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Synthesis of carbon nanotubes – polyphenylene sulfone composite membranes for waste water treatment from petroleum sources

By

Jacob Phasha

MSc report presented to the University of the Witwatersrand

In the fulfillment of the requirements for the degree of

Master of Science in Engineering

School of Chemical and Metallurgical Engineering

Faculty of Engineering and the Built Environment

University of the Witwatersrand

Johannesburg

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Declaration

I, Jacob Phasha, declare that this research report is my own work, executed under the supervision of Dr. Diakanua Nkazi. It is being submitted to the degree of Master of Science in Chemical Engineering at the Faculty of Engineering, University of the Witwatersrand. In my knowledge, it has never been submitted before for any degree or examination.

…….

(Signature of candidate)

…….

(Signature of supervisor)

26th day of April 2017

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Synopsis

Oil and gas operations produce high volumes of wastewater in the form of finely dispersed oil/ water (o/w) emulsions, which have detrimental effects on the environment. The current most feasible method used to mitigate the environmental impacts caused by the emulsion (produced water) from oil and gas operations is polymer membrane technology. However, polymer membranes are susceptible to fouling and concentration polarization, which leads to the necessity for frequent membrane replacement, thus loss of operating time and high operation cost. This motivates the need to investigate ways of modifying the polymer membrane in order to make it more resistant to fouling and concentration polarization. This study is concerned with circumventing the challenges experienced by polymer membrane during crude oil/ water mixture ultra-filtration by infusing the polymer membrane with nano particles. The aim of the research was to investigate the influence of addition of CNTs on the modified membranes in treatment of waste water from petroleum source.

The Wet Impregnation method was used for the preparation of the bimetallic catalyst (Fe-Co catalyst supported on Zeolite), Chemical vapor deposition (CVD) method was used to prepare the carbon nanotubes (CNTs) and Phase inversion (PI) method was used for the preparation of the polymer nanocomposite membrane. The bimetallic catalyst was characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD). The CNTs were characterized using Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and Transmission electron microscopy (TEM). The prepared polymer nanocomposite membranes were characterized using SEM, FTIR, goniometer (for contact angles) and TAXT plus texture analyzer (for tensile strength test).

Functionalized carbon nanotubes were used as membrane fillers or modifiers to improve the filtration properties of the polymeric membrane, ultimately forming nanocomposite polymer membranes. This increased hydrophilicity, chemical, mechanical and physical properties of the polymer membrane, made them to perform better during filtration than pristine polymer membranes.

The performance of the nanocomposite membranes were evaluated and it was determined that the nanocomposite polymer membrane with a loading 0.4 wt.% functionalized carbon nanotubes performed better than pristine membrane and other CNTs loaded nanocomposite polymer membranes.

The pristine membrane (0 wt% CNTs) showed a higher contact angle (79^{o}) which crosses ponds to the inability to soak up water. The 0.4 wt% nanocomposite polymer membrane showed the lowest contact angle of 72 ^{o}, this validated an improvement in the properties of the membrane, in particular hydrophilicity. The 0.4 wt% nanocomposite polymer membrane showed a superior mechanical strength, with a breaking force at 4 N relative to the other membranes of the same thickness.

0.4 wt% nanocomposite polymer membrane showed the highest permeate flux of 120 $L/m^2.h$ compared to the pristine membrane, which showed a permeate flux of 63 $L/m^2.h$. The permeate flux of 0.4 wt% nano-composite polymer membrane increased with the operating pressure.

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Nomenclature

Abbreviations

O/w	Oil/water
A	The effective area of the membrane
DMF	Dimethyl formamide
ID	The intensity of the D-band
IG	The intensity of the G-band
SEM	Scanning electron microscope
CVD	Chemical vapour deposition
CNTS	Carbon nanotubes
XRD	X-ray diffraction
TEM	Transmission electron microscopy
FTIR	Fourier transform infrared spectroscopy
UF	Utrafiltration
RO	Reverse osmosis
NF	Nanofiltration
MF	Microfiltration
PES	Polyether sulfone
PS	Polysulfone
MD	Membrane distillation
PPSU	Polyphenylene sulfone
SWNTs	Single walled CNTs

MWNTs Multi-walled CNTs

PEDGE Penta-ethyleneglycol-dodecylether

wt% Weight fraction percent of the CNTs to polymer solutin

fCNT Functionalized carbon nanotubes

w/w Weight fraction of CNTS to polymer solution

Chemical formulas

HNO_3	Nitric acid
HF	Hydroflouric acid
$Fe(NO_3)_3.9H_2O$	Iron Nitrate nonahydrate (III)
$Co(NO_3)_2.6H_2O$	Cobalt(II) nitrate hexahydrate
Fe	Iron
CO	Cobalt
Ar	Argon
C_2H_2	Ethylene

1. Introduction

1.1 Background and motivation

It is inevitable for processes deployed during crude oil production not to produce high volumes of waste water in the form of water-in-oil (w/o) or / and oil-in-water (o/w) emulsions (produced water). It is reported in literature that oil and gas industry accounts for high production of oily wastewater (o/w emulsions) relatively compared to several industries such as food processing, metallurgical, transportation, petrochemical, pharmaceutical and etc. on a yearly basis (Maphutha, *et al*.,2013). This can be attributed to fact that oil and gas reservoirs co-exist with water (formation water, up to 50% volume) (Weideman, 1996; Khatib and Verbeek, 2003).

Although, crude oil production is essential for the survival of human kind, the oily water emulsions may cause risk to the survival in the form of health, safety and environment (Daminger, *et al.*, 1995). The oil concentrations in oily wastewater produced by crude oil production processes are reported to range from 50-1000 mg/L where else the acceptable discharge limit range is 10-15 mg/L (Maphutha, *et al.,* 2013). Therefore, delmulsification of these emulsions is critical to the process associated with crude oil production in order to comply with the environmental regulations and for economic reasons.

Delmulsification of the oil emulsions is commonly achieved by the use of conventional separations processes such as floatation, skimming, electric field, ultrasonic separation and coagulation / flocculation (Qin, *et al.*, 2003; Yi, *et al*., 2012).However, Chakraborty, *et al*., (2008) highlighted that these methods fail to produce clean water with minimal oil content when dealing with low-concentration of finely dispersed oil emulsions.

Over the years, cost-effective technologies have been developed and still in development in order to extend water resources and mitigate water pollution. Currently polymer membranes separation technology is the most widely used membrane type for water treatment (Yin and Deng, 2015). It is also known (polymer membranes) to have major technical and commercial advantages over inorganic equivalents (Mori *et al*., 1994; Goto, *et al*., 1989).

However, the polymer membrane separation technology is not without significant drawbacks. Two major problems experienced by polymer membrane are fouling and concentration polarization (Maphutha, *et al.*, 2013). These drawbacks can be offset by modifying the polymer membrane in such a way that the membrane will have controlled pore size, high permeate flux and have good anti-fouling properties (Yin and Deng, 2015). The modification can be achieved by infusing the polymer membrane with nano-materials in order to alter their structure and physiochemical properties (hydrophilicity, porosity, thermal & mechanical strength and charge density) thus making the membrane more effective (Yin and Deng, 2015).

Therefore, in order to study the effects of addition of nano-materials, in particular carbon nanotubes to enhance polymer membranes properties for better performance during the filtration of wastewater from oil sources, it becomes a vital necessity to be able to synthesis carbon nanotubes and impregnate them onto the polymer membrane.

Chemical vapour deposition (CVD) and phase inversion (PI) are reported to be the effective ways to synthesize carbon nanotubes and nano composite polymer membrane respectively (Iyuke, *et al*., 2013).

1.2 Research objectives

The aim of the research was to investigate the influence of addition of CNTs on the modified membranes in treatment of waste water from petroleum source. The study further investigated the physical and chemical properties of the modified membrane.

The objectives of the research were as follows:

- Synthesizes of Fe - Co catalysts supported on zeolite for the preparation of carbon nanotubes using the chemical vapor deposition method
- Functionalize the produced CNTs
- Preparation of nanocomposite polymer membrane with varying CNTs loading
- Investigate the effect of CNTs loading on the mechanical properties and hydrophilicity of the membrane
- Investigate the effect of CNTs loading on the performance of the membranes during filtration.

2. Literature Review

2.1 Crude oil, formation water and on and offshore operation process

Crude oil is well defined by Cadwallaer (1993) as a colloidal mixture of huge number of hydrocarbon and non-hydrocarbon, the source material for nearly all petroleum products (Diesel, Jet fuel, Gasoline (petrol) and etc.). Crude oil is formed from the decomposition of plant and animal organic matter under elevated temperature and pressure over millions of years and it is important as both fuel source and commodity (Gay, *et al*., 2010).

Crude oil production or extraction sites are usually onshore or offshore sites where the production proceeds via drilling (Humphries, 2014). The oil reservoir are usually a multi-phasic reservoirs consisting of the crude oil, natural gas or associated gas (usually methane) and water (also known as formation water) (Khatib and Verbeek, 2003).The oil is usually trapped in the reservoir with gas and water. The formation water located at the bottom due to the fact that water is denser than oil and with associated gas at the top because gas is less dense than oil as illustrated in figure 2.1.

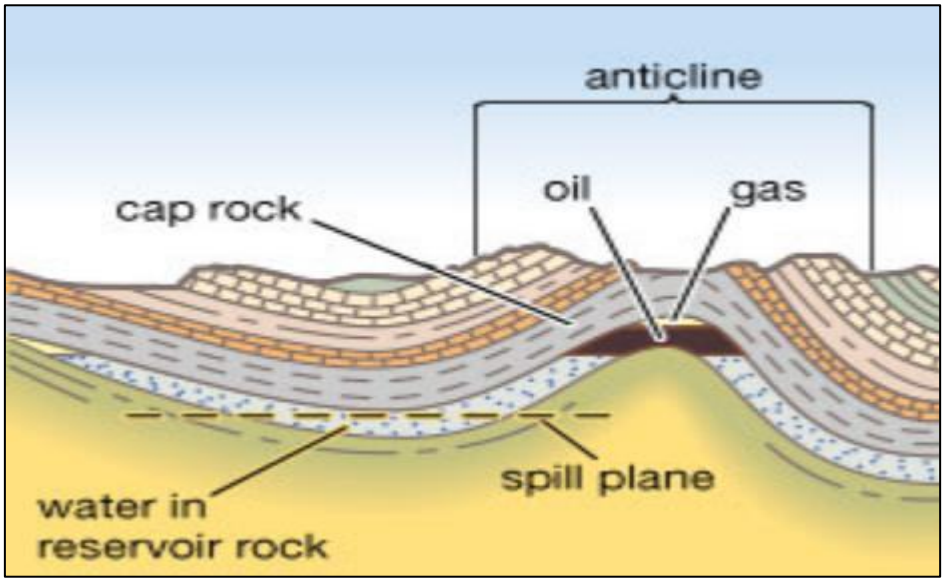


Figure 2.1. Typical Oil reservoir (adapted from Jukic, 2013)

.The formation water may account up to 50% of the oil reservoir volume and as a result water usually contains finely dispersed oil (Khatib and Verbeek, 2003).The formation water and the associated gas usually complicate the process of extracting crude oil (Kearns, *et al*., 2000).The gases are usually flared or injected into the well to enhance the recovery of crude oil and small amount of formation water may also be injected into the well to enhance oil production (Kearns, *et al*., 2000; Burnett, 2004). Since water is contaminated by oil with oil concentration in water ranging from 50 -1000 mg/l. Purification process is needed before the water can be injected into the well or discharged elsewhere.

2.2 Types of oil-water emulsions

Basically, essentially there are different kinds of oil existing in oily waste water emulsions namely unstable, stable o/w emulsions and free - floating oil (Rhee*et, et al.*, 1983). Delmulsification of these emulsions differs greatly. Unstable o/w and free-floating can be easily separated by conventional separations such as floatation, skimming, electric field, ultrasonic separation and coagulation / flocculation (Qin, *et al.*, 2003 ; Yi, *et al*., 2012).

Luo, *et al.* (2015) stated that the stable emulsions containing small size droplets (submicron) needs to be broken down before treatments and also mentioned that conventional emulsification techniques such as chemical coagulation and thermal treatment are ineffective, also Benito, *et al*., (2002) highlighted that although conventional methods may be able to reduce the oil concentration in oil water emulsion to about 1% of the total wastewater, they cannot efficiently remove oil droplets below 10 µm size and thus results in environmental pollution and resources utilization problems.

2.3 The environments impacts of crude oil – water mixture (oily wastewater, o/w emulsion)

Crude oil production is essential for the survival of human kind, but its water pollution in the form of oily water emulsions, may cause risk to the survival in the form of health, safety and environment (Daminger, *et al.*, 1995). The extraction of crude oil is a complicated process that has the potential for detrimental effects on the environment (Gay, *et a*l., 2010). Leaks, spills and other release mechanisms of

petroleum products such as gasoline, diesel, fuels and heating oil normally results in the contamination of soil and water (Edema, 2012). In addition, Gay, *et al*. (2010) conducted a study of health effects of oil contamination and found that oil contamination can have significant effects on people living in close proximity to the pollution.

Oil pollution basically occurs when oil is introduced into the environment directly or indirectly resulting in unfavorable change in such as way the safety and welfare of any living organisms is endangered (Edema, 2012). Most of the oil pollution occurs during oil and gas exploration and production because of the complicated process involved in extracting the hydrocarbons (Khatib and Verbeek, 2003). In addition to the hydrocarbons, oil contains wide array of components such as Oxygen, Nitrogen, Sulphur and some metals related porphyrin oxygen containing compounds such as carboxylic acids, esters, ketones etc. (Odu, 1981). When oil is released into the environment, these compounds may exacerbate the pollution.

When oil is introduced into water, the oil in water undergoes a variety of physical, chemical and biological changes including evaporation of high volatile fractions, dissolution of water-soluble fractions, photochemical oxidation, emulsification, microbial degradation and sedimentation (Edema, 2012). Depending on the concentration and the type of the hydrocarbons released into the water environment, they may be toxic to organisms (Neff and Anderson, 1981).

It is clear that the effects of oil on water and environment are detrimental and it remains a challenge to ensure that the concentration of the oil released into the environment are reduced to acceptable levels in order to mitigate its environmental impacts and comply with environmental regulations.

2.4 Membrane technology

The application of membranes for water treatment dates back several decades ago, it emerged as a viable way of water purification in the 1960s alongside the development of high performance synthetic membranes (Sagle and freeman, 2004). Due the scarcity in fresh water sources, ways to produce fresh water from alternative water resources such as ocean water were investigated using membranes. Membranes proved successful in producing portable water from salty water and

membrane became viable alternative to evaporation - based technologies in water treatment industry (Sagle and freeman, 2006). The use of membranes for water treatment gained reputation because of the ability to perform efficiently and effectively (Sagle and freeman, 2006).

Al-Alawy and Al-Musawi (2013) well defines a membrane as a synthetic barrier, which prevents the transport of certain components based on various characteristics. Membranes are different in the physical and chemical properties but have a common purpose of separating matrix into desired components or mixtures. Essentially a membrane is a filter, made up of a pores support layer and a dense layer that makes up the actual part of the membrane.

The membrane may have an inherit properties such as chemical, physical or biological properties that selectively aid in permitting certain particles or molecules which are compatible with properties of those membrane to pass through (known as permeate) while rejecting other molecules (known as Retentate) as illustrated in figure 2.2.

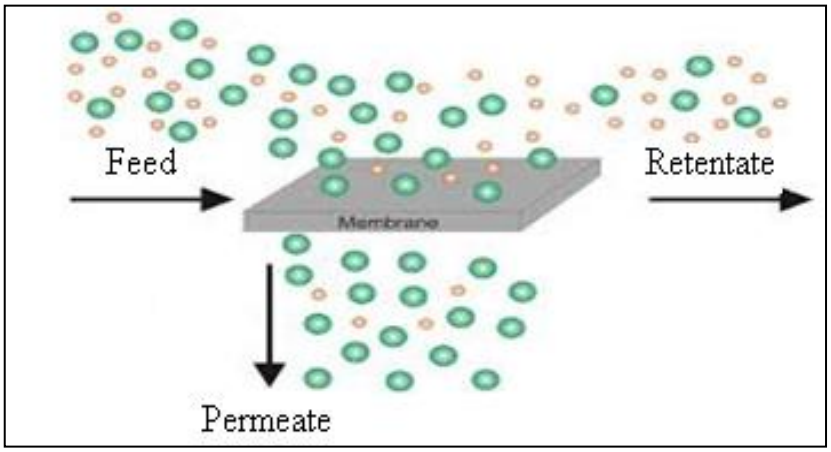


Figure 2.2. Illustration of membrane process (adapted from Strathham, et al., 2006).

The molecules are forced through the membrane (or filter) by use of driving forces such as pressure, temperature, concentration, and basic properties of the membrane such as membrane pore size, hydrophilicity, structure or morphology, electric potential, membrane arrangement etc. (Mulder, 2006).

2.4.1 Types of membranes and separation (filtration) process

Water treatment process employs different types of membranes depending on the separation objective that needs to be achieved (Amjad, 1993). The membrane includes ultra - filtration (UF), reverse osmosis (RO), nanofiltration (NF) and Microfiltration (MF) (Perry and Green, 1997). These membrane differ in pore sizes, ultimately effectively permitting molecules based on their sizes, figure 2.3, illustrate range of nominal pore size.

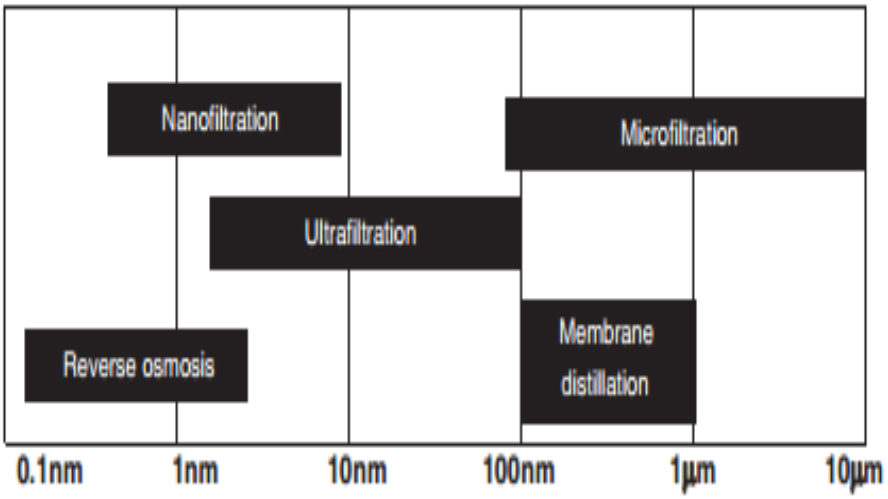


Figure 2.3. Range of nominal membrane pore size (adapted from Perry and Green, 2013)

As evident from figure 2.3, Microfiltration membranes have the largest pore size and usually reject large particles and various microorganisms (Sagler and Freeman, 2004). A filtration or separation process using this membrane can effectively remove particles or biological entities in the 0.025 µm to 10.0 µm (Baker, 2004).

Ultrafiltration membranes (UF) have small pore size compared to those of MF, implying that a filtration process using this membrane can reject bacteria and soluble macromolecules such as proteins in addition to large particles and microorganisms (Sagler and Freeman, 2004).

Reverse osmosis membranes are effectively non-porous, hence a filtration process using this types of membranes can effectively remove or exclude particles and even low mass species such as salt ions, organics (Perry and Green, 1993). The

Nanofiltration membranes are quite recent and they are porous membrane and they usually show performance between that of RO and UF membranes (Baker, 2004)

2.4.2 Membrane operating configuration or geometry during filtration

There are different configurations of operating a filtration process: Dead-end filtration, cross-flow filtration,

2.4.2.1 Dead-end filtration

The most common form of filtration configuration is the dead-end filtration in which the feed flow is forced through the membrane and the filtered matter accumulates on the surface of the membrane, the drawback with this configuration is the decrease in the efficiency of filtration due to blockage caused by the accumulated matter on the membrane system which requires the accumulated matter to be removed resulting in loss of operating time. Usually this configuration is ideal for concentrating compounds (see figure 2.4 for configuration) (Iritani, *et al*., 1995).

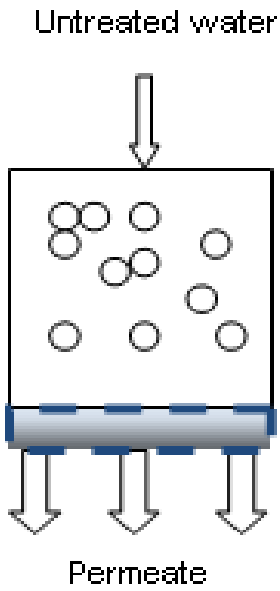


Figure 2.4. Dead end filtration configuration

2.4.2.2 Cross flow filtration

The cross-filtration has a constant turbulent flow along the membrane surface which ultimately prevents the accumulation on matter on the membrane surface (Baker, 2004). The feed flow passes the membrane tube at high pressures and high speed in order to create turbulent conditions. It is praised as an excellent way to filter liquids with high concentration of filterable matter. Figure 2.5 illustrate this configuration.

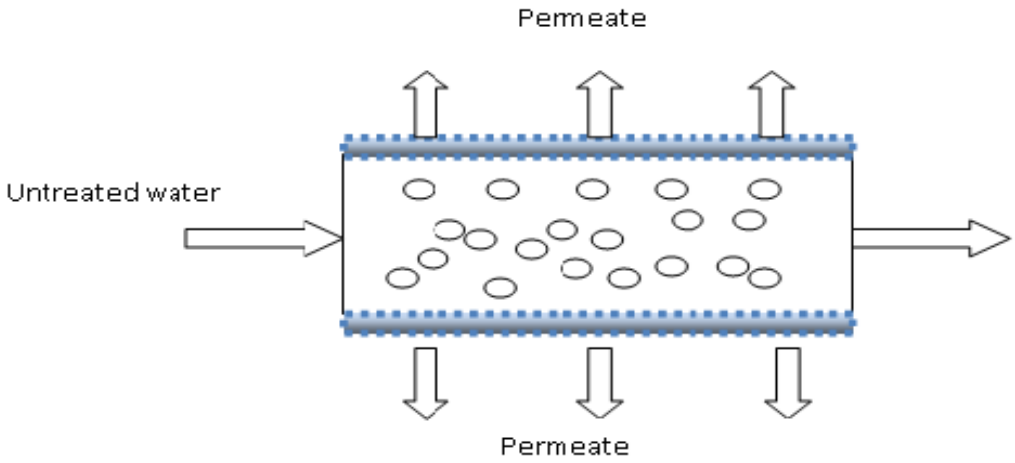


Figure 2.5. Cross -flow configuration

Other uncommon configuration includes hybrid-flow filtration and submerged filtration (Baker, 2004). During the submerged filtration process the membranes are submerged in the liquid that has to be filtered and the filtration is performed from the outside to the inside of the membrane operated in vacuum.

The hybrid-flow filtration process combines the dead-end and the cross-flow technique (Munir, 2006). The filtration process has two phases: the production phase; the tubes are closed both side and dead filtration is performed and the flushing phase; the tube is open on both side and the fraction that does not pass thought the membrane is removed in order to clean membrane as in cross-flow (Munir, 2006).

Essentially, all these configurations work the same to same to separate matrix but differs in the efficiency to do so.

2.4.3 Membrane characteristic

According to Mulder (2006) membranes can be either natural (mainly biological) or synthetic in the origin. The synthetic membranes are categorized as organic or inorganic membranes depending on the constituents that make up the membranes. Organic membranes are commonly made up from polymers such as Polyether sulfone (PES), Polysulfone (PS) etc. and Inorganic membranes represent membranes made up from materials such as ceramic, glass and metal etc. (Mulder, 2006). Synthetic membranes can be further classified as isotropic and anisotropic (Sagle and Freeman, 2004).

Sagle and Freeman (2004), describes Isotropic membranes as membrane which are uniform in composition and physical nature across the cross-section of the membrane. Whilst anisotropic membranes are defined as non-uniform over the membrane cross-section and consisting of layers which vary in structure and/or chemical composition. Figure 2.6 depicts or illustrates the difference in cross-sections of isotropic and anisotropic membranes.

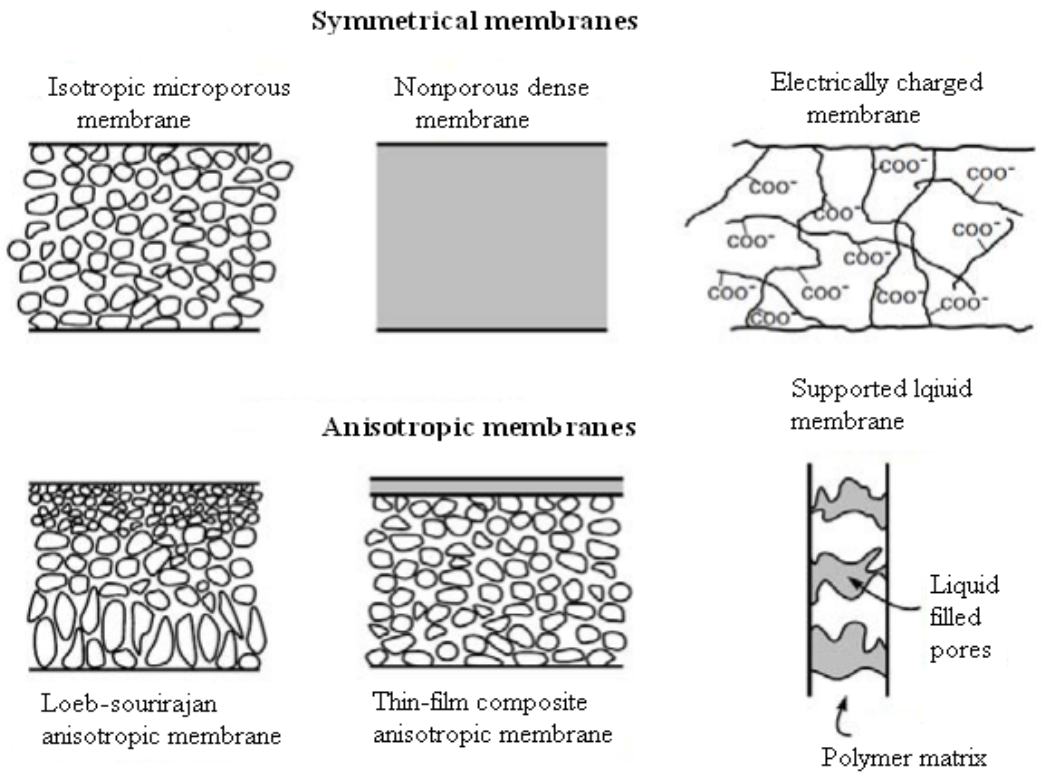


Figure 2.6. Cross section of Isotropic and anisotropic membranes (adapted from Baker, 2014).

The isotropic membrane can be further divided into certain subcategories such as microporous membranes which are commonly prepared from rigid polymeric materials with large voids that create interconnected pores e.g. Phase inversion membrane, expanded-film membrane and track-etched membrane (Sagle and Freeman, 2004; Baker, 2004). It should also be noted that isotropic membranes can also be dense films which either lack pores or contain pores are so small as to render the membrane effectively non-pores (Baker, 2004).

Sagle and Freeman (2004), reports two main types of anisotropic membranes namely thin-film composite membrane and phase separation membranes Phase separation membranes are homogeneous in chemical composition but different in structure and they can be prepared via phase inversion techniques with the exception that there is variance in pore size and porosity across the membrane (Sagle and Freeman, 2004).

Baker (2004) describes the thin-film composite membranes as membranes that are both chemically and structurally heterogeneous, consisting of a highly porous substrate coated with a dense film of a different polymer prepared via several methods such as interfacial polymerization, solution coating, surface treatment or plasma polymerization.

Membranes that are of organic origin, those that are made up from polymers (such as natural rubber, silicon rubber, polysulfones) are commonly used in water treatment compared to those that are of inorganic origin. This is because of the fact that polymer membranes have major technical and commercial advantages over inorganic equivalents (Mori , *et al*., 1994).

2.4 .4 Polymer membranes

Polymers are defined as molecules that arranged orderly in repetition of small simple chemical units (Ebil, 1999). The repetition may be liner or nonlinear to form a three dimensional networks exhibiting rubbery or glassy states depending on the temperature (Ebil, 1999). For an example polymer such as polysulfones (PS) tend to exhibit a glassy state at room temperature, meaning they have glass like properties with low permeability but with high selectivity (Ebil, 1999).

Depending on the type of o/w emulsion different techniques (skimming, electric field, ultrasonic separation and coagulation / flocculation) can be used to reduce the concentration of oil in oily wastewater in order to mitigate the detrimental effects it has on the environment (Qin, *et al.*, 2003; Yi, *et al*., 2012). However conventional methods cannot effectively reduce the concentration of oil in wastewater in an economical viable way relatively compared to polymer membranes as highlighted by Yin and Deng (2015).

Polymer membranes separation technology is reported to be the most widely used membrane type for treatment water (Yin and Deng, 2015) and it is said to have major technical and commercial advantages over inorganic equivalents (Mori, *et al*., 1994). The technology to effectively treat the oil water emulsions according to Luo, *et al*. (2014). The use of polymer membrane technology to treat oil wastewater is versatile and is increasingly applied in industry (Syed*et, et al*., 2000).

Reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF) and nano-filtration (NF) are some of examples of pressure driven processes that use polymer membrane technology (Syed*et, et al.,* 2000). One of the advantages of polymer membrane is that the quality of the treated water is uniform independent of influent variations and there is no need to use extraneous chemicals (Cheryan and Rajagopalan, 1998).

2.4.4.1 Polymer membrane preparation methods and fabrication geometry

There are a number of polymeric membrane preparation path ways reported in literature (Apel, 2001; Sa-nguanruksa, *et al*., 2004; Baker, 2000; Mackenzie, 2000). However there are five of them that are commonly used for the preparation of polymeric membranes, these include phase inversion, interfacial polymerization, stretching, track-etching and electrospinning (Lalia, *et al*., 2013). The choice of polymer and the desired structure detects the selection of the preparation method (Lalia, *et al*., 2013).

Phase inversion method

Phase inversion is practically a process whereby polymers are dissolved in suitable solvents such as DMF (dimethyl formamide) to achieve a homogenous polymer solution which is then converted in a controlled manner to a solid state from liquid

state (Driol and Giorno, 2009). Mulder (1996) outlines various ways of converting a liquid polymer solution to a solid state, namely:

(i) Immersion precipitation. In the immersion precipitation, the polymer solution is cast on a suitable support such as glass, then the polymer solution is immersed in a non-coagulation bath (usually water), where an exchange of solvent and non-solvent takes place and the membrane is formed. (Driol and Giorno, 2009; Boussu, *et al*., 2006).

(ii) Thermally induced phase separation. Lalia, *et al*. (2013), alludes that the method is based on the fact that the quality of the solvent decreases with decreasing temperature and the solvent is then removed by extraction, evaporation or freeze drying after demixing

(iii) Vapour - induced phase separation. According to Lalia, *et al*. (2013), the transformation or conversion of liquid polymer solution to solid state is accomplished by exposing the polymer solution to an atmosphere containing a non-solvent and demising or precipitation occurs as the result of the absorption of the non-solvent

(iv) Evaporation – induced phase separation method. The polymer solution is made in a solvent or in a mixture of a volatile non-solvent, and the solvent is allowed to evaporate, leading to precipitation or demixing/precipitation. This technique it is also known as a solution casting method (Lalia, *et al*., 2013; Baker, 2000).

Interfacial polymerization

Thin-film composite (TFC) RO and NF membranes are fabricated for this method (Lalia, *et al*., 2013). Cadotte, *et al*. (1980) is credited for being the first to develop the interfacially polymerized TFC membranes. The procedure for interfacial polymerization (IP) involves immersing a micro porous polysulfones support in an aqueous solution of a polymeric amine and then immersing the amine impregnated membrane into a solution of a di-isocyanate in hexane and cross-linking the membrane by heat-treatment at 110^{o}C (Cadotte, *et al*.,1980 ; Lalia, *et al*., 2013).

Track-etching

Lalia, *et al*. (2013), describes this technique as whereby a nonporous polymeric film is irradiated with energy heavy ions leading to the formation of linear damaged tracks across the irradiated polymeric film. The technique is soundly known for great control of the pore size distribution of the membrane and; pore density and pore size are independent parameters and can be controlled in a wide range from a few nanometres to tons of micrometres (Lalia, *et al*., 2013).

Stretching

Basically the procedure for preparation of membrane using this method involves, extrusion followed by stretching technique. The membranes produced in this manner are commonly used in MF, UF and MD (Membrane distillation) (Lalia, *et al*., 2013). It is a method that does not need a solvent, in which the polymer is heated above its melting point and extruded into thin sheet forms followed by stretching to make it porous (Sadeghi, 2007; Zhu, *et al*., 1996; Trommer and Morgensten, 2010).

Electrospinning

This technique is quite recent for fabrication of porous membranes for a wide number of applications including desalination and fabrication. It works by applying a high potential between the polymer solution droplet and the grounded collector (Lalia, *et al*., 2013). Upon the electrostatic potential becomes sufficiently high and overcomes the surface tension of the droplet, a charge jet is formed (Lalian, *et al*., 2013).

2.4.5 Factors affecting polymer membrane performance

Although polymer membrane emerged as the most promising method that can effectively reduce the concentration of oil in oily wastewater to acceptable level compared to its inorganic membrane equivalents, it is still restricted by several challenges such as trade-off relationship between permeability and selectivity and low resistance to fouling (Yin and Deng, 2015).

To offset these challenges the concept of polymer-matrix nanocomposite membranes was developed, originally to overcome the Robeson upper boundary in the field of gas separation in the 1990s (Robeson, 1991; Chung, *et al.,* 2007), where

highly selective zeolite were incorporated into polymers to improve both permeability and selectivity (Duval, *et al*.,1993). Because of the ability of nano-composite membranes to overcome the trade – off relationship between permeability and selectivity as well as mitigating membrane fouling problem during water treatment application, nano-composite membranes gained considerable attention and it is considered as the cutting edge of creating the next generation of high performance membranes (Yin and Deng, 2015).

As reported in literature, polymer membrane suffer concentration polarization (also known as cake formation) and pore blocking (Baker, 2000), and these results in the necessity for frequent cleaning and replacement of the membrane. Pore blocking results in the need to increase trans - membrane pressure in other to achieve a constant membrane performance (constant permeate), however increase trans-membrane pressure may results in making the membrane less efficient (Maphutha, *et al*., 2013).

Pore blocking and cake formation results in membrane fouling. The fouling decrease the life spans of the membrane and as well its performance which leads to high utility cost (Vrijenhoek, *et al*., 2001; Zularisam, *et al*., 2007). To circumvent these challenges it is reported static turbulence promoters such as rods, differently shaped inserts and static mixers can be utilized to minimize the fouling in polymer membranes (Mulder, 1996).

However, the current effective trend is to increase the properties (hydrophilicity) of polymer membrane in order to minimize fouling, charging the membrane is reported to be another way of making an “anti-fouling” membrane (Zhao, *et al*., 2010; Mulder, 1996). To achieve this, inclusion of nano-sized inorganic materials such as CNTs, catalyst and other organic barrier layers are used. The incorporation of these materials change the porosity and pore size of the polymer membrane and as a results change the membrane permeability and solute rejection (Yin and Deng, 2015).

Another factor that is mentioned in literature that can help mitigate membrane fouling is the membrane geometry, i.e. cross flow filtration or dead end filtration (Al-Alawy and Al-Musawi, 2013). According to Al-Alawy and Al-Musawi (2013), cross flow

separation is where only part of the feed stream is treated and the reminder of the feed is passed through the membrane untreated, while the dead-end filtration all the feed is treated.

The benefits of cross-flow filtration over dead end filtration lies in the fact that there is a constant turbulent flow along the membrane surface preventing accumulation of matter on the membrane surface and its ideal to filter liquids with high concentration of filterable matter whilst dead end is ideal for less concentrate filtrate matter and also to concentrate matter (Song and Elimelech, 1995).

2.4.6 Polymer membrane Modification

As evident from literature discussed, modification of polymer membrane is imperative to ensure that membrane performance reasonably well and it remains operational for longer periods. The modification of polymer membrane basically means tuning or altering the structure and physiochemical properties (hydrophilic, porosity, charge density, chemical, thermal and mechanical stability) of the membrane (Luo, *et al*., 2015). The modification is achieved by addition of organic materials, biomaterials, inorganic materials or hybrid materials depending on the desired membrane type, insertion of these materials into the polymer membrane results in fabrication of composite polymer membrane.

Modification of membranes has been reported to yield better results compared to the respective unmodified membrane. For an example, in a study by Luo, *et al*.(2015), oil/ water emulsion was separated via ultra-filtration by novel triangle-shape tri bore hollow fiber membranes from polyphenylenesulfone (PPSU) and they observed that the modified membrane always exhibited higher permeate fluxes and lower total resistance than the pristine PPSU membranes.

In another study by Maphutha, *et al. (*2013) ,they fabricated and tested carbon nanotubes (CNTs) – infused polymer composite membrane with PVA (polyvinyl alcohol) as a barrier layer for treatment of oily wastewater and the membrane was effective to achieve concentration below 10 mg/L and oil rejection of over 95%. In addition to the satisfying results obtained by Maphutha, *et al*. (2013), the composite polymer membrane showed an increase of 119% tensile strength, 77% in Young's

modulus and 258% in the toughness for *ca.*7.5% Concentration CNT in the polymer composite.

Literature reports numerous materials that can be infused into the polymer membrane to make it able to overcome the challenges of selectivity, permeability and low resistance to fouling. For the purpose of this study only CNTs as nanofillers CTNS will be discussed.

2.4.6.1 Carbon nanotubes

Carbon nanotubes were first brought to attention of the scientific arena by Iijima in 1991. Carbon Nanotubes (CNTs) are allotropes of Carbon, a carbon nanotube is a one-atom thick sheet of graphite rolled into a seamless cylinder with a diameter of the order of a nanometer (Rafique and Iqbal, 2011). According to Sears, *et al*. (2010), they have exceptional properties such as high mechanical strength, high aspect ratio and large specific surface area (see figure 2.7).

Essentially there two main types of CNTs namely; single walled CNTs (SWNTs) which have outer diameters in the range of 1-3 nm with inner diameters of 0.4-2.4 nm (see figure 2.7 and table 2.1) and Multi-walled CNTs (MWNTs) which can have outer diameters ranging from *ca*. 2nm – 100nm (see table 2.1, for comparisons of the two types) (Sears, *et al*., 2010).Because of exceptional properties, there have been studies that concentrated on finding wider application of CNTs (Park, *et al.,* 2006).

Carbon nanotubes are widely used in water treatment, they are commonly infused to polymer membrane in order to enhance the membrane properties (such as mechanical strength, hydrophilicity, pore diameter and etc.) in order to make the polymer membrane less susceptible to fouling thus increasing the membrane performance during filtration (Yin and Deng, 2015).

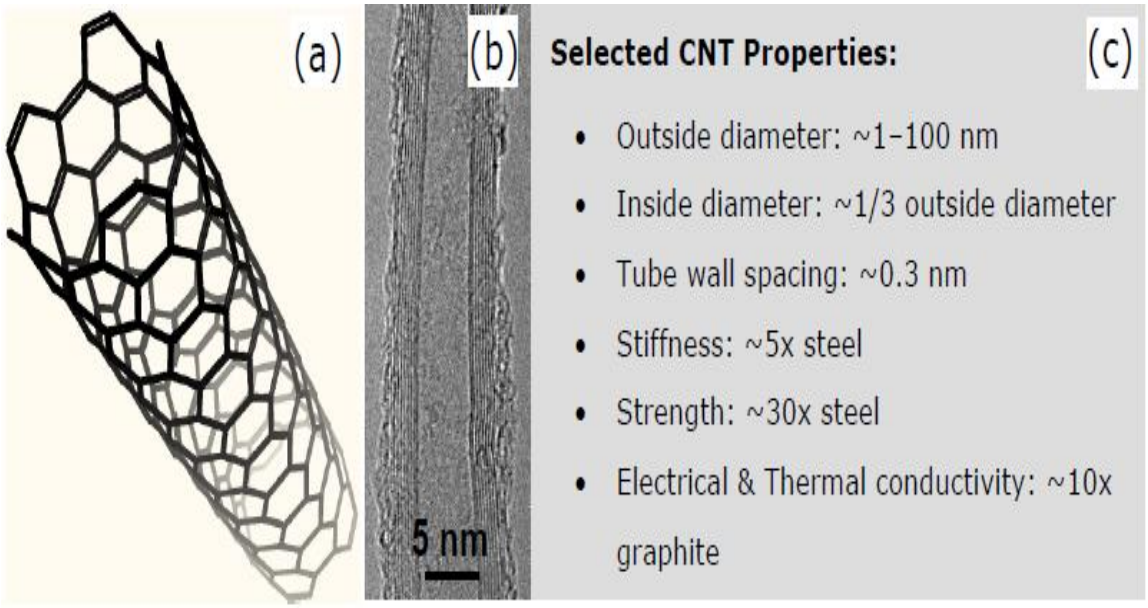


Figure 2.7. a) Schematic of a CNT, (b) TEM image of CNT showing concentric graphitic walls and (c) a list of selected CNT properties (adapted from Sears, *et al*., 2010)

Table 2.1. Comparison of SWNT and MWNT (adapted from Sears, *et al*., 2010).

SWNT	MWNT
Single layer graphene	Multiple layer of graphene
Catalyst is required for synthesis	Can be produced without catalyst
Bulk synthesis is difficult as it required proper control over growth and atmospheric conditions	Bulk synthesis easy
Low purity	High purity
Less accumulation in the body	More accumulation in the body
Characterisation and evaluation is easy	Complex structure
Easily twisted	Cannot be easily twisted

2.4.6.2 Production of Carbon nanotubes.

There are various methods of synthesizing CNTs and the oldest method of synthesizing them is known to be the electric arc discharge (Szabo, *et al*., 2010). Other methods include production by laser ablation, flame synthesis, high pressure carbon monoxide (HiPco), electrolysis and pyrolysis and they are mainly classified into physical, chemical and miscellaneous processes (Rafique and Iqbal, 2011).

Physical Processes

According to Rafique, *et al.* (2011), physical processes make use of physical principles of carbon conversion into nanotubes and example of this processes are arch discharge and laser ablation. The major issues with physical processes that limits their use are the fact that they are energy intensive, require solid carbon or graphite which has to be evaporated to obtain nanotubes and the process produces nanotubes of low purity (Rafique and Iqbal, 2011).

Arc Discharge method

The arc discharge is known to be the oldest method for the production of carbon nanotube(s). It is reported that the method was used in the early sixties to synthesise carbon fibres called whiskers and in 1990, it was used to produce fullerenes in good in yields (Szabo, *et al*., 2010). In 1991, Iijima discovered the carbon nanotubes from analysing samples produced by arc discharge in Helium (He) atmosphere. The method was then later improved and applied in the synthesis of Multiwall (MWNT) and single (SWNT) carbon nanotubes (Szabo, *et al*., 2010).

According to Szabo, *et al*. (2010), the arc discharge method concerns the use of two high-purity graphite electrodes as depicted in figure 2.8. The anode can be pure graphite or consisting of metals. In the case of the metals, Szabo, *et al*. (2010), states that the metals are transitorily brought into contact in a manner and an arc is struck. In a similar fashion, the electrodes are also brought into contact and an arc is struck.

The production is conducted in a controlled environment composed of inert and/or reactant gas at low pressure (30-130 torr or 500 torr) and the distance is reduced until the current flow is between 50-150 A (Szabo, *et al*.,2010). Carbon sublimes at

the consumed positive electrode (anode) due to the high temperature in the inter-electrode zone and the position of the anode can adjusted in order to maintain the constant gap between the cathode and the anode (Szabo, *et al*.,2010).

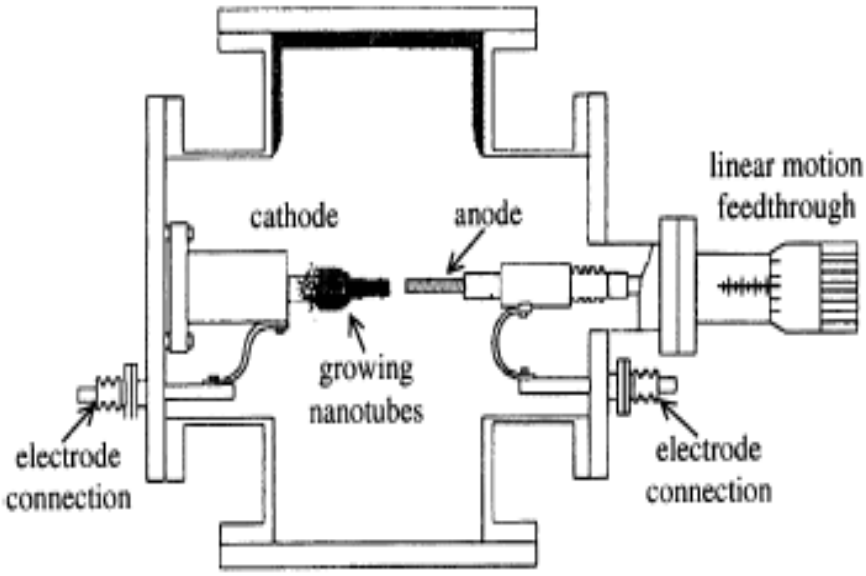


Figure 2.8. Schematic representation of the arc-discharge method (adapted from Saito, *et al*., 1996)

The plasma formation take place between the electrodes and by controlling the distance between the electrodes via voltage control (25-40 V), and the plasma can be stabilized for longer reaction time (varies from 30-60 seconds to 2-10 minutes) (Szabo, *et al*., 2010).

Szabo, *et al*. (2010), states that various kinds of products are formed within the different sections of the reactor: large quantities of rubbery soot on the reactor walls, web-like structures between the chamber walls and cathode, spongy collaret around the cathodic deposit and grey hard deposit at the end of cathode.

When no catalyst is used, only the soot (contains fullerenes) and the deposit (comprising of MWNTs (ID: 1-2 nm, OD: 2-25 nm, length: less than / equal to 1 µm and have closed tips) and graphite carbon nanoparticles) are formed (Szabo *et al*., 2010). When metals catalyst are evaporated in parallel with the carbon in the arc discharge, the core deposit contains MWNTs, metal filled MWNTs (FMWNTs), graphitic carbon nanoparticles (GNP), metal filled graphite carbon nanoparticles (FGNP) and metal nanoparticles (MNP), while the powder- like or spongy soot

contains MWNTs, FMWNTs and SWNTs (Szabo, *et al*., 2010). Szabo, *et al*. (2010), reports that the formed SWNTs (1.14-1.4 nm ID and several microns long) have closed tips, free of catalyst and are either isolated or in bundles and that the formed collarette (formed in the presence of certain catalysts) mainly consists of SWNTs (80%), isolated or in bundles.

There several physical and chemical factors that influence the arc discharge process, namely: carbon vapor concentration, the carbon vapor dispersion in inert gas, the temperature in the reactor, the composition of catalyst, the addition of promoters and the presence of hydrogen (Szabo, *et al*., 2010). Szabo, *et al*. (2010), states that these factors affect the nucleation and growth of the nanotubes and the physical characteristics.

Other types of discharge methods are reported to be but not limited to:

- Intermittent arc discharge process; the method permits several millisecond pulse duration which is much longer than that of the pulsed arc method with microsecond pulse duration (Szabo, *et al*., 2010). The product can be either floating powder containing uniformly dispersed fine spherical particles or sediment composed of straight MWNTs with length in the range 100-500nm and aggregated onion-like nanoparticles (Imasaka*, et al*., 2006; Szabo, *et al*., 2010).
- Plasma rotating arc discharge process, Lee, *et al*. (2002), used this method to synthesis CNTs and observed that the nanotube yield was directly increased as per increase in the rotation speed of the anode and the collector being closer to the plasma.

Laser ablation Method

This method was initially used for the first synthesis of fullerenes and over the years it was enhanced to cater the production of single walled carbon nanotubes (Erik, *et al*., 2001; Rinzler, *et al*., 1998; Thess, *et al*., 1996; Zhang and Iijima, 1999). Szabo, *et al*. (2010), states that the nanotubes produced via the utilization of this method have higher purity (up to 90% pure) and the structure is better graphitized than those produced in arc discharge method.

It also stated that the disadvantage of this method is imbedded in the small carbon deposit and that it only favors single walled nanotubes over multi walled carbon nanotubes (MWNT produced under special reaction conditions) (Szabo, *et al*., 2010). Figure 2.9.; represent a general set –up or arrangement of this method.

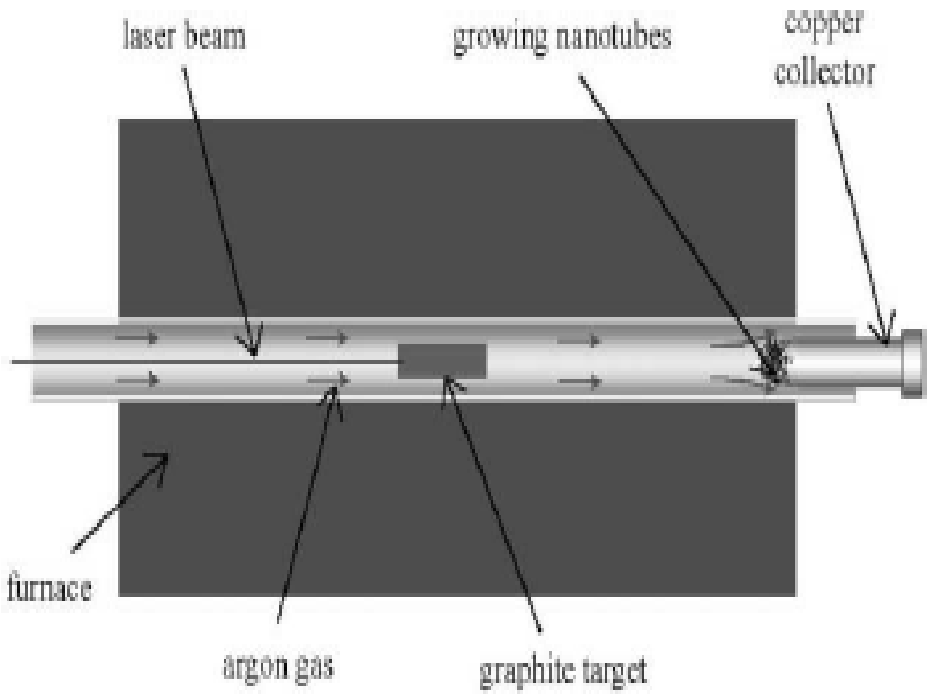


Figure 2.9 . Schematic illustration of the laser ablation method (adapted from Collins and Avouris, 2000)

In this method, a laser is used to vaporize a graphite target held in a controlled atmosphere oven at temperatures close to 1200 ^{o}C (Erik*, et al*., 2001). In a study by Rinzler, *et al*. (1998), SWNT were produced by doping the graphite target with cobalt and nickel catalyst and the condensed material was them collected on a water-cooled target.

Erik, *et al*. (2001), highlights that the two methods (arc-discharge and the laser ablation methods or techniques) are constricted in the volume of sample they can produce in relation to the size of the carbon source and the fact that there is a need for subsequent purification steps in order to ensure that tubes are separated from undesirable by-products.

Due to these limitations, gas-phase techniques such as chemical vapour decomposition were developed in order to overcome the challenges, the short

comings experienced by arc-discharge and laser ablation techniques or methods (Erik, *et al*., 2001).

Chemical Processes

The chemical process use chemical principles of carbon conversion to nanotubes and example of these processes are chemical vapour deposition, high pressure carbon monoxide reaction (HiPco) and CoMoCAT® process (Li, *et al*., 1996; Nikolaev ,*et al.,* 1999; Tang, *et al*., 2001). The chemical processes are reported to have many advantages compared to physical processes and some of the advantages include but no limited to: ease control and manipulation of reaction, easy to produce CNTs directly to substrate and are cheap in terms of unit price (Rafique and Igbal, 2011).

Chemical vapour deposition (CVD) method

This method was developed following the short comings (impure nanotubes) experience by laser ablation and arc discharge methods. In this method nanotubes are formed by the decomposition of a carbon containing gas (Erik, *et al*., 2001). This method is known to offer the best chance to obtain a controllable process for the selective production of nanotubes with predefined properties (Sinnot and Andrews, 2001).

The purity of the as-produced nanotubes obtained using this method can be high thus minimizing the need for subsequent purification steps (Erik, *et al*., 2001). The ability to synthesise aligned array of carbon nanotubes with controlled diameter and length and the fact that this process can be acquiescent to a continues process since the carbon source is continually replaced by the flowing gas makes this method attractive for large scale production of nanotubes (Erik, *et al*., 2001; Seo, *et al*., 2007). This method, the catalytic chemical vapour decomposition method is considered as the only economically viable for large-scale CNT production and the integration of CNTs into various devices (Seo, *et al*., 2007).

Chemical vapour deposition is well described by Szabo, *et al*. (2010 as a catalytic decomposition of hydrocarbon or carbon monoxide (CO) feedstock with the aid of supported metal catalyst generally in a flow furnace at atmospheric pressure. Figure

2.10, illustrates CVD methods, vertical and horizontal configurations (the most commonly used) (Szabo, *et al*., 2010).

In the application of the horizontal configuration, the catalyst is place in a ceramic or quarts boat which is place into a quartz tube as demonstrated in figure 2.10, the reaction mixture containing a source of hydrocarbon and an inert gas is passed over the catalyst bed at temperatures ranging from 500 ^{o}C to 1100 ^{o}C and then the is cooled down to room temperature.

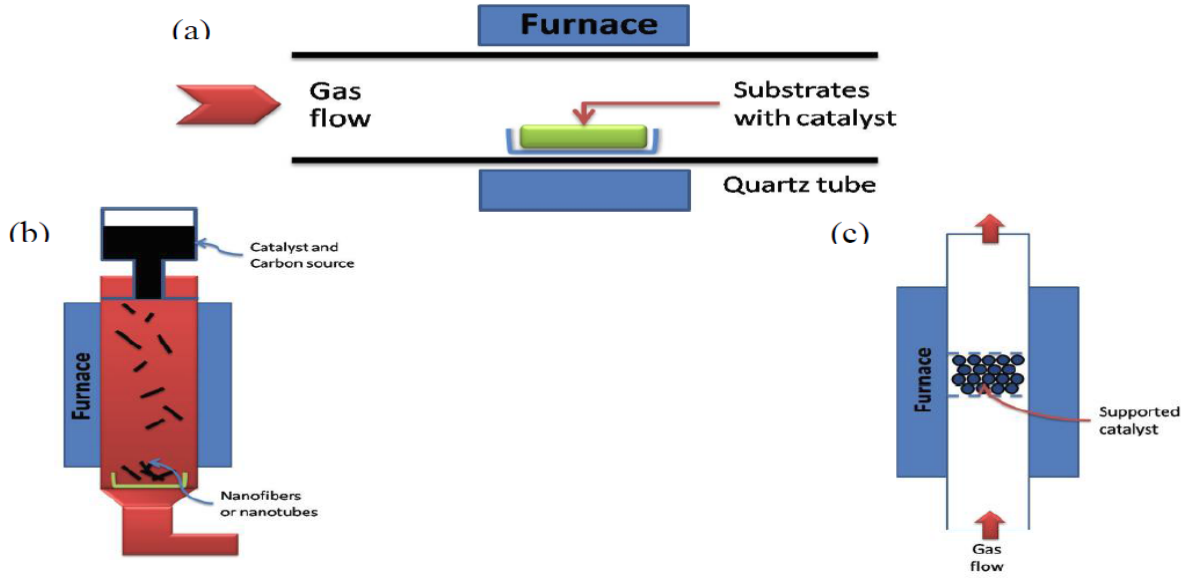


Figure 2.10. Schematic demonstration of CVD Method. (a) Horizontal furnace. (b) Vertical furnace. (c) Fluidized bed reactor (adapted from Szabo, *et al*., 2010)

The vertical furnace configuration is commonly utilized for the continuous mass production of carbon fibers or nanotubes, the catalyst and the carbon source is injected at the top of the furnace as a result filaments grow during flight and are collected at the bottom of the chamber (Szabo, *et al*., 2010).

According to Szabo, *et al*. (2010), fluidized bed reactor, is basically the variation of the vertical furnace in which supported catalyst are placed in the centre of the furnace and an upward flow of carbon feedstock gases is used. Teo, *et al*. (2003), asserts that in this case the fluidization process involves the supported catalysts to remain much longer in the furnace than in the vertical floating technique.

Several structures forms of carbon are formed when using the chemical vapor method, these includes amorphous carbon layers on the surface of the catalyst, filaments of amorphous carbon, graphite layers covering metal particles, SWNTs and MWNTs made from well-crystallized graphite layers (Szabo *et al*., 2010).

Other processes are those processes that are not commonly used and they include helium arc discharge method, electrolysis and flame synthesis ((Rafique *and* Iqbal, 2011; Wal, *et al*., 2001 & 2002).

Table 2.2, gives a comparison of three most widely used CNTs production methods with respect to their potential to be scaled up as large scale methods for production of carbon nanotubes (Rafique *and* Iqbal, 2011). From table 2.2, it is very clear that chemical vapor deposition method is the most technically and economically viable method mainly because of the excellent advantages presented.

Table 2.2. Comparison of Carbon Nanotube Production Methods (adapted from Rafique and Igbal, 2010)

Process /property	Arc-discharge	Laser ablation	Chemical vapour deposition (CVD)
Raw Materials availability	Difficult	Difficult	Easy, abundantly available
Energy requirement	High	High	Moderate
Process control & reactor design	Difficult	Difficult	Easily automated &large scale process
Production rate	Low	Low	High
Unit per cost	High	High	low
Post treatment requirements	Require refining	Require refining	Less refining required

Carbon precursor

It is clear that chemical or gas phase production of carbon nanotubes is more favourable than the physical process. In chemical processes, particularly Chemical vapour decomposition, a number liquid and gaseous hydrocarbon feedstocks may be used to produce nanotubes via thermal catalytic decomposition (Szabo, *et al*., 2010). Sinnot and Andrews ,2001; Dai, *et al*.,1996 ; Maruyana, *et al*., 1992;Hernadi ,*et al*., 2000 & Nikolaev, *et al*., 1999, have used different kinds of hydrocarbons as source for production of nanotubes, it included light gases such as C_2H_4 and C_2H_2 to heavier aromatic liquids such as Xylene or benzene.

In the case where liquid carbon source(s) are used, a vaporisation stage is required before the reaction chamber stage to turn the liquids carbon source into gas phase (Szabo, *et al*., 2010).

Catalyst preparation pathways for preparations of CNTs

From aforementioned discussion, it is clear that catalysis plays an important role in production of carbon nanotubes. A number catalysts have been investigated in effort to improve the quality and yield of CNT production by various researches and the results showed that quality and the yield of the CNT depended on the choice of catalyst (Sinnot and Andrews, 2001; Su ,*et al*., 2000; Li, *et al*., 2001; Ciambelli ,*et al*., 2005). In most cases, transition metal catalyst such nickel, iron, molybdenum and cobalt are often used in CVD to synthesis carbon nanotubes (Moisala, *et al*., 2003).

However, not only does the choice of the catalyst affect the quality and yield of the CNTs but also the size of the catalyst, and the preparation method are reported to play an important role in the quality and yield of the carbon nanotubes (Dupuis, 2005).

With respect to the particle size, it was observed that when the catalyst are prepared in holes or pores, the diameter of the former is subjected to the size of the latter and as result yielding CNTs that have diameter almost equal to the diameter of the hole or pore (Duesberg, *et al*., 2002; Terrones, *et al*., 1997). The direct connection between the catalyst particle size and CNTs size was also quantified by Cheung et al. (2002): iron nanoparticles with average mean diameter of 3 nm, 9 nm and 13 nm,

yielded CNTs with wall diameter of 3, 7 and 12 nm respectively, similar trend was observed.

However, it is also worth noting that the size of the catalyst particle size depends on the catalyst preparation method, for instance precipitation methods usually lead to wide particle size distribution which effectively implies that catalyst prepared using this method will yield CNTs with varying size (Moisala, *et al*., 2003).

Other factors that may affect the yield and quality of the CNTs are catalyst support and chemical composition of the catalyst. For instance, with regards to chemical composition it was observed that the use of bimetallic catalysts resulted in an increase in the yield of the catalyst (Alvarez, *et al*.,2001 ;Harutyunyan, *et al.,* 2002 and Flahaut, *et al*.,1999).

It is clear that the effect of the catalyst particle size on the yield and quality of the carbon nanotube cannot be ignored and that catalyst preparation method plays a key role in controlling the catalyst particle size thus the quality and yield of the carbon nanotubes.

An enumerate catalyst preparation methods have been developed over the past years for the preparation of supported metal catalyst and of those developed methods, the most common technique involves the introduction of a salt ion containing the metal to the support (Hicks, 2004;Ponec and bond, 1995). Typical catalyst preparation methods include but not limited to reverse miscele (micro-emulsion technique), sol-gel, impregnation, Ion-exchange precipitation and etc.

Micro-emulsion technique

Micro-emulsion technique also known as reverse micelle technique has been used to prepare catalyst (nanoparticles) with nano range size. Narrow particle size distribution can be achieved and the support material does not have negative impact on the formation of particles (Barber, 2005). Desired particle size and thus membrane pore size can be achieved by using this method by varying water to surfactant ratio (Eriksson, *et al*., 2004).

