

Impact of Carbon Nanotubes on the Polymeric Membrane for Oil – Water Separation

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Abstract

In this research, the classical phase inversion method was used to produce the polysulfone (PSF) membrane by using three different solvents: N, N-dimethylformamide (DMF), chloroform (CHCl₃) and tetrahydrofuran (THF). Furthermore, different concentrations of functionalized multi – walled carbon nanotubes (MWCNTs) were added to PSF membranes by the classical phase inversion method. MWCNTs were synthesized using chemical vapour deposition (C.V.D) then functionalized by acid treatment. The morphology and the structure of the membrane and MWCNTs were characterized by using the scanning electron microscope (SEM) and transmission electron microscope (TEM). The characterization of the functionalization of the MWCNTs was performed by using the Raman spectroscopy. It was found that the chemical, physical and mechanical properties of the polymeric membrane improve with the content in functionalized MWCNTs concentration in the polymeric membrane matrix. The membrane with the MWCNTs concentration of 0.4% w/w showed the highest flux of 117 L/m².h and solute rejection. The selectivity and permeate flux of the polymeric membrane were increased with functionalized MWCNTs content for the membranes produced with the three different solvents.

Keywords: Multi - walled carbon nanotubes, Organic solvents, Polysulfone membrane, Contact angle.

1. INTRODUCTION

Knowledge of the process of membrane separation is of great importance in mechanical (metalworking fluids), metallurgical, petroleum, and pharmaceutical industries, especially in solving problems related to environmental protection. Oily wastewater produced from the aforementioned industries released a very high oil concentrations [1-2]. While, the tolerable discharge ranges between 10–20 mg/L. Polysulfone (PSF) membranes are the most common membranes used for filtration process of oily wastewater due to

its mechanical robustness and structural and chemical stability [3-4]. The membrane separates immiscible solids and solutes that are dissolved, acting as a selective barrier allowing the passage of certain components while preventing the passage of others [5-7]. In the process of separating two streams are produced: the concentrate stream (retentate) containing the contaminants initially present in the feed stream and permeated or purified fraction of liquid passing through the membrane [6-7]. PSF membranes possess

a unique asymmetric structure and are available in a wide range of pore sizes from 0.03 to 1.2 μm . A high degree of asymmetry provides built in prefiltration through the depth of the membrane and results in exceptionally high throughput and dirt holding capacity (DHC) [6 - 8]. The pore diameters on one surface of the membrane are over 100 times larger than the micron-rated pores on the opposite surface. Microfiltration (0.1-10 μm), Ultrafiltration (0.01- 0.10 μm), Nanofiltration (order of nanometers) and reverse osmosis have all been successfully used in the separation of oil from water [9-10]. These techniques are useful because of the high quality water produced, simple module design, low amount of chemicals used and low energy consumption compared to other treatment techniques. Membrane filtration technology is widely used for wastewater purification, but still suffers from major disadvantages, including irreversible membrane fouling and concentration polarization [11-12]. Membrane fouling may occur due to the following reasons: biological fouling which is the growth of biological species on the membrane surface, colloidal fouling which leads to a loss of permeate flux through the membrane, organic fouling due to the deposition of organic substances, and scaling, defined as the formation of mineral deposits precipitating from the feed stream to the membrane surface [13-14]. Membrane fouling is still regarded as the major drawback of the membrane filtration process and without improved anti-fouling membrane this highly efficient technology will remain handicapped [15]. To improve PSF membrane performance, a considerable research effort has focused on the addition of inorganic materials such as MWCNTs sieves to polymers [16]. This so called blended membrane (BM) combine useful molecular sieving properties of inorganic molecular sieves with the desirables mechanical, chemical and other processing properties of polymers [17]. However,

despite their stable structures and good properties, single walled carbon nanotubes (SWCNTs) do not disperse properly in the polymeric membrane and it leads to a poor interfacial compatibility of the SWCNTs with the polymer. This dispersion problem can be used to justify the choice made on MWCNTs production, due to their good dispersions in the organic solvent and inside the matrix of the polymeric membrane [18-19]. Another advantage of using MWCNTs instead of SWCNTs is based on the fact that MWCNTs are easier to be produced in high volume quantities than SWCNTs [19]. Attempt to improve the compatibility between MWCNTs and PSF membrane by introducing the interest of using nanoparticles in membrane structures mainly focuses on their assumed beneficial effect on fluxes and fouling resistance [18-20]. Vahid and Van der Bruggen [20-22] reviewed potential applications of nanoparticles-enhanced membranes in general. They conclude that the use of nanoparticles in the development of low-fouling membranes allows for a high degree of control over membrane characteristics as well as the ability to produce ceramic membranes in the nanofiltration membrane range mutually interactive functional groups on the PSF membrane, thus hindering separation performance.

The main purpose of this study was to assess the effect of acid functionalized MWCNTs on a PSF membrane for oil–water separation. Since the organic solvents play a very important role in the preparation of polymeric membranes, the effects of three solvents: N, N-Dimethylformamide (DMF), Chloroform (CHCl_3) and Tetrahydrofuran (THF) on polymorphism of PSF membranes by phase inversion were investigated. SEM, TEM were used to analyze the morphology and crystalline structure of the membrane. The physical, chemical and mechanical performances of the PSF membranes with different concentration of functionalized MWCNTs were also studied.

2. EXPERIMENTAL AND CHARACTERIZATION METHOD

2.1. Fabrication of PSF Membrane

The phase inversion method was used in the preparation of the PSF membrane [23-24]. Using a magnetic stirrer, 10 g of PSF was dissolved in 50 ml of three different solvents (e.g. DMF, CHCL₃ and THF) for 24 h. An ultra sonicator, set to a frequency of 60% was used to sonicate the solution for 10 min. A casting blade or doctor blade (which is a film casting knife that can be used to cast a membrane on a glass substrate) was used to cast the solution onto a casting glass under constant casting speed and left in ambient conditions for 20 to 30 seconds before being immersed in a bath of deionized water. The membrane was then allowed to dry in the bath for another 24 h. A 1wt% (w/v) solution of polyvinyl alcohol (PVA) was prepared and poured over the membrane. This was left in contact with the membrane for 3 min and the excess solution was drained off. A 0.2 wt% (w/v) maleic acid solution was also poured over the membrane and then drained off after 3 min. Finally the membrane was placed in an oven at 125 °C for 30 min and the final produce allowed cooling.

2.2. Fabrication and Functionalization of MWCNTs

The MWCNTs were synthesised using chemical vapor deposition (C.V.D) process at the temperature range: 800°C – 900°C [25-26]. MWCNTs were produced instead of single walled carbon nanotubes (SWCNTS) due to its good dispersion in the organic solvent and inside the matrix of polymeric composites [26]. The nanotubes were produced by passing acetylene and argon (which are the carbon source and carrier gases respectively) through a furnace with a ferrocene which was acting as both a carbon source and a catalyst. The MWCNTs were immersed in a 35% nitric acid solution and was refluxed in oil for 4 h at 110 °C. The functionalized MWCNTs were then

filtered and washed with distilled water until a neutral pH was attained. The washed MWCNTs were dried in an oven at 120 °C for 12 h.

2.3. Fabrication of Functionalized Multi - Walled Carbon Nanotubes - Polysulfone Membrane (Blended Membrane)

The functionalized MWCNTs were blended with the polymer solution in varying concentrations: 0.1%, 0.2 %; 0.3%; 0.4%; 0.5% and 0.6% w/w. The functionