control of the catalyst preparation. *Carbon* 43 (2), 375–383.
- Gao, Y., Li, B., Zhong, L., Zhang, L., Ding, Z., Sep. 2014. Effect of nano-amphiphilic cellulose as a modifier to PSf composite membranes. *Vacuum* 107, 199–203.
- Ghaemi, N., Madaeni, S. S., Alizadeh, A., Daraei, P., Badieh, M. M. S., Falsafi, M., Vatanpour, V., Aug. 2012. Fabrication and modification of polysulfone nanofiltration membrane using organic acids: Morphology, characterization and performance in removal of xenobiotics. *Separation and Purification Technology* 96, 214–228.
- Ghiazza, M., Vietti, G., Fenoglio, I., 2014. 8 - carbon nanotubes: properties, applications, and toxicity. In: Njuguna, J., Pielichowski, K., Zhu, H. (Eds.), *Health and Environmental Safety of Nanomaterials*. Woodhead Publishing, pp. 147–174.
- Ha, T.-J., Park, H.-H., Jang, H. W., Yoon, S.-J., Shin, S., Cho, H. H., Aug. 2012. Study on the thermal stability of ordered mesoporous SiO₂ film for thermal insulating film. *Microporous and Mesoporous Materials* 158, 123–128.
- Hernadi, K., Fonseca, A., Nagy, J. B., Bemaerts, D., Fudala, A., Lucas, A. A., Nov. 1996. Catalytic synthesis of carbon nanotubes using zeolite support. *Zeolites* 17 (5–6), 416–423.
- Hou, P.-X., Liu, C., Cheng, H.-M., Dec. 2008. Purification of carbon nanotubes. *Carbon* 46 (15), 2003–2025.

- Khulbe, K. C., Matsuura, T., Mar. 2000. Characterization of synthetic membranes by raman spectroscopy, electron spin resonance, and atomic force microscopy; a review. *Polymer* 41 (5), 1917–1935.
- Kořtuniewicz, A. B., Field, R. W., Jun. 1996. Process factors during removal of oil-in-water emulsions with cross-flow microfiltration. *Desalination* 105 (1–2), 79–89.
- Kumar, M., Ando, Y., Jun. 2010. Chemical vapor deposition of carbon nanotubes: A review on growth mechanism and mass production. *Journal of Nanoscience and Nanotechnology* 10 (6), 3739–3758.
- Li, Y. S., Yan, L., Xiang, C. B., Hong, L. J., Sep. 2006. Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes. *Desalination* 196 (1–3), 76–83.
- Mackenzie, K. J., 2000. Film and sheeting materials. In: *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc.
- Maphutha, S., Moothi, K., Meyyappan, M., Iyuke, S. E., Mar. 2013. A carbon nanotube-infused polysulfone membrane with polyvinyl alcohol layer for treating oil-containing waste water. *Nature* 3.
- Mhlanga, S. D., Mondal, K. C., Carter, R., Witcomb, M. J., Coville, N. J., 2009. The effect of synthesis parameters on the catalytic synthesis of MWCNTs using Fe-Co/CaCO₃ catalysts. *South African Journal of Chemistry* 62 (67).
- Motchelaho, M. A. M., Xiong, H., Moyo, M., Jewell, L. L., Coville, N. J., Feb. 2011. Effect of acid treatment on the surface of multiwalled carbon nanotubes prepared from Fe-Co supported on CaCO₃: Correlation with Fischer–Tropsch catalyst activity. *Journal of Molecular Catalysis A: Chemical* 335 (1–2), 189–198.
- Pagidi, A., Saranya, R., Arthanareeswaran, G., Ismail, A. F., Matsuura, T., Jul. 2014. Enhanced oil–water separation using polysulfone membranes modified with polymeric additives. *Desalination* 344, 280–288.
- Pattinson, S. W., Windle, A. H., Koziol, K. K. K., Feb. 2013. Facile processing of zeolite based catalyst support for carbon nanotube synthesis. *Materials Letters* 93, 404–407.
- Phao, N., Nxumalo, E. N., Mamba, B. B., Mhlanga, S. D., 2013. A nitrogen-doped carbon nanotube enhanced polyethersulfone membrane system for water treatment. *Physics and Chemistry of the Earth, Parts A/B/C* 66, 148–156.
- Tetana, Z. N., Mhlanga, S. D., Bepete, G., Krause, R. W. M., Coville, N. J., 2012. The synthesis of nitrogen-doped multiwalled carbon nanotubes using an Fe-Co/CaCO₃ catalyst. *South African Journal of Chemistry* 65, 39–49.

Vatanpour, V., Madaeni, S. S., Moradian, R., Zinadini, S., Astinchap, B., Jun. 2011. Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multi-walled carbon nanotube/polyethersulfone nanocomposite. *Journal of Membrane Science* 375 (1–2), 284–294.

Chapter 5

Conclusions and recommendations

5.1 Conclusions

This research explored the performance of modified membranes in the treatment of synthetically made produced water. Two different techniques were employed in synthesizing the membranes; the PI method and the solution casting method. The membranes were modified with CNTs and a polyester NWF. From the property and filtration tests performed on both the CNTs and the membranes, the following conclusions were drawn:

- CNTs can be successfully grown from both a Fe/Co catalyst supported on either a CaCO_3 or zeolite support using the CVD method at 700 °C. Acetylene was used as the carbon source and nitrogen as the carrier and inert gas. The synthesized CNTs were functionalized and characterized using the TEM, Raman, FTIR, TGA/DTG and the SEM/EDS.
- The wet impregnation method successfully impregnates metals catalysts onto the supports. The choice of catalyst support influences the sizes of CNTs grown, the yields of CNTs produced and the purities of the synthesized nanotubes.
 - CNT grown from a zeolite supported catalyst produce tubes with smaller diameter ranges of 10 nm to 40 nm while those grown from CaCO_3 yield larger diameter tubes, from 20 nm to 80 nm.
 - CNTs grown from the CaCO_3 catalyst support produce almost twice as much CNTs as the CNT grown from the zeolite support. This is attributed to the larger pore sizes and surfaces of the CaCO_3 supported catalyst.
- Concentrated HNO_3 can be used to purify and functionalize CNTs. This acid removes both CaCO_3 supports and any remaining metals from the CNT-cs without affecting their wall structures.
 - HNO_3 however fails to completely purify CNT-zs due to the thermally and chemically

stable nature of the zeolite support. The acid failed to remove about 37 % of SiO₂ from the CNTs.

- Concentrated HF however effectively removes the SiO₂ and yields very pristine CNTs with no residual materials without destroying the nanotubes.
- Both the PI and solution casting methods can be used to successfully produce polymeric membranes.
 - These methods however produce two different types of membranes.
 - The PI method produces very porous anisotropic membranes while the solution casting method produces very dense and non-porous isotropic membranes.
 - This is due to the liquid-liquid exchange in the two techniques; the former being rapid and efficient compared to the slow exchange in the solution casting method.
- PI membranes are rougher and more hydrophilic than the SC membranes. The AFM, contact angles and FTIR were used to characterize and confirm the roughness and hydrophilicities of the membrane.
 - The SC membranes are more thermally stable at higher temperatures compared to the PI membranes.
- CNTs improve the porosity, permeability, hydrophilicity, and tensile strength of the membrane. The interaction of the fCNTs with the membrane introduces O-H bonds, which makes it more hydrophilic. This interaction however makes the membrane slightly less thermally stable at high temperature and also reduces its rigidity.
- Polyester NWF increases the roughness and permeabilities of the membrane. The membranes supported on a fabric and imbedded with CNTs are more thermally stable at high temperatures. The tensile strength of the membrane is drastically increased with the addition of the fabric.
 - The introduction of the fabric introduces subsurface voids to the SC membrane and this in turn increases the hydrophilicity of the membranes.
- Increase in the filtration pressure increases the permeate flux across the membrane. This is because of the increased pressure difference across the membrane.
- The permeate flux through the membrane decreases with time. This is attributed pore blockage in the membrane and the formation of an oil layer across the membranes, which hinders flow across the membrane.
 - Pore blockage occurs a lot faster and has a greater influence on the flux decline than concentration polarization.

- CNTs help reduce this flux decline *via* pore blockage
- The fabric makes the membrane more susceptible to fouling *via* pore blockage.
- The membranes are effective in removing the oil particles from the produced water and yielding clear permeates with oil rejections between 78 % and 90 %.
- Though these concentrations are high, the oil concentrations are still above the allowable discharge limits of 50 mg/l

This research successfully treated wastewater prevalent in the oil and gas industry using the cost effect and scalable membrane technology. The physical properties of the membrane show that they are effective in separating oil water emulsions. The filtration tests performed confirm this with very high oil rejections. Further modifications of the membranes will however be required to reduce this oil concentrations to allowable discharge limits. This would prove very useful for oil and gas platforms in deep or ultra deep platforms.

5.2 Recommendations for further studies

Due to time constraints, not all the parameters that influence the membrane's performance could be investigated. The following list provides recommendations for further investigation that could help improve the quality of the membrane in treating produced water.

- It has been shown that CNT increase the hydrophilicity of the membrane and help control fouling *via* pore blockage. The effect of the CNT sizes imbedded into the membranes and their alignment could be further studied to determine if they would further improve the membrane's properties.
- This research showed that the polyester NWF influenced the permeability and hydrophilicities on the membranes. Further studies could be carried out on the how the various types of fabrics (A, TH and HS types) affect the properties and performance of the membrane for both the PI and solution casting methods.
- Further studies could be carried out to investigate further additives that could attract or rejection oils across the membrane. This could help reduce the oil concentrations in the permeates to below allowable discharge limits or completely remove the crude oil from the emulsion.
- Further fouling studies could also be conducted on the membrane to determine the best membrane cleaning agent and the best membrane cleaning procedure.
- Further studies could be conducted on the solution casting method; filtration conditions, effect of various additives in enhancing the properties and performances of these membrane *etc.*

Appendix A

Preparing oil-water emulsion (synthetic produced water)

A 1000 mg/l oil water mixture was prepared using Millipore water. This was sonicated for 30 min until the oil was adequately dispersed in the water. This solution was left untouched in ambient conditions for a month to ensure the dispersed oil did not naturally separate into the different phases.



Figure A.1: Synthetic produced water after a month with an oil concentration of 1000 mg/l

Appendix B

Wet impregnation calculations

This appendix presents the calculations used for the preparation of the CNT catalyst *via* the wet impregnation method.

A 10% Fe-Co on Zeolite catalyst was prepared. Equal amounts of the metals were used i.e. 5% of each. So this makes up

$$\frac{5}{100} \times 10g \text{ Zeolite} = 0.5g$$

For Iron Nitrate ($Fe(NO_3) \bullet 9H_2O$) that has an atomic mass of 55.845g and a molecular mass of 404g/mol, 0.5g of *Fe* will have

$$= \frac{0.5g}{55.845g} \times 404.0g/mol$$

$$= 3.62g/mol \text{ of iron nitrate}$$

Similarly

For Cobalt Nitrate that has an atomic mass of iron of 58.933g and a molecular mass of 291.03g/mol, 0.5g of *Co* will have

$$= \frac{0.5g}{58.933g} \times 291.03g/mol$$

$$= 2.46g/mol \text{ of iron nitrate}$$

These are the masses of metals that are measured.

Appendix C

Tensile strength

Figure C shows a typical stress-strain plot used for the calculation of the tensile strength.

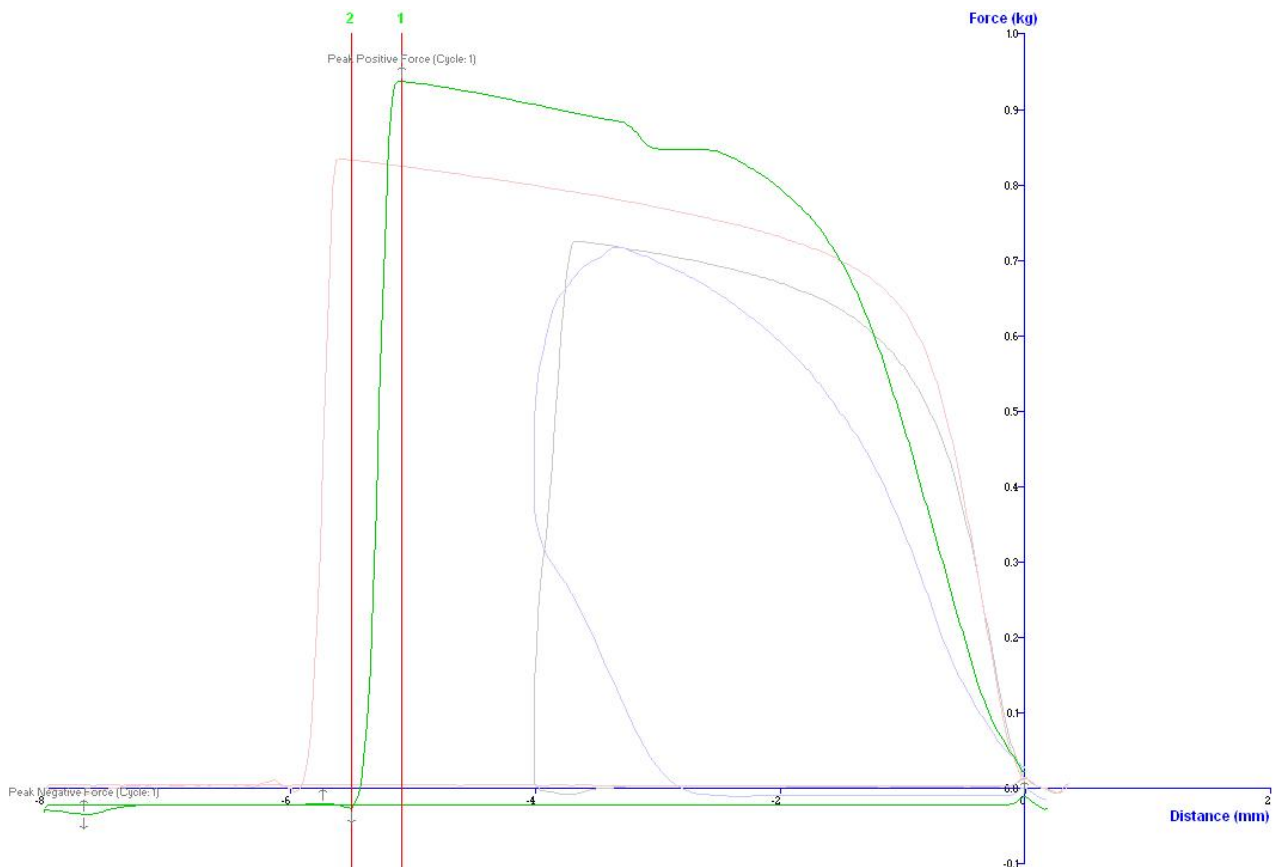


Figure C1: Information from a stress-strain graph

To determine the Young's modulus the gradient taken before the curve starts bending as shown in Figure C.

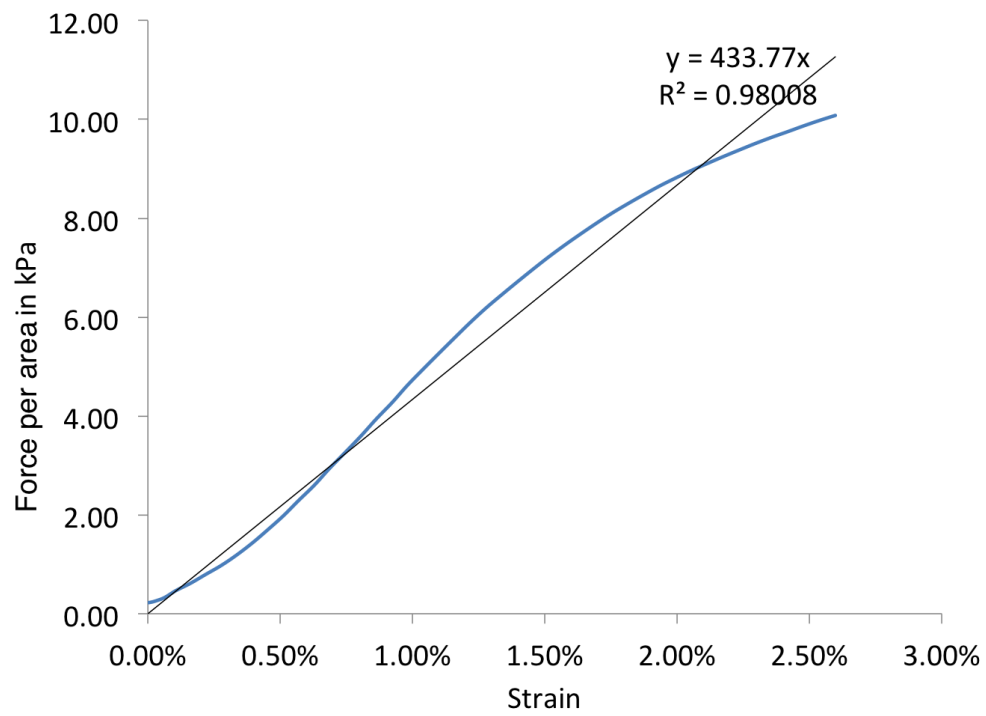


Figure C2: Information from a stress-strain graph