Micro-emulsion is defined by Danielsson and Lindman (1981) as a thermodynamically stable, optically isotropic solution of water, hydrocarbon and at

least one amphiphilic compound (surfactant).This technique basically involves formulating water in oil micro emulsion from a ternary water/oil/ surfactant system (Barber, 2005). The figure 2.11 depicts an example of a ternary phase diagram. The preparation of metal nanoparticles from microemulsions can be achieved mixing a microemulsion containing a metal precursor a microemulsion containing a precipitating agent (see figure 2.12) (Eriksson, *et al*., 2004; Maboso, 2005, Fischer, *et al*., 2011).

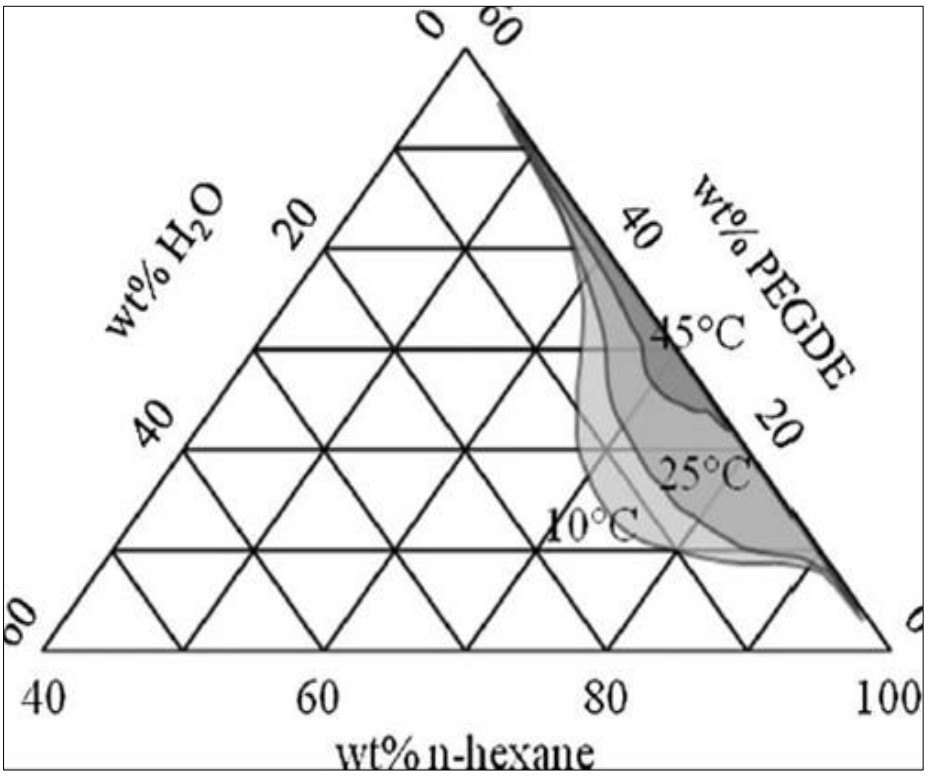


Figure 2.11. Ternary phase diagram of PEGDE; n-hexane and water mixture (adapted from Fischer, *et al.*, 2011)

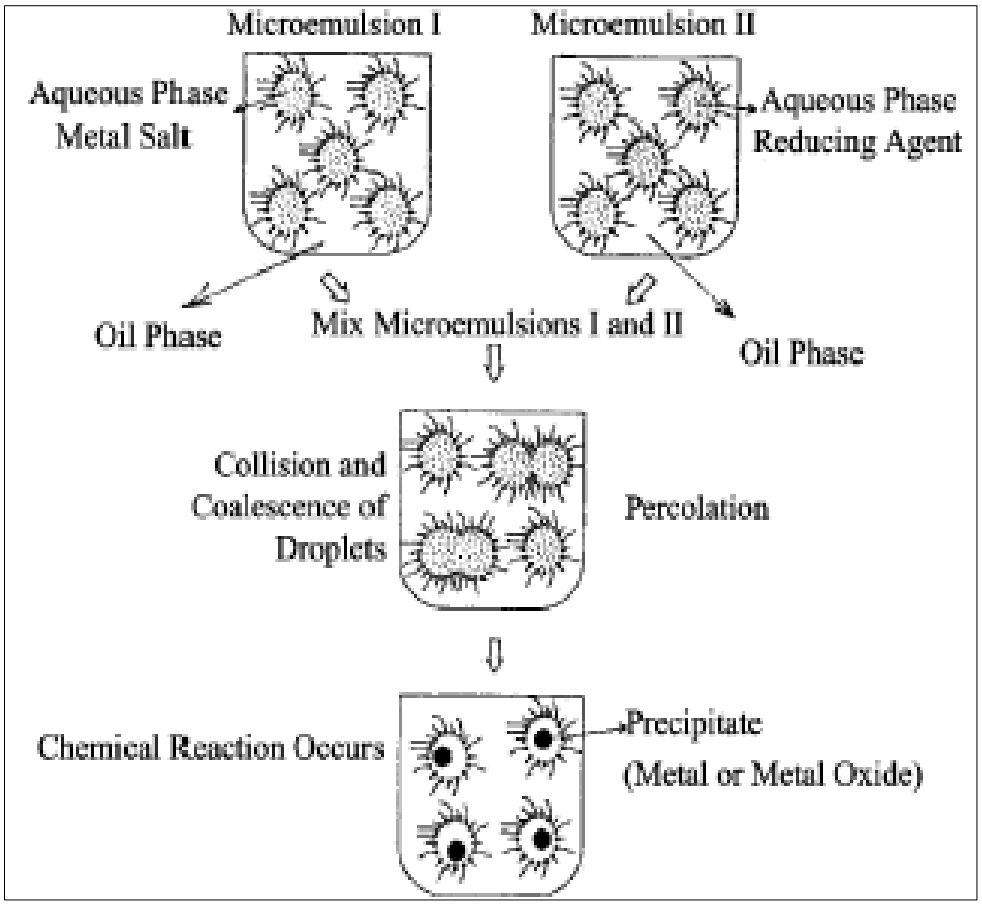


Figure 2.12. Mechanism for the formation of metal particles using microemulsion method (adapted from Capek, 2004)

The use of this method to prepare catalyst is important to this study for the preparation of nanocomposite membrane. The method has been deemed to be effective in synthesising nanoparticles with a size of ca. 2 nm. For an example Lisieki and Pileni (1993) synthesized cupper (Cu) nanoparticles on the range of 2-20 nm by dissolving bis (2-ethylhexyl)-Sulfosuccinate (Cu $(AOT)_2$) in a mixture of cyclohexane, Isooctane and sodium bis (2-ethyhexyl)-sulfosuccinate (NaAOT).

In another study, Chen, *et al. (*1995) were able to synthesize cobalt (Co) nanoparticle in the range of 1.8 to 4.4 nm diameter via borohydride reduction of $COCl_2$ in reverse micelle system of toluene and didodecyldimethyl ammonium bromide (DDAB). These studies substantiate the fact that this method can yield nanoparticles of a narrow size.

However, according to Eriksson, *et al*. (2004), the drawbacks of this method are:

- Large volumes of solvents required
- Low yield of the catalyst from single micro emulsion
- Not commercial feasible

Impregnation method

Dupuis (2005), describes the method as the method that concern(s) or involves dissolving a catalyst precursor (e.g, iron nitrate) firstly and then followed by addition of support on the prepared solution. The precursor deposits onto or into the substrate and then the solvent is then evaporated and the catalyst is dried. The last step involves calcination, reduction or another appropriate method. The advantage of this method is that is very simple method to use to prepare supported catalysts.

There are two types of impregnation methods:

I. Dry impregnation: in dry impregnation or pore volume impregnation, the exact amount of liquid required to fill the pore volume of the support is used (Srojas, 2013).
II. Wet impregnation: the amount of liquid is only controlled by the solubility of the metal precursor (Srojas, 2013).

In both types of impregnation method discussed, the electrostatic force controls the adsorption mechanisms and uniform distribution of particles is achieved by using weakly interacting precursors plus mild drying (Srojas, 2013).

Many more preparation methods are reported in literature for the preparation of supported catalyst (Dupuis, 2005). The effectiveness of these methods depends greatly on desired chemical and physical properties of the catalyst (type of the catalyst prepared), metal support interactions, stability, selectivity, activity, mechanical strength, time and cost (Kohler, 2006). These factors make it challenging to select the most viable method as results certain improvisations are made which indirectly might limit the quality of the research.

2.4.6.3 The dispersion of CNTs

The application or usefulness of the CNTs, particularly in the field of CNTs/polymer nanocomposite is limited, due to the fact that their application depends more on the dispersion of CNTs in the matrix and interfacial interactions between the polymer (Ma, 2010).The full potential application of carbon nanotubes is limited because of the difficulties associated with the dispersion of entangled CNTs during processing and poor interfacial interaction between CNTs and polymer matrix (Ma, *et al.,* 2010).

Ma, *et al*. (2010) alluded that the nature of dispersion problem for CNTs is relatively different from other conventional fillers such as spherical particles and carbon fibers due to the fact that CNTs are small of diameter in nanometer scale with high aspect ratio and hence extremely large surface area. In a study conducted by Ma, *et al*. (2010), the dimensions of commonly used fillers corresponding to uniform filler volume fraction of 0.1% in a composite of 1.0mm^3 cube, shed a light to why the dispersion of CNTs in a polymer matrix is more difficult than other fillers. It was observed that size effect of fillers and the physical nature of particles were somewhat the controlling factors in the dispersion of CNTs in polymer matrix.

Nonetheless, there have been a lot of effort devoted to finding ways to modify the surface of nanotubes in order to improve the interactions with foreign molecules, to make them soluble in any solvent (Lin, *et al*.,2003; Valentini, *et al*.,2006).Some of the method used to overcome the dispersion problems in order to facilitate the dispersion of CNTs in polymer matrix includes but not limited to mechanical dispersion (Ultrasonicaton, Calendering process, Ball milling, Stir & extrusion) and Functionalisation of CNTs (Chemical and physical) (Ma, *et al*., 2010).

Ultra-sonication

According to Ma, *et al*. (2010), ultrasonication is the act of applying ultrasound energy to unsettle particles in a solution for various applications and is known to be the most used method for dispersion of nanoparticles. This method produces shock waves and the production of the shock waves promotes the “shaving off” of the individual nanoparticles located at the outer part of the nanoparticles bundles and thus results in the separation of individualized nanoparticles from bundles (Ma*, et al*, 2010).

Although this method is the most frequent used and the most effective method (Ma, *et al*., 2010), its limitation arises from the fact that the liquid in which the CNTs are dispersed has to be of a low viscosity, this implies that this will not be effective in dispersing the CNTs in some polymers solutions since most polymers are viscous, thus using this method will require the solution to be diluted as to make it less viscous before dispersing the CNTs (Ma, *et al*., 2010).

Ma, *et al*. (2010) also highlighted another limitation pertaining to this technique is that the technique can generate substantial heat rapidly, therefore CNTs dispersed in volatile solvents, such as acetone and ethanol requires to be kept cold and the sonication to be conducted over short intervals. This complement the findings from literature that the CNTs can be damaged with ease if the sonication treatment is too aggressive and/or too long.

The findings were supported by Kim, *et al*. (2006), it was observed from the Raman spectroscopy that the long period of CNTs ultra sonication resulted in a significant increase in the intensity of D band, which implies generation of defects on the surface of CNTs. Mukhopadyay, *et al*. (2002), found that in extreme cases, the graphene layers of CNTs are destroyed completely and the CNTs are converted into amorphous carbon nanofibers. As a results of the damage to the CNTs the electrical and mechanical properties of the CNTs /polymer composites diminishes (Ma, *et al*, 2010).

Ball milling

Ball milling was suggested by Ma, *et al*. (2010) as one of the techniques that can be used to facilitate the dispersion of CNTs in chemicals. Ball milling is essentially a type of grinding method used to grind materials into fine method for use in paint, ceramics and pyrotechnics (Ma, *et a.,* 2010).During the process of milling high pressure is generated locally due to the impact between tiny, rigid balls in a concealed container, the internal cascading effect of balls reduces the material to fine powder (Ma*, et al*., 2010).

An added advantage to this method is that it does not only enhance CNTs dispersibility but also introduces some function groups onto the CNTs surface (Ma et al., 2010). For an example in a study conducted by Ma, *et al.* (2008 & 2009), a

chemo-mechanical method was used to achieve in-situ amino functionalization of CNTs using ball milling and the results showed that the CNTs milled with ammonium bicarbonate were more effectively disentangled and shortened than those the chemical and the CNTs length was controlled by selecting the an appropriate milling period. The drawback to this method is that high-quality ball mills can grind mixture particles to as small as 100 nm (Ma, *et al*., 2010), it is a limitation in the sense that the smallest size is limited to 100 nm.

Stir and extrusion

According to Ma, *et al*. (2010), Stir is a common technique to disperse particles in liquid systems and it can be used also to disperse CNTs in a polymer matrix and extrusion is a common or popular technique to disperse CNTs into solid polymers like thermoplastics, where thermoplastics pellets mixed with CNTs are fed into the extruder hopper.

In the case of Stir technique, size and shape of the propeller and the mixing speed regulates the dispersion outcome (Ma, *et al*., 2010). Sandler, *et al*. (1999) highlighted that when using the Stir technique, an intense stirring of CNTs in polymer matrix is necessary to achieve relatively fine dispersion. Apart from the fact that MWCNTs tend to re-agglomerate as a results of frictional contacts and elastic interlocking mechanisms, this method tend to favor the dispersion of MWCNTs over SWCNTs (Schmid, *et al*, 2000).

The extruder technique is reported to be useful to produce CNT/polymer nanocomposites with higher filler content (Li, *et al*., 2007).

Calendering process

Calendaring process is a machine tool that uses the shear force created by rollers to mix, disperse viscous materials (see figure 2.13) (Ma, *et al*., 2010). The common configuration of a calendaring machine consists of three adjacent cylindrical rollers each of which runs in different velocity (Gojny, *et al*., (2004) and Thostenson and Chou (2006)). One of the advantages of this technique is that the easy control and narrow size distribution of particles in viscous materials can be obtained by mechanically or hydraulically adjusting and maintaining the gap between the rollers

and also the desired level of particle dispersion can be achieved by gradually decreasing the width of the gaps (Ma*, et al*., 2010).

The application of calendaring process to disperse CNTs in a polymer matrix emerged recently as a promising method to achieve relatively good CNT dispersion as accord to some recent literature (Gojny*, et al*., (2004) and Thostenson and Chou, 2006). However, in order to be effective a high shear stress is required to be applied to disentangle CNT bundles and distribute the dispersed CNT into polymer matrix (Thostenson and Chou, 2006).

Although this seems to be a promising technique to disperse the CNT into polymer matrix as according to recent reports (Gojny, *et al*., (2004) and Thostenson and Chou, 2006), there are several drawbacks to using this technique for dispersion of CNT. Ma, *et al*.,*(*2010) highlighted that the minimum gap between the rollers is about 1-5 µm, which is larger than the diameter of a single CNTs suggesting that the calendering can better disperse large agglomerated CNTs into small one sat sub-micron level.

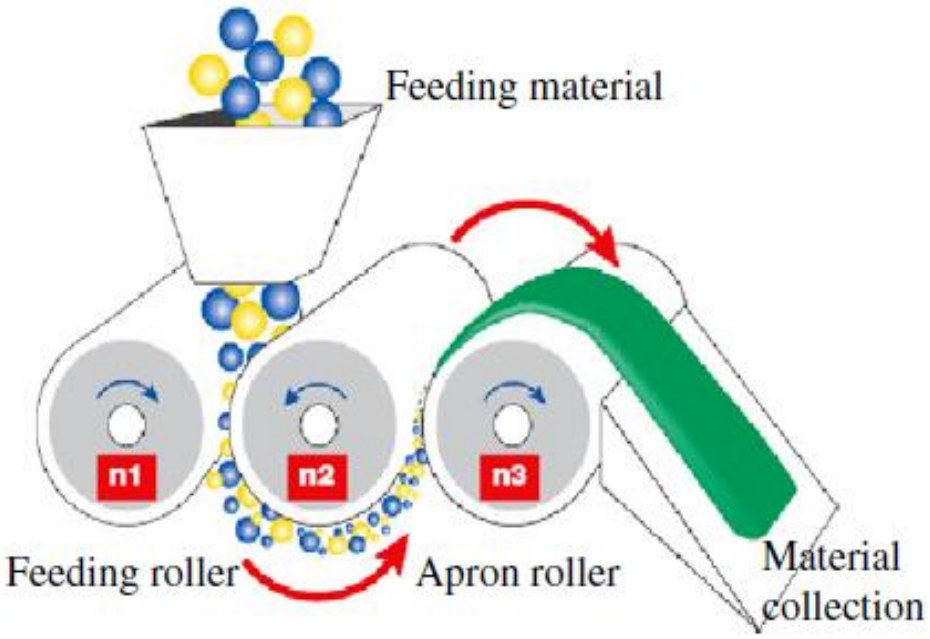


Figure 2.13 . General configuration of calendering machine (adapted from Ma, *et al*, 2010)

It should be noted that the dispersion of CNTs onto polymer matrix are not limited to those aforementioned. For an example, some literature reports the use of combination of ultrasonic and microwave-assisted acid digestion and Ultrasonic-assisted digestion to disperse the CNTs into polymer matrix (Tsai, *et al.,* 2013). Table 2.3, provides characteristics comparison of number CNT dispersion techniques that may be used as a guideline for the selection of appropriate dispersion technique to prepare CNT/polymer nanocomposites.

Table 2.3. Comparison of various techniques for CNT dispersion in polymer composites (adapted from Ma, *et al*., 2010)

Technique	Damage to CNTs	Suitable polymer matrix	Governing factors	Availability
Ultrasonication	Yes	Low viscous polymer, soluble polymer	Power, sonication time and mode of sonicator	Easy operation and clean after use, commonly used in lab
Calendering	No, CNTs may be aligned in matrix	Liquid polymer or oligomer monomer	Rotation speed, distance between adjacent rolls	Easy operation and clean after use, commonly used in lab
Ball milling	Yes	Powder (polymer or monomer)	Milling time, rotation speed, size of balls & balls/CNT ratio	Easy operation and clean after use, commonly used in lab
Shear Mixing	No	Low viscous polymer, soluble polymer	Size & shape of the propeller, mixing rate	Easy operation and clean after use, commonly used in lab
Extrusion	No	Thermoplastics	Temperature, configuration and rotation speed of the screw	Easy operation and clean after use, commonly used in lab

2.4.6.4 Functionalization of carbon nanotubes

Functionalization of carbon nanotubes is a process of adding the functional groups such as alky, aryl groups, ester groups, carboxyl group and etc. onto carbon nanotubes (single walled (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) in order to make them susceptible to participate in many reactions (Ma, *et al*, 2010). Functionalization of CNTs is necessary in order to enhance their properties to offer CNTs a potential for wide applications in the field emission, conducting plastics, thermal conductors, conductive adhesives, fibers, catalyst support, biological application, water filtration and so on (Dresselhaus, *et al.,* 1995; Ajayan, *et al.,* 2003;, Coleman, *et al.,* 2006; Ma, *et al*., 2010).

There are several methods to modify the surface properties of CNTs for various applications (Ma, *et al*., 2010). Literature describe the chemistry of functionalized CNTs and the reaction mechanisms between the CNTs and functional groups (Hirsch, 2002 & 2006, Tasis, *et al*., 2006, Balasubramanian, 2005).The mechanisms can be divided into chemical and physical functionalization methods based on the interactions between the active molecules and carbon atoms on the CNTs (Ma, *et al*.,2010).

Chemical Functionalization

The chemical functionalization of CNTs depends on the covalent bonding or linkage of functional groups onto the CNTs (Ma, *et al*., 2010). It is well reported in literature that chemically modified carbon nanotubes are more soluble than pristine nanotubes and are more easily compatible with the polymer matrix (Zhu, *et al*., (2003), Mitchell, *et al*., (2002) and Sen*, et al*., (2004)). Their findings emphasize the necessity to modify the surface of the CNTs as to make them useful for various applications. The chemical functionalization is to be performed at the termini of the tubes or at their sidewalls (Ma et al., 2010). There are two ways to functionalize the carbon nanotubes in chemical functionalization; there is direct covalent functionalization and defect functionalization (Tchoul, *et al*., 2007& Ma*, et al*., 2010).

Direct covalent functionalization

The direct covalent side wall functionalization can be attributed to the change in the hybridization from sp^2 to sp^3 and a simultaneous loss of π-conjugation system on the graphene layer. The process is carried out by reaction with some molecules of high chemical reactivity, such as fluorine (Ma, *et al*., 2010). Kelly, *et al., (*1999), demonstrated the effectiveness of this process, it was portrayed that the fluorination of purified SWCNTs occurred at temperatures up to 325 ^{0}C and the process was reversible. The fluorinated CNTs had C-F bonds that were weaker than those in alkyl fluorides making them susceptible for additional functionalization via substation sites (Touhara*, et al*., (2002).

Defect functionalization

Defect functionalization is another type of method of covalent functionalization of CNTs and the process takes advantage of chemical transformation of defects of sites on CNTs. The defects can be holes or/ and open end in the sidewalls, pentagon or heptagon irregularities in the hexagon graphene framework (Ma*, et al*., 2010). According to Esumi, *et al.* (1996), Oxidative process with strong acids such as HNO_3, H_2SO_4 or a mixture of both (Yu, *et al*., 1998), can be employed to create defects on the sidewalls as well as on the open ends of CNTs.

Other strong oxidants such as $KMnO_4$, Ozone, and reactive plasma have been reported as alternative oxidants to creating defects (Yu, *et a*l., 1998, Sham and Kim, 2006, Wang, *et al*., 2009 &Avila-Orta, 2009). It is stated that the created defects can be stabilized by bonding with carboxylic acid (-COOH) or hydroxyl (-OH) groups (Ma, *et al*., 2010). Because of the fact that these functional groups have rich chemistry, the CNTs with these functional groups can be used as precursors for further chemical reactions such as polymer grafting, esterification, alkylation and etc. (Liu (2010), Hamon*, et al*., 2002 and Liu*, et al*., 1998).

CNTs functionalized in this fashion are soluble in many organic solvents because of the fact that the hydrophobic nature of CNTs is changed to hydrophilic nature due to the attachment of polar groups (Ma, *et al*., 2010). Figure 2.14, shows some of possible reactions that CNTs functionalized via covalent bonding fashion can participate in.

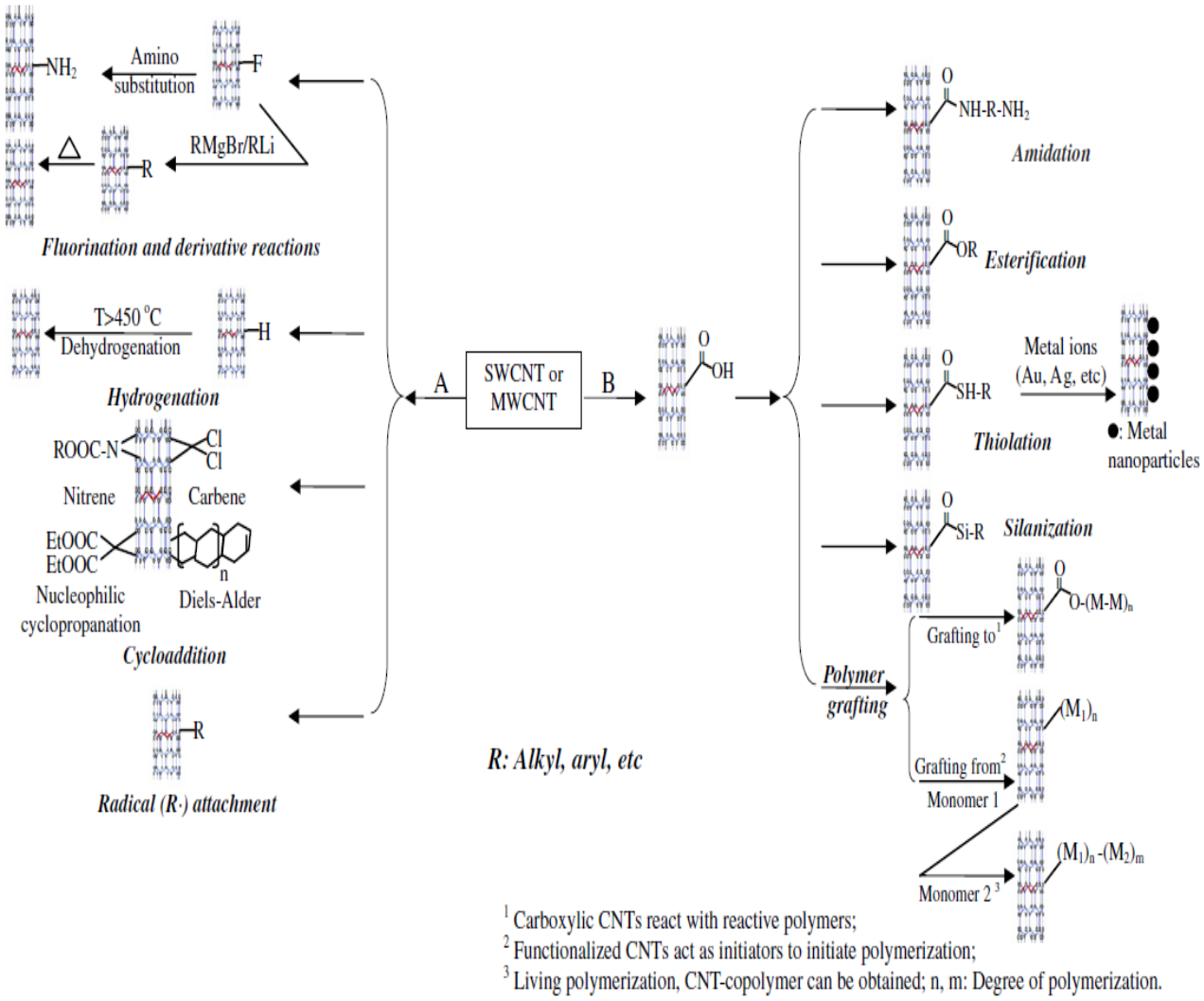


Figure 2.14. Strategies for covalent functionalization of CNTs (A: direct sidewall functionalization; B: direct functionalization) (adapted from Ma, *et al*.,2010).

Ma, *et al*.,(2010) alluded that the chemical functionalized CNTs can produce strong interfacial bonds with many polymers, providing CNT based nanocomposites to inherit high mechanical and functional properties. However, although the covalent functionalization of CNTs provide a useful functional groups onto the CNT surface, at some time, the oxidation damages nanotubes which results in structural defects, shortening of the nanotubes, accumulation of carbonaceous impurities, diminishing of diameter and overall loss of material (Zhang, *et al*., 2003; Liu, *et al*., 1998; Yang, *et al*., 2002 & 2005; Miyata, *et al*., 2006 ; Dilon, *et al*., 1999).

These observation are further supported by Datsyuk, *et al.,* (2008), the same conclusion that oxidation treatment of CNTs may compromise the structural integrity of carbon nanotubes (MWCNTs) was reached. In their study (Datsyuk, *et al*., 2008), MWCNTs were oxidized by subjecting them in reagents of different oxidation degree or power. The electron microscopy and them gravimetric analysis showed that the nitric acid treated material under reflux conditions suffered the highest degree of degradation such as nanotube shortening whilst material subjected under basic oxidation treatment led to the complete removal of amorphous carbon and metal oxide impurities (Datsyuk, *et al*.,2008).

It stems out from literature that achieving maximum degree of functionalization with minimum material degradation remains a challenge and that a balance has to be made between achieving highest degree of functionalization vs. minimum damage to the CNTs. This may be made possible by choosing the oxidation carefully in such a way that there is chemical functionalization at minimum damage to the CNTs (Tchoul, *et al*., 2007).

Physical functionalization

Physical functionalization also referred to as non-covalent functionalization is another method to alter the interfacial properties of nanotubes (Ma, *et al*., 2010). A typical example of non-covalent functionalization includes the suspension of CNTs in the presence of polymers such as polystyrene, this proceed to the wrapping of polymer around the interfacial properties of nanotubes and the wrapping process is achieved through the van der waals interactions and π-π building up between the CNTs and polymer chains containing aromatic rings (Ma, *et al*., 2010).

In addition to polymers, surfactant can also be used to functionalize CNTs, the surfactants can be non-ionic surfactants such as polyoxyethylene 8 lauryl, anionic surfactants such as sodium dodecylsulfate (SDS) and cationic surfactants such as dodecyl tri-methyl ammoniumbromide (DTAB) (Ma, *et al*., 2010).

Endohedral methods is another kind of non-covalent method for functionalization of CNTs,in this method, foreign molecules or atoms are kept in the inner cavity of CNTs via capillary effect (Ma, *et al*.,2010). The attachment usually takes place at defect sites localized at the end or on the sidewalls (Ma, *et al*., 2010). A typical example of

endohedral method includes but not limited to the attachment of inorganic nanoparticles into the tubes such Ag, Au, Pt and C_{60} (Geirgakilas, *et al*., 2007).

From the literature presented it seems as if the physical functionalization have more advantage over the chemical functionalization of the CNTs as argued by Ma, *et al.,*(2010), that during the chemical functionalization reactions large defects are inevitably and in some extreme cases, the CNTs are fragmented into smaller pieces.

These damages affect results in degradation in mechanical properties of CNTs as well as disruption of π electron system (Ma, *et al*., 2010). The other concern is the acids or strong oxidants that are often used for CNT functionalization which are environmentally unfriendly (Ma, *et al*., 2010). On the other hand the advantage of the non-covalent functionalization is that the structure and original properties of CNTs remain intact after modification (Van Thu Le, *et al*., 2013).

However, the shortcoming(s) of non-covalent functionalization of CNTs using surfactants, polymer chains and electric acceptor are limited, their dispersion is not very stable and it is difficult to further modify CNTs with different functional groups, thus making chemical functionalization more attractive functionalization method regardless of the prevalent associated disadvantage(s) (Van Thu Le, *et al*., 2013).

Table 2.4, provides a comparison of the two functionalization methods discussed. Each method they have its own inherit drawbacks, for instance if a strong CNT/polymer matrix interaction is desired, one will have to consider the using chemical method instead of physical method and vice versa. The use of chemical methods to functionalize the carbon nanotubes is likely to lead to damage the CNTs; where else the physical methods have less chances of damaging the carbon nanotubes.

Table 2.4. Advantages and disadvantages of various CNT functionalization methods (adapted from Ma, *et al.*, 2010).

Method		Principle	Possible damage to CNTs	Easy to use	Interactions with polymer matrix	Re-agglomeration of CNTs in matrix
Chemical method	Side wall	Hybridization of C atoms from Sp2 to sp3	√	√	S	√
	Defect	Defect transformation	√	√	S	√
Physical method	Polymer wrapping	Van der waals force, π-π stacking	X	√	v	x
	Surfactant adsorption	Physical adsorption	x	√	w	x
	Endohedral method	Capillary effect	x	x	w	√

S: strong, W: weak, V: variable

It can be surmised that overcoming dispersion challenges of CNTs and functionalization are the two key issues that unlocks or makes the CNTs to be useful for many applications, most importantly compatible in CNT/polymer matrix. However it should be noted that the findings favorable dispersion and functionalization ways remains a major challenge, in the sense that many factors has to be considered such as dispersion method and functionalization method to use for optimum dispersion and functionalization of the CNTs without altering their perfect structure and the original properties (Van thu Le, *et al*., 2013).

2.4.7 Nano-composite membranes

Fabrication of the nanocomposite membrane depends on all the issues that were discussed in the previous sections. This section concerns the preparation of nanocomposite membrane, different fabrication pathways are discussed.

2.4.7.1 Classification of nano-composite membranes

Depending on the membrane structure and location of nanomaterials, nanocomposite membranes can be classified into four categories namely: Conventional nanocomposite; thin-film nanocomposite (TFN); thin-film composite (TFC) with nanocomposite substrate; and surface locate nanocomposite membranes (Yin and Deng, 2015). Figure 2.15, illustrates nanocomposite membranes types, typical structures and location of nanomaterials. The red dots represent but not limited to the representation of the nanocomposite materials as they may represent nanotubes, nanofibers or nanosheets.

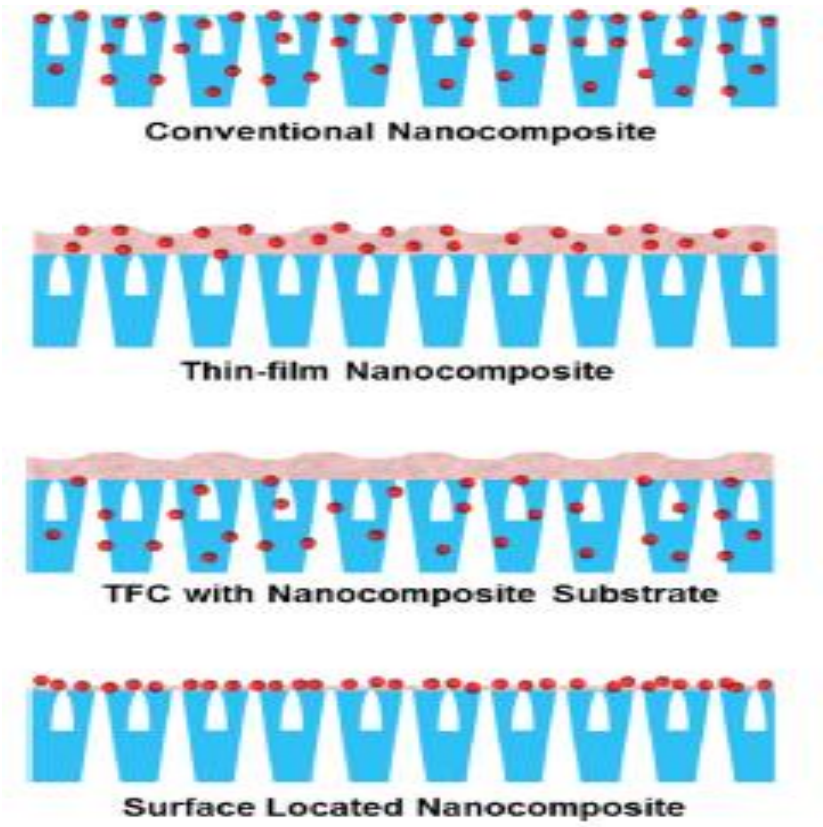


Figure 2.15. Nano-composite membrane types, typical structures and location of nanomaterials (adapted from Yin and Deng, 2015)

Conventional nano-composite membrane

Nanofillers fall into one of the four categories in the conventional nanocomposite membranes namely: organic material, inorganic material, Biomaterial and hybrid material with two or more material types. According to Yin and Deng (2015), fabrication of conventional nanocomposite membrane is mostly based on phase inversions (PI) method in which nanofillers are dispersed in polymer solution before the PI Process and can be prepared in either flat sheet or hollow fibre configuration.

Due to the membrane porous structure, it is typically used in microfiltration (MF) or Ultrafiltration (UF) processes (Yin and Deng, 2015). Figure 2.16, illustrates the fabrication of conventional nanocomposite membranes through the PI process and the main effects on nanofillers on the final products.

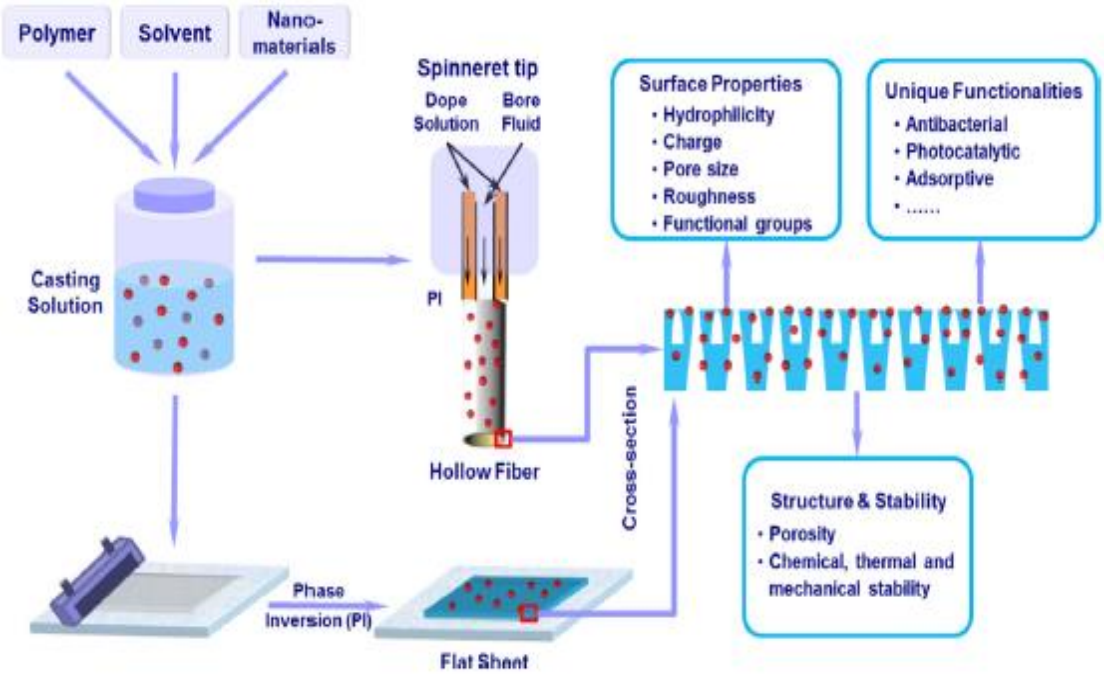


Figure 2.16. Illustration the fabrication of conventional nanocomposite membranes through the PI process and the main effects on nano-fillers on the final products (Adapted from Yin and Deng, 2015).

The Thin-film nanocomposite membrane (TFN)

The thin-film nano-composite membrane differs from the conventional nanocomposite membrane in that the fabrication typically proceeds via the in-situ interfacial Polymerization (IP) process between aqueous m-phenykenediamine (MPD) and trimesoyl chloride (TMC) organic solution (Yin and Deng, 2015). The film composite membrane consist of ultra-thin barrier layer and it was been used mostly as the main membrane in RO/NF. Figure 2.17, demonstrates TFN membrane via the IP process.

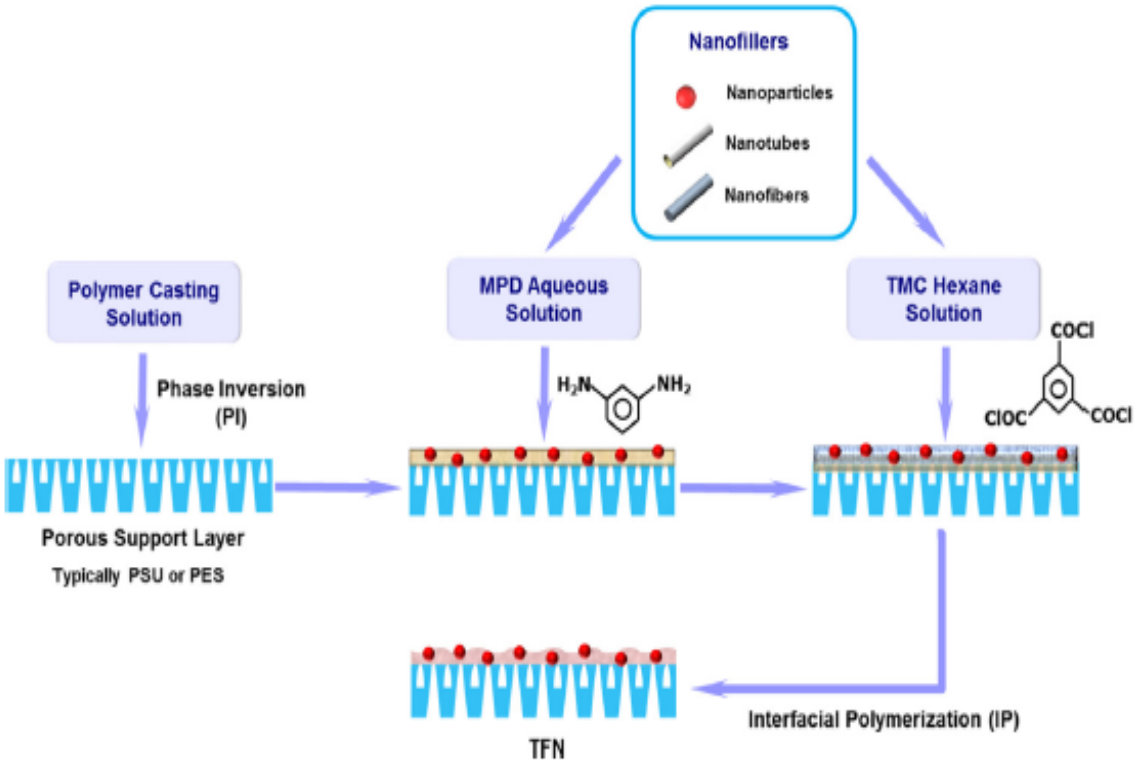


Figure 2.17 Fabrication of TFN Membrane via IP process (adapted from Yin and Deng, 2015).

TFC with nanocomposite substrate

According to Yin and Deng (2015), these kinds of membranes were developed to investigate the effects of nano-fillers on the membrane compaction behavior and are produced similarly to TFN membrane with addition of substrate.

Surface located nanocomposite membrane.

These kind of membranes could be fabricated based on methods such as self – assembly, coating/ deposition and chemical grafting and these fabrication methods can be implemented individually or be involved simultaneously (Yin and Deng, 2015). This process of preparing this kind of membrane is said to have minimal effects on the membrane's intrinsic structures and thus there is a good potential of implementing such an approach on commercially available membranes (Yin and Deng, 2015).

3. Experimental procedures and Analytical techniques

3.1 Materials

Synthetic crude oil was used in preparation of synthetic oil-water emulsion. All the chemicals used were analytical grade chemicals purchased from Sigma-Aldrich, unless stated otherwise. 50% hydrofluoric acid (HF) and zeolite support were denoted by the University of the Witwatersrand department of chemistry. The chemicals and / or gases used entails:

- Polyphenylene sulfone beads
- Iron Nitrate nonahydrate (III) (($Fe(NO_3)_3.9H_2O$, 98%),
- Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, 98 + %)
- 55% nitric acid (HNO_3)
- 50% Hydrofluoric acid (HF)
- 1-methyl-2-pyrrolidinone (NMP ≥ 99%)
- N,N – Dimethylformamide, anhydrous, ≥ 99.7 % (DMF)
- Technical grade nitrogen (purchased from Afrox)
- Acetylene (purchased from Afrox)
- Crude oil (NATREF laboratorium in Sasolburg)

3.2 Preparation of Fe-Co bimetallic catalyst supported on Zeolite

The bimetallic catalyst was prepared using wet impregnation method as outlined by Dupuis (2005);Phao*, et al*., (2013) ,the method is basically similar to that outlined by Owusu-Ansah (2014) with slight change in the support. Cobalt (II) nitrate hexahydrate and Iron Nitrate nonahydrate (III) were used as the metal precursors, while the Zeolite was used as the support.

The metal precursors were dissolved in 30 ml of distilled water and stirred until a homogeneous mixture or solution was obtained. The dissolved mixture was then added drop wise to 10g of the Zeolite - support and stirred slowly for half an hour.

The solution was stirred for another 30 min and dried in the oven for 8 hours at 60 ^{o}C. The nitrates were then removed by calcining the resultant product at 400^{o}C for an hour.

3.3 CNT preparation

The catalytic chemical vapour deposition (CCVD) was utilised or adopted for the production of CNTs using acetylene as the carbon source. Nitrogen was used to purge the system. 1g of catalyst was weighted and loaded onto a quartz boat and place in the centre of horizontal furnace. The furnace was operated at temperature of 700 ^{o}C at the heating rate of 10 ^{o}C /min. Nitrogen gas purge the system at flow rates of 180 ml/min and thereafter acetylene and nitrogen were allowed to flow into the system at the flow rate of 90 ml/min in order to initiate CNT growth. Figure 3.1, illustrates the CNTs synthesis set up using CCVD.

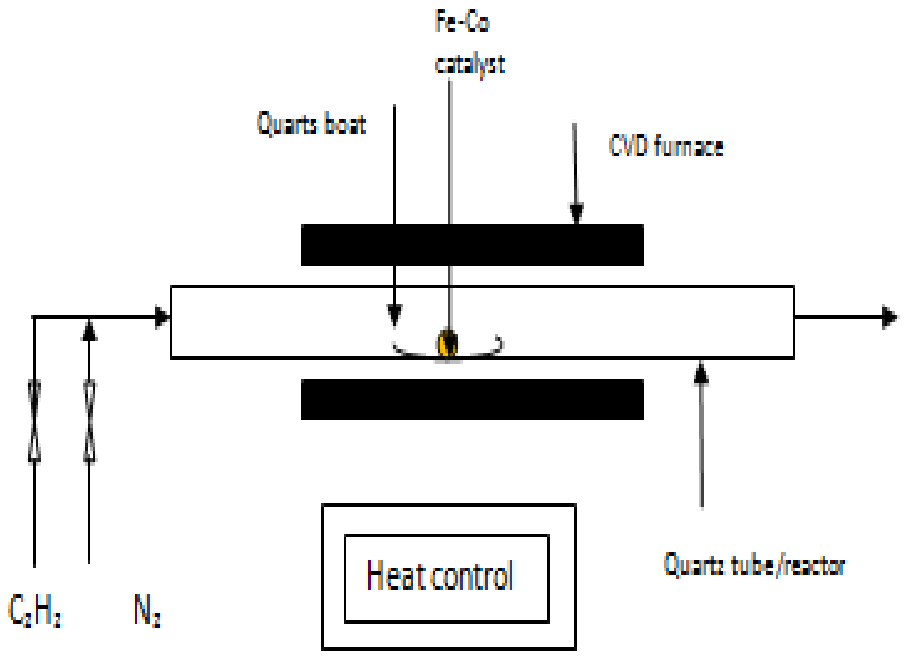


Figure 3.1 CNT synthesis setup

3.3.1 Functionalization of CNTs

The produced CNT was functionalised using chemical methods; they were soaked in different concentration (15%, 25%, 35%, 45%, and 55%) of HNO_3. They were soaked and then refluxed for 4 hours at 110^{o}C. Once the period of 4hours elapsed, the refluxed mixture(s) were allowed to cool at room temperature and then the functionalised CNTs were washed thoroughly with distilled water until a neutral pH was attained. The fCNTs were then dried in the oven at ca. 120^{o}C before being characterised.

Transmission electron microscope (TEM, FEI Tecnai Spirit G2) was used to ascertain the existence of the CNTs while the Raman spectroscope was used to confirm the presence of graphite structure (G-band) and disorder in the sidewall structure (D-band) of the CNTs.

3.3.2 Purification of functionalised CNTs

The functionalised carbon nanotubes (fCNT) were purified by being immersed in 50 ml of 50% hydrofluoric acid (HF) under constant stirring for 8 hours. The resulting products were washed and characterized.

3.4 Membrane preparation

The preparation of the polymeric nanocomposite membrane proceeded via phase inversion (PI) method. The pristine membrane (0wt% CNTs) was prepared by using polyphenylene sulfone (PPSU) pellets; PPSU is said to have outstanding physical and chemical properties compared to other bispheno-A- modified polysulfones (Arockiasamy *et. al*, 2013). The PPSU beads were dissolved in the solvent (1-Methyl-2-pyrrolidinone (NMP, ≥ 99%)) under magnetic stirring for 24 hours to ensure that a homogenous mixture or solution was obtained. The resulting solution was then cast in a water bath at room temperature.

For the nanocomposite polymeric membranes (fCNT/PPSU), the preparation was as follows:

- Various weight concentrations (0, 0.2, 0.4, 0.6 wt %) of CNTs were dispersed in the solvent, facilitated with ultra-sonication to achieve homogenous solution

- Once homogenous mixture was obtained, PPSU beads were added to the solution.
- Then the mixture was placed under magnetic stirring for 24 hours, to form a casting solution.
- The casting solution was cast using a casting blade set at *ca*.250 µm to form the polymeric nanocomposite membrane.
- The casting solution was then immersed in distilled for phase separation step
- The formed membranes were then immersed in distilled water for 24 hours to ensure complete liquid-liquid transfer of the liquid and solvent.

3.4.1 Membrane Characterization

The membranes were then characterised using SEM to determine the cross-section view and surface morphologies. FTIR analysis was used to confirm the presence of the f-CNTs in the membrane. The contact angles of the membrane were determined using goniometer.

3.4.2 Membrane Performance evaluation

The separation performance or efficiencies of the fCNTs / PPSU nano-composite and the pristine membranes were determined with respect to permeability and rejection was evaluated using cross-flow membrane configuration cell. The membrane flux (or permeate) was determined from equation 3.3.2.1. The flux, J ($L/m^2.h$) of the nano-composite membrane was determined by measuring the volume of permeate (V) per unit area (A) per unit time.

$$J = \frac{V}{\mathrm{A}\times\Delta t} \qquad (3.3.2.1)$$

The membranes were compacted by passing distilled water at 100psi for a minimum of 4 hours, in order to stabilize the permeate fluxes for true representation of the fluxes. Distilled water fluxes were calculated at pressures for each membrane ranging from 1 to 5 bar. The prepared oil-water emulsion was the passed through the membranes and the permeate fluxes were determined. The volumes of the permeate were collected for every 15 minutes.

Figure 3.2, depicts experimental setup or procedure to be followed in order to collect data required to analyze the efficiency of the nano composite membrane.

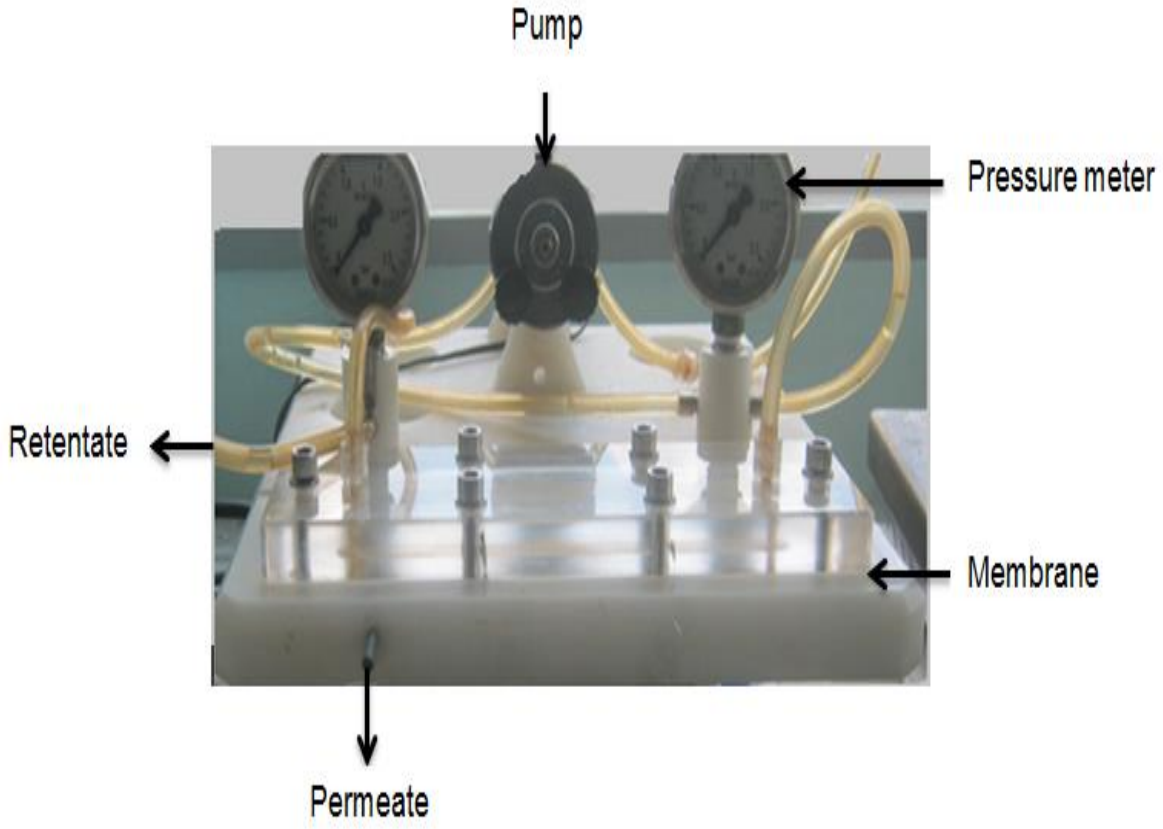


Figure 3. 2 Experimental setup

4. Results and discussion

This chapter presents and discuss results obtained from the experimental methods as presented in chapter 3 and determine the objective(s) of this research study were achieved or not. The characterization techniques conducted on the catalyst are presented firstly, then the carbon nanotubes, and produced membranes and finally the filtration test. The performance of the membrane is monitored or evaluated based on the ability to separate water from the water-oil emulsion.

The effect of adding the functionalized multi - walled carbon nanotubes (MWCNTs) on the membranes is also investigated and discussed in detail.

4.1 Characterization of the Fe Co catalyst.

4.1.1 SEM Analysis results

Figure 4.1 present SEM Micrograph of the Fe - CO catalyst supported on the zeolite. The SEM analysis was conducted in order to determine the morphology of the particles and as well as to determine the average sizes. When taking into consideration figure 4.1, it can be observed that the catalyst particles appear to have a square or cubic morphology. The average particles determined to be *ca*. 4 nm. This validates the ability of the wet impregnation methods to yield nano-sized particles.

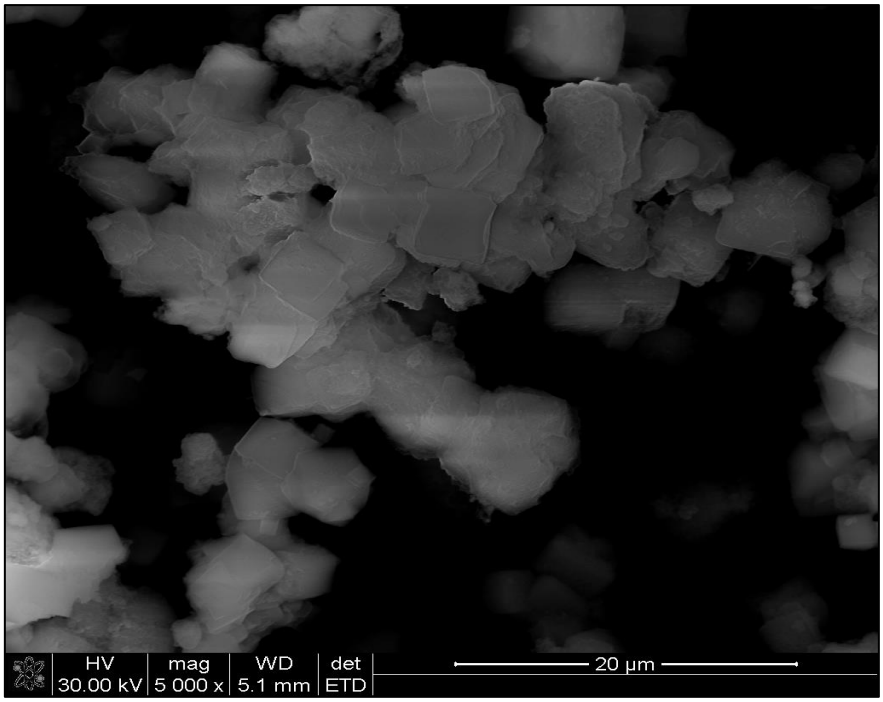


Figure 4. 1 SEM Image for Fe - CO catalyst supported on Zeolite

4.1.2 XRD analysis results

XRD analysis was used to characterize the zeolite supported catalyst. It was conducted in order to determine the composition of the catalyst. The results of the analysis are graphically portrayed in figure 4.2. The spectrum confirms the present of cubic or square crystalline structures of the zeolite. The blue peaks represent the existence of the zeolite support in the catalyst.

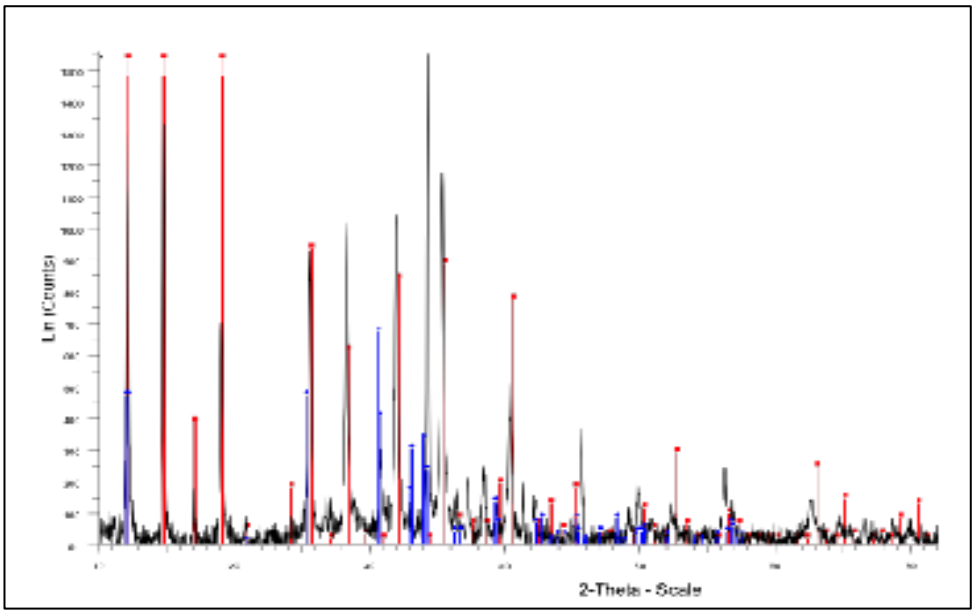


Figure 4. 2 XRD spectrum for FE CO catalyst supported on zeolite

4.2 CNT characterization

4.2.1 TEM analysis

Figure 4.3 and 4.4 portrays the TEM micrographs obtained for pristine (un--functionalized) MWCNTS CNT and Functionalized MWCNTs respectively prepared using methods outlined in chapter 3. TEM was used in order to determine the morphology of the particles and also to determine the average particle size. The un - functionalized MWCNTs (figure 4.3) seem to be scattered all over, with tendency to aggregate whereas the functionalized MWCNTs (figure 4.4) appears to be well consolidated.

When comparing figure 4.3 and 4.4 it can be seen that figure 4.3 (CNT) has noticeable dark spots than fCNTs. The dark spots are not noticeable in the fCNTs, Even at small scale of 200 nm it was still not easy to notice the dark spots,(figure 4.4), which indicates the present of impurities in the synthesized CNTs. The impurities may be amorphous carbon, metallic or other nano particles from the catalyst – support system (Hou, *et al.*, 2008; kwame 2015). This observation justifies the need to functionalized synthesized CNTs in order to reduce impurities there by increasing the chances of obtaining qualitative results.

It was worth mentioned the difference in the sizes between the CNTs and fCNTs, The image shows that the CNTs with a size distribution from 30 to 90 nm whereas the fCNTs shows a size distribution from 15 to 75 nm. This difference may be attributed to the use HNO_3 (In the case of fCNTs), which may have interacted with the walls of the nano-tubes thus reducing the size of the diameters (Phao, *et al.,* 2013)

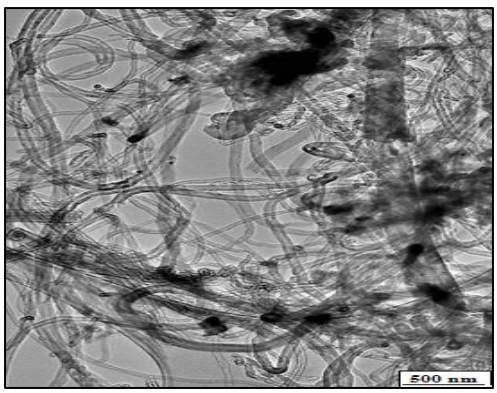


Figure 4. 4 TEM image of CNT

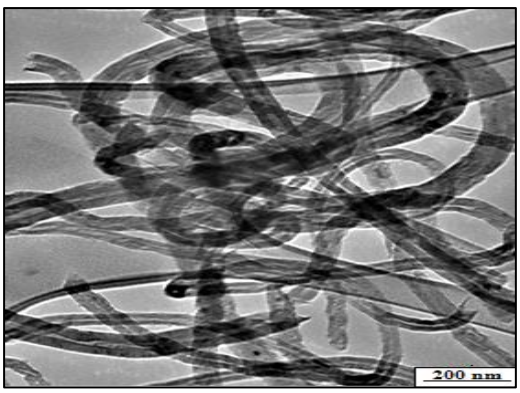


Figure 4. 3 TEM image of fCNT

4.2.2 FTIR

The FTIR analysis was conducted on the synthesized multi walled carbon nano tubes (functionalized and unfunctionalized). The analysis was conducted using the Bruker TENSOR 27 FTIR spectrometer. This device or equipment helps to indentify the functional groups present in the walls of the multi walled carbon nano-tubes. Figure 4.5 present the FTIR spectra as synthesized (as produced) and functionalised MWCNTs.

The two peaks at 1600 cm^{-1} and 1030 cm^{-1} indicating the presence of C=C and C-O functional groups. These groups indicate and validates that the MWCNTs were well synthesised and functionalized. The peaks at 1900 cm^{-1} and 2400 cm^{-1} may suggests the presence of C=O and –OH functional groups respectively.

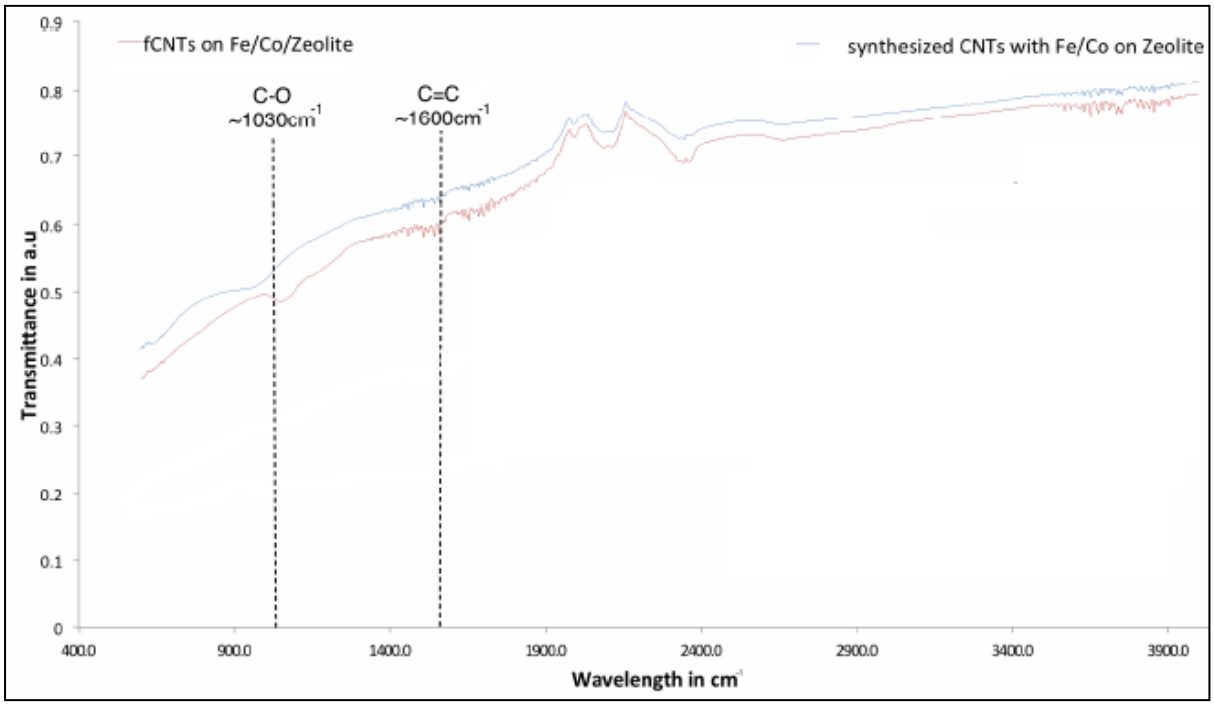


Figure 4. 5 FTIR spectra for synthesized MWCNTs

4.2.3 Raman spectroscopy

Figure 4.6, shows the raman spectroscopy of unfunctionalized and functionalized MWCNTs.

Of particular interest is the shape of the graphs and the decrease in the intensity as a function of HNO_3 concentration increases. From the shape of the graph it can conclude that the functionalization process did not alter the qualitative properties of the MWCNTs. From the decrease in intensity it can be concluded that the purified MWCNTs had some defects.

The D and G band are *ca.* 1350 cm^{-1} and *ca*. 1600 cm^{-1} respectively. The D band indicates the present of graphene sheets, while the G band serves to indicate the disorder present in the graphene structure. The intensity ratio (s) of D and G (I_D/I_G) yields the degree of disorder introduced into the MWCNTs wall matrix. Table 4.1, summarizes the I_D/I_G values.

Table 4.1, reflect that the I_D/I_G ratio increased by about 4%, the increase reflect that there were defects on the walls of the MWCNTs. This justifies the need for functionalizing the MWCNTs.

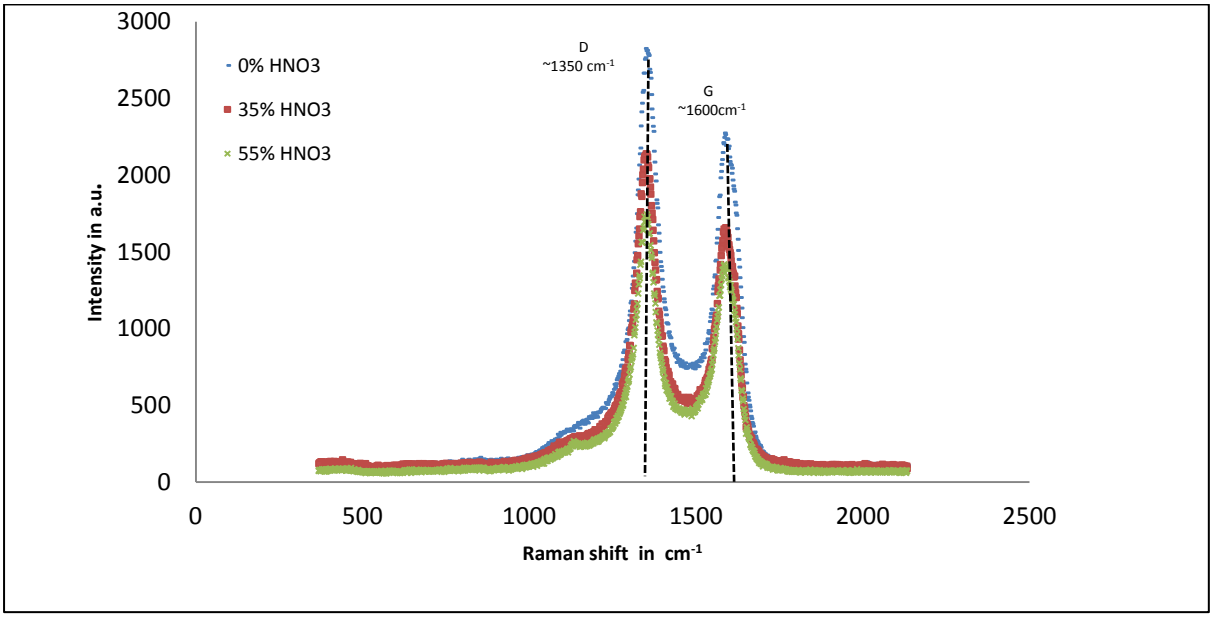


Figure 4. 6 Raman spectra for synthesized nano-tubes

Table 4. 1 Intensity ratio for functionalized and unfunctionalized MWCNTs

	0% HNO_3		35% HNO_3		55% HNO_3	
	D Band	G Band	D Band	G Band	D Band	G band
Raman Shift (cm^{-1})	1370	1650	1360	1620	1350	1600
Intensity (a.u)	2800	2300	2150	1750	1700	1340
I_D/I_G	1.217		1.228		1.259	

4.3 Membrane characterization

4.3.1 Contact angles

In order to determine the water contact angles of the membranes a sessile drop experiment was conducted. The contact angle of the membrane is an indication of the hydrophilicity and flux behavior of membranes.

Figure 4.7 shows a trend of contact angles vs. wt% CNTs blended with PPSU. These values provide an indication about the hydrophilic nature of the membranes. The contact angles for 0wt% (pristine), 0.2 wt%, 0.4 wt% and 0.6 wt% were determined to be 79^o, 76^o, 72^o & 74^o respectively.

The pristine membrane (0 wt%) shows to have a higher contact angle which cross ponds to the inability to soak up water. The ability of the membrane seems to show an increase with increase in CNTs wt% (decrease in contact angle). The permeability of the blended membranes increases with decreasing contact angle. The decrease in the contact angle can be attributed to a polar surface as a result of increasing the – COOH and improved by increasing the polarity of the blend. This will then increase the flux rate.

The optimum CNTs loading is observed to be at 0.4 wt%, at optimum permeability.

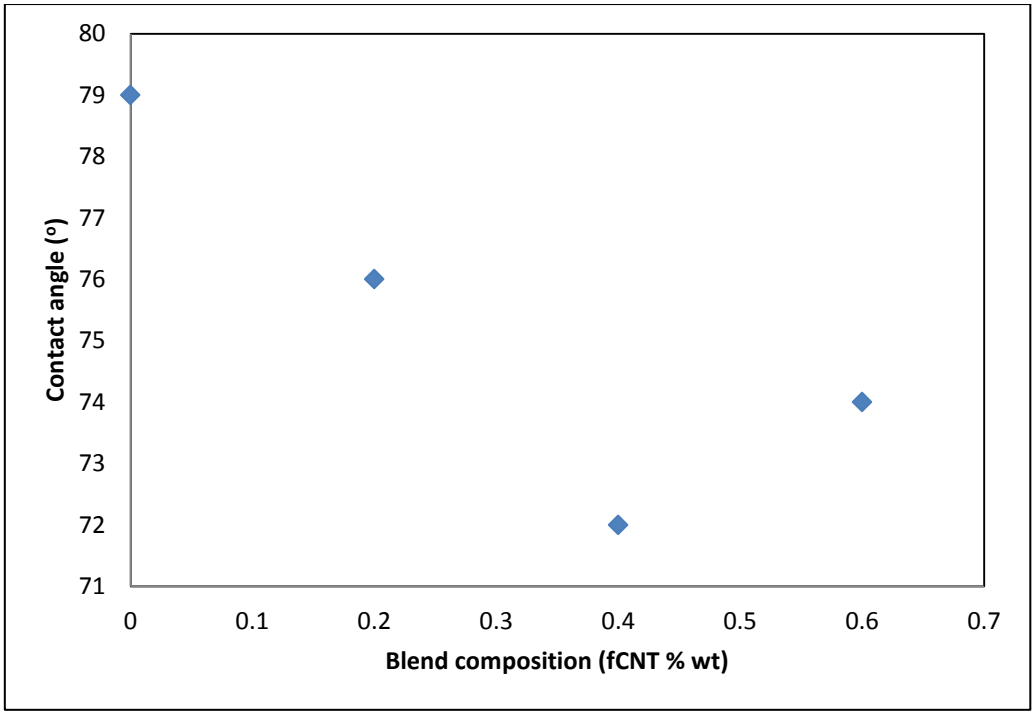


Figure 4. 7 Contact angle of the fCNTs as per composition

4.3.2 Mechanical performance

The idea of fabricated nano-composite membranes is to reinforce the membrane making them strong and less susceptible to damage. By infusing CNTs into the polymer solution to make nano-composite increases the life usage of the membranes.

The mechanical properties were determined by observing the breaking point force (N) of the membranes. Figure 4.8 summarizes the results. It can be noticed that the 0.4 wt% CNTs/ PPSU blended membrane has a highest breaking force. This implies that optimum tensile properties can be obtained at 0.4 wt% CNTs loading. The mechanical properties were obtained using the TAXT plus Texture Analyzer. The increase or the improvement in the strength of the membranes due to the addition of MWCNTs in the PPSU matrix relates to what is reported in literature elsewhere (Maphutha *et* al., 2013).

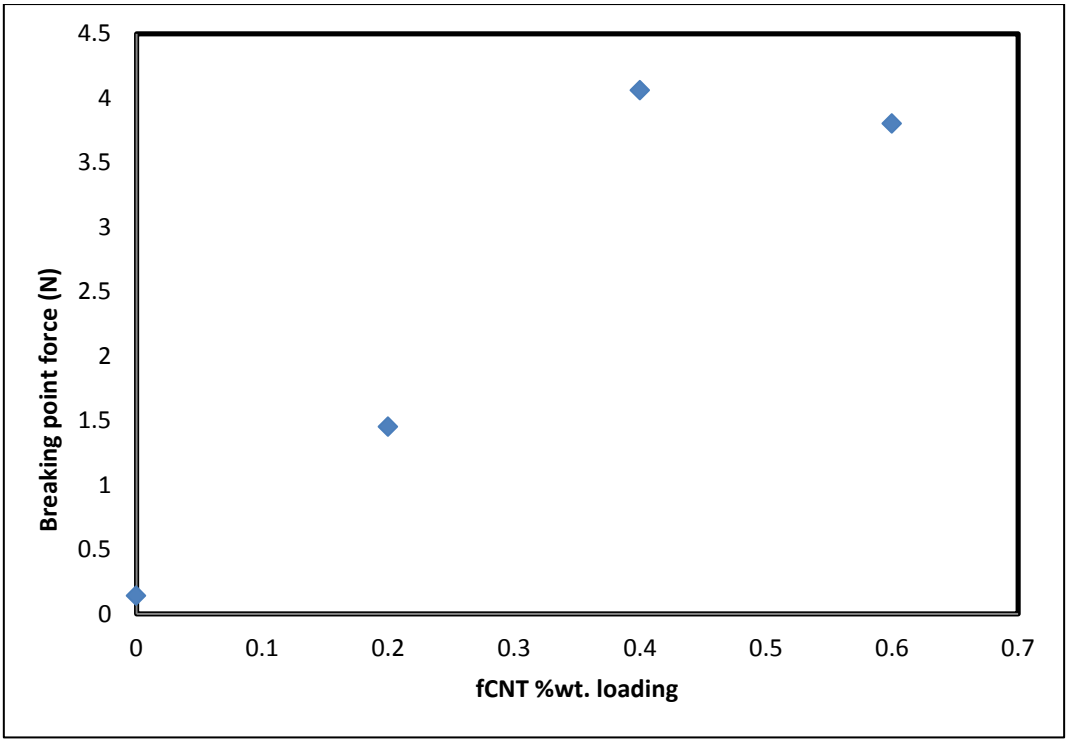


Figure 4. 8 Breaking force of the nanocomposite polymer membranes as a function of CNTs loading

4.3.3 SEM characterization

SEM is critical analysis for determination of the morphology of the materials. SEM provided critical information about the surface and cross – sectional structure of the membrane. These information will aid in determining or explaining the extend or limitation of the membranes ability towards permeation and rejection. The sole purpose of infusing or blending the PPSU membranes with f/MWCNTs, was to manipulate the morphology of the structure of the membranes in order to attain a high rejection/permeation performance of the membranes.

Thus, to understand the morphology of the prepared membranes (pristine and fCNTs/PPSU), morphological studies were conducted using SEM. Figure 4.9, shows the SEM micrographs of top surface of pristine PPSU and fCNTs/ PPSU composite membranes.

PPSU membrane seems to show an asymmetric membrane structure, which has a porous middle layer, macropores at the bottom and a dense layer. Whilst, the PPSU/fMWCNTs showed an asymmetric membrane structure: again with a dense

top layer, porous middle layer but with bottom spongy layer. This may be attributed to the change in the thermodynamic behavior as the result of the –COOH group in the nano material.

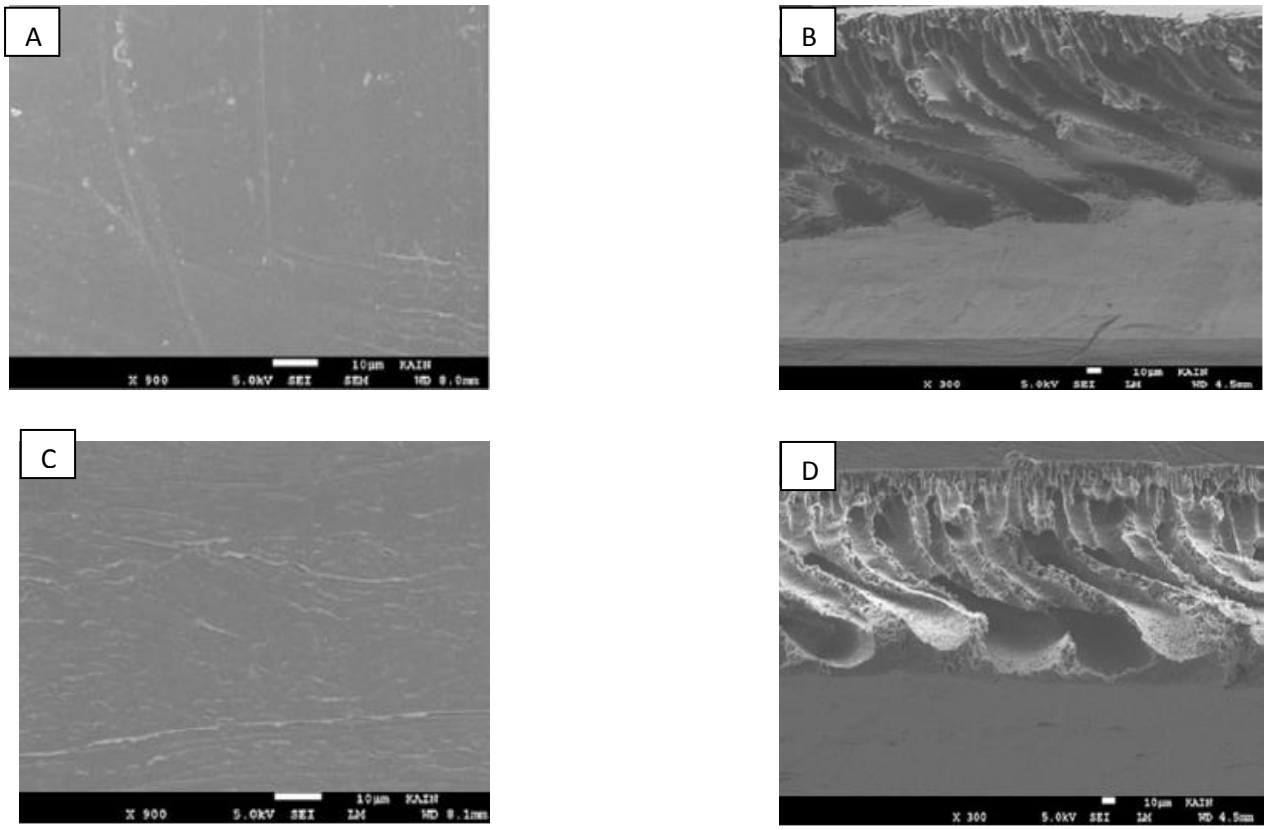


Figure 4. 9 SEM surface image of PPSU (A), cross section of PPSU(B), SEM surface PPSU - fCNTS (C) cross section of PPSU – fCNTS (D)

4.3.4 Membrane FTIR

Figure 4.10 portrays the FTIR spectra of the membrane surfaces of the pristine PPSU and fMCNT/PPSU composite membrane with 0.4 wt% CNTs. There is no noticeable difference between the pristine and composite membrane. The carboxyl groups (–OH) peak can be seen at 1500 cm^{-1}. This observation might suggests that the formation of the composite membrane was caused by the results of the hydrogen bonding interaction between the sulfonic groups of PPSU and carboxylic groups of the fMWCNTs, (Rong, *et al*., 2010).

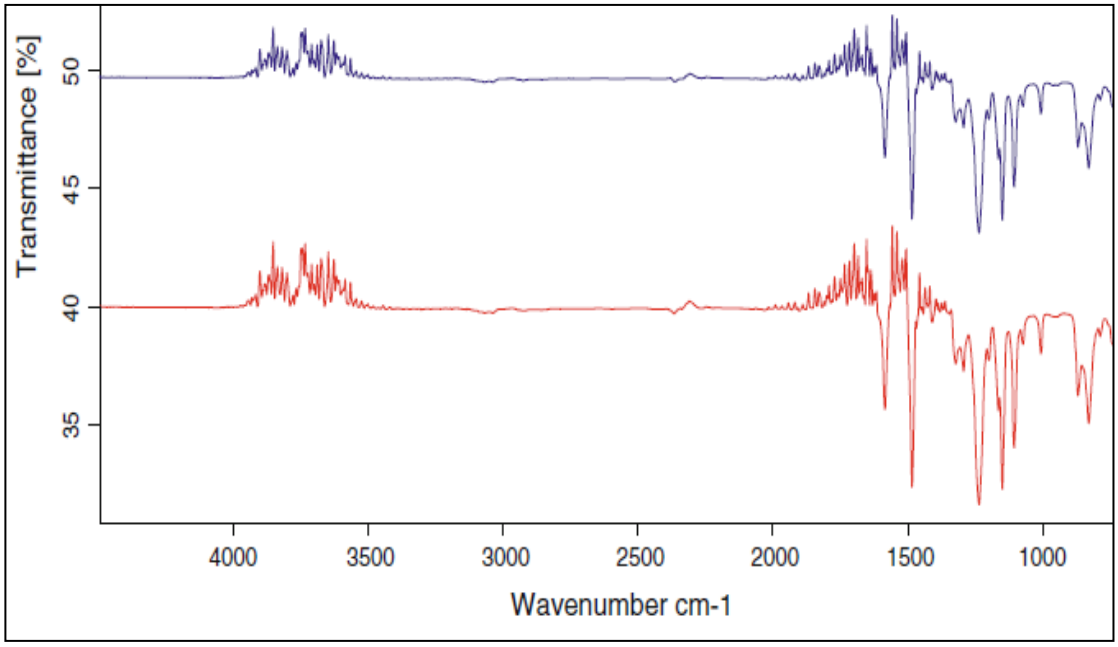


Figure 4. 10 FTIR of PPSU polymer membrane, and PPSU – fCNTS nanocomposite polymer membrane

4.4 Filtration test

Understanding the effect or the influence of the CNTs loading on the synthesized membrane performance during filtration is presented in this section. The results obtained from the filtration test of the membrane are presented in this section and are discussed to better understand the significant of adding CNTs on the PPSU membrane.

The membranes were compacted for at least 1 hour as discussed in section 3. The distilled water fluxes through the membrane were recorded and studied, prior the filtration of the waste water.

4.4.1 Permeate flux

Figure 4.11 , present the results of water flux as a function of fCNTs loading at a constant pressure of 2 bar using the cross flow filtration system. It can be observed that the water flux increase as per increase in fCNTs loading. It is also observed that the flux plateau is reached at a loading of 0.4 wt% fCNTs, at *ca.*120 L/m^2.h.

A decrease in water flux is observed at a loading greater than 0.4 wt %. fCNTs, this can be attributed to the increase in the density of the functionalized CNTs. The increase in the density of the functionalized CNTs results in sterric hindrance which causes the CNTs to group or agglomerate in the polymer matrix during membrane preparation using the phase inversion method.

An increased flux maybe attribute to the increase in hydrophilicity of the membrane and increase in the surface pore size, although there is an increase in the hydrophilicity per increase in the CNTs loading, decrease in the flux for CNTs loading above 0.4 wt% CNTs is due to the decrease in the surface pore size because of increased density. The presence of the –OH bonds in the CNTs maybe be credited for the increase in the flux, as this alters the contact angles (hydrophilicity) and pore size of the membranes.

This observation suggests that in order to ca.0.4 wt% CNTs loading is the optimum CNTs loading for high performance of the nano - composite polymer membrane.

This observation complements the conclusion reached by other researchers elsewhere (Maphutha*, et al.*, 2013).

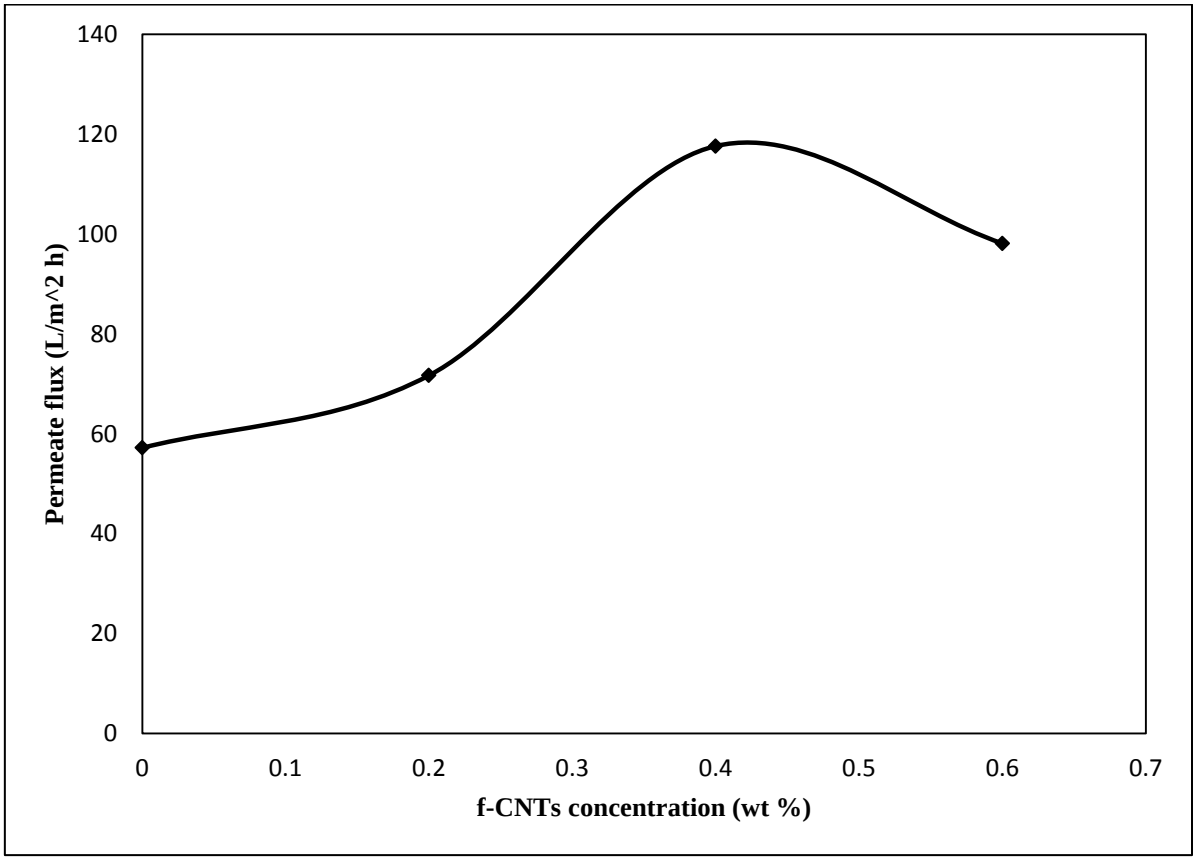


Figure 4. 11 Pure water flux for different % fCNTs loadings (at constant pressure of 2 bar for 1 hour)

4.4.2 Pressure influence on the membrane performance

The effect of pressure on the membranes performance during the filtration process shows that the composite membrane fCNTs/PPSU was more rigid and strong compared to the pristine polymer membrane and can be operated at elevated pressure.

High pressure facilitate the filtration process which results in increase in the permeate flux. Therefore pressure is another variable to optimize in addition to the wt.%CNTs loading in order to complement the overall membrane performance.

Figure 4.12, presents the flux results of the synthesized pristine PPSU polymer membrane and 0.4 wt% fCNTs/PPSU composite PPSU membrane) as a function of

operating pressure. 0.4 wt% fCNTs/PPSU composite polymer membrane proved to yield optimum results. The experiment lasted for *ca*. 1 hour.

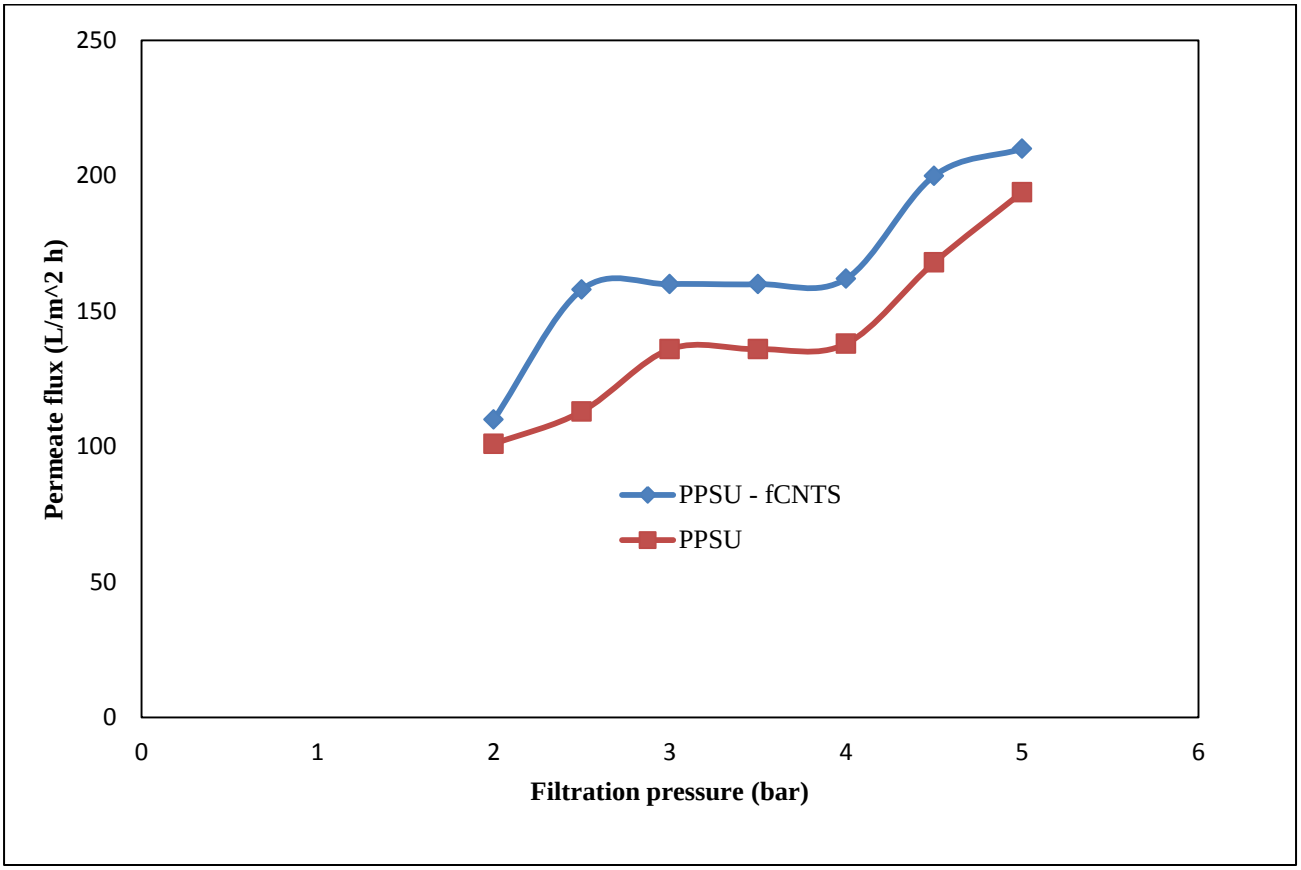


Figure 4. 12 Water flux for different filtration pressure (at constant fCNTs loading 0.4% for 1 hour)

It can be observed from Figure 4.12 that the flux through the membrane increases with increasing pressure. There is a flatting or constant permeate flux at pressure ranging from 3 to 4 bar for all the membranes. There are different reasons that can explain the observed behavior: a) Fouling of the membrane on the surface – this reduces the pore size or available pores.

However, the PPSU/fCNTs composite membrane shows the best flux results and this can be attributed to the increase porosity and hydrophilicity. The deviation from constant flux after 4 bar for both membrane suggest that indeed the membrane was fouled and increase in pressure was required to overcome the membrane inefficiency induced by the fouling.

However, increase pressure at industrial level is not practical because these could result in increasing the in operational cost. In addition, the membrane strength is also a limiting factor: higher pressurizing membrane may results in damaging the membranes and affecting the downstream process and interrupting the production process.

Therefore, it is critical to determine the optimum operating pressure that membranes can withstand and simultaneously yielding good results at the most cost effective manner possible. In this case it can be seen that optimum pressure is ca. 3 bar.

4.4.3 Flux decline

Figure 4.13 present the decrease in flux as a function of time for nano-composite polymer membrane with 0.4 wt% CNTs loading and the pristine polymer membrane (0 wt% CNTs). The operation pressure was selected to be 3 bar, the figure shows the permeate flux decline over ultra-filtration time of the pristine polymer membrane and the fCNTs /PPSU composite polymer membrane.

The PPSU polymer membrane shows strange behavior in the sense that the trend started by slight increased and decrease after an hour; however the flux still low than fCNTs/PPSU composite polymer membrane over the same period of time. Better results are observed after *ca.* 20 min for both membranes.

The slight increase in flux in the case of PPSU polymer membrane might be attributed to the fact that pore size of the pristine polymer membrane deformed, when subjected to the operating pressure (In this case 3 bar). This implies that water molecules and small oil droplets may be forced through the pores which over time tend to accumulate within these pores and thereafter blocking the pores. Blockage of the pores results in the decreased of permeate flux over time.

The decreased in permeate flux for both membranes can be attributed to adsorption of oil droplets on the surface of the membranes (concentration polarization). Because the retentate stream was recycled back into the feed this meant that the surface of the membrane became more concentrated thus forming a cake layer on the surface of the membranes.

These results suggest that in order to increase the life span of the membranes, backwashing should be considered. The backwashing process will help clean the membrane surface. This will results in an increase in the flux because the blocked pores will then be freed of any material (s) that were blocking the pores which resulted in decrease in the flux.

This is achieved by pushing water through the membrane in reverse direction in order for the foulants on the membrane surface to be lifted off. It is worth noting that the addition of the CNTs aided in the control of the flux decline by controlling membrane fouling.

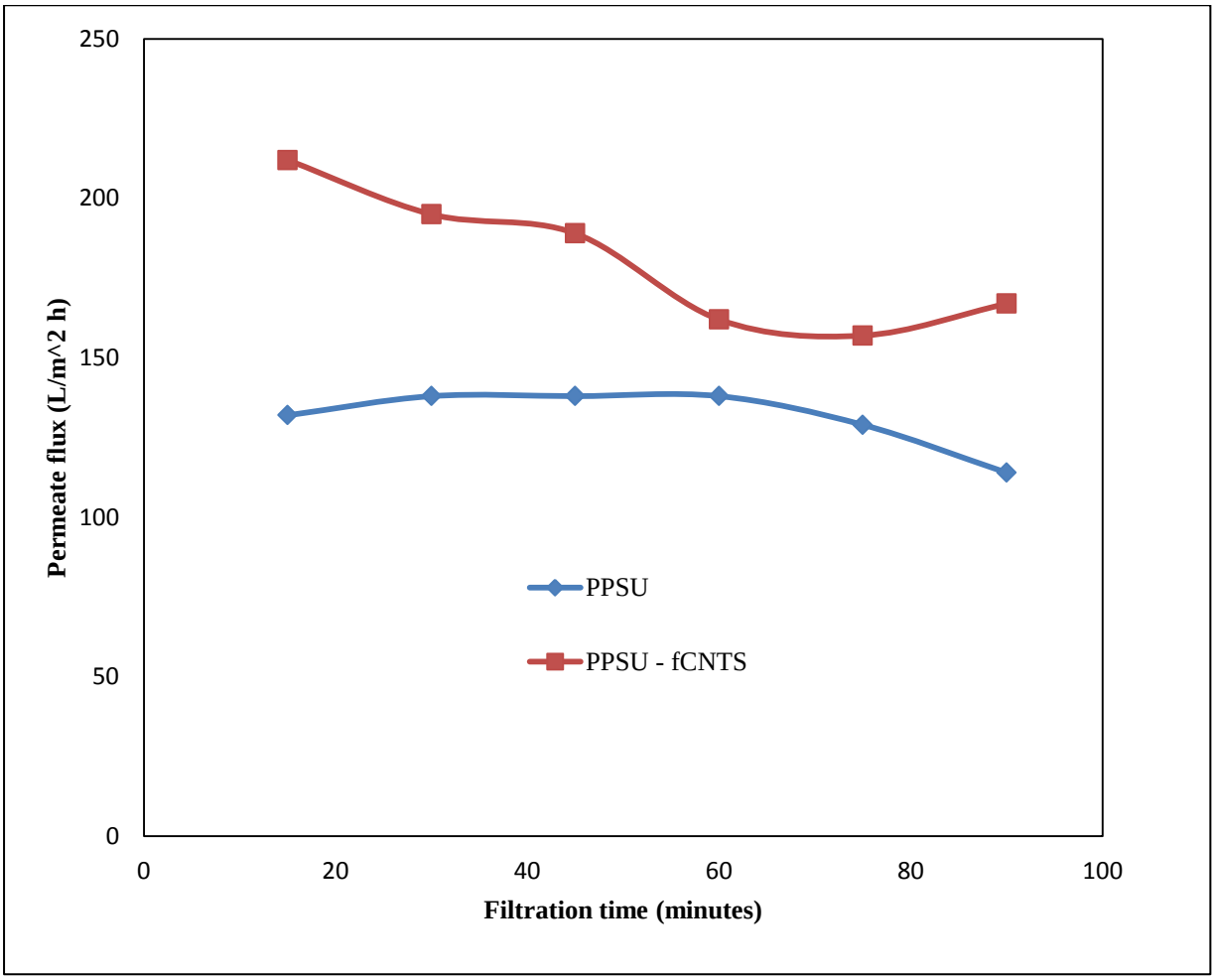


Figure 4. 13 Water flux for different time (at constant fCNTs loading 0.4% and 4 bar

5. Conclusions

The results showed that the wet impregnation method successfully synthesised nano sized Fe-Co crystallites supported on zeolite. This method well impregnates metal precursor on the zeolite metal support.

CVD method was successfully utilised to produce the MWCNTs at 700˚C. In this method, acetylene was used as the carbon source and the carrier gas was nitrogen.

The produced MWCNTs were functionalised using HNO_3 and purified using HF in order to remove any impurities and to add new functional groups (e.g. –OH group) on the surface of the MWCNTs without altering any of their physical properties (wall structure).

The Phase inversion method was used to synthesise polymer membranes. To produce nano-composite polymer membrane, certain concentration of MWCNTs were added to the polymer solution and sonicated to achieve a homogenous mixture. The addition of carbon nanotubes resulted in improving the porosity, permeability, hydrophilicity of the membrane and the mechanical behaviour.

However addition of nanotubes to produce nanocomposite membrane is limited to fCNT loading. In this study it was found that 0.4 wt% CNTs was the optimum loading. This loading produced better hydrophilicity, mechanical strength and permeability results relatively compared to the other membranes.

During the filtration studies it was found that an increase in filtration pressure results in an increase in the permeate flux and this may be attributed to an increase in differential pressure across the membrane.

However, it should be noted that high pressure may results in damages to the membrane, therefore an optimum pressure should be used in order to avoid the damage of the membrane. Also it would be interesting to used pressure similar to those used in industry.

The permeate flux showed a decrease over longer operational period for all the membranes; this may be caused by pore blockage of the membrane and the accumulation of oily matter (concentration polarization) on the surface of the membrane.

The study showed that addition MWCNTs onto the polymer membrane has positive impact on the membrane performance; increase in hydrophilicity, mechanical strength, permeability and etc.

However, the key in achieving an optimum nano - composite polymer membrane lies in the CNTs loading which is further dependent on the choice of catalyst, carbon source, the choice of the functionalizing & purifying agent, membrane preparation method and operating conditions (pressure, temperature & etc.).

Understanding how the aforementioned parameters or variable affect the process of filtration or the performance is important for suggesting recommendation that would results in synthesizing nanocomposite polymer membrane that has an optimum performance.

6. Recommendations

It remains very clear that it is a challenge to synthesize a high performing nanocomposite membrane because of many contributory factors. This results in the need to probe into the controlling factor (s), these may be physical or chemical related factors or properties. It is therefore important to provide recommendations from catalyst preparation, membrane preparation and operation conditions.

Catalyst:

There are many numerous catalyst preparation methods, it is therefore recommended to compare the effects of catalyst preparation methods on the end product i.e. nanocomposite membrane. This may include the choice of the catalyst, choice of support and preparation method e.g. wet impregnation method vs reverse micelles and dry impregnation method.

The choice of catalyst and support may influence the final CNTs sizes, which indirectly affect the properties of the nanocomposite membrane (the influence small CNTs vs large CNTs sizes on the nanocomposite membrane performance).

The preparation method influences the narrow size distribution of catalyst, which influences the surface area available for reaction thus the CNTs growth, thus it is recommended that different catalyst preparation methods should be used and compared in order to establish qualitatively their effects on the CNTs produced.

Membrane Chemistry/ preparation

It was established that the optimum MWCNTs loading was 0.4 wt% but no knowledge exist that shed light into understanding how this has an influence on the performance of nanocomposite polymer membrane prepared using different methods e.g. Phase inversion vs. Solution casting.

Phase inversion methods are said to produce a very porous anisotropic membrane and the solution casting methods yields dense and non-porous isotropic membrane. It also worth mentioning that the solution casting methods membranes are less rougher and less hydrophilic than the phase inversion methods.

Thus it is recommended that different preparations methods at this loading should be compared to determine the best or optimum performing nanocomposite polymer membrane. It is also interesting to determine the effect of addition of polyester non-woven fabric (different kinds) unto the membrane as it is reported in literature that it has an increasing effect on the roughness, permeability and strength of membranes although this might make the membrane more susceptible to fouling through pore blockage.

Membrane additives

Apart from the CNTs other additives should be used to establish the extent of their enhancing properties and performance of the nanocomposite polymer membranes.

Operation conditions

It is recommended that the research should be conducted under conditions similar to industry in order establish the application limit of the synthesized nanocomposite membrane.

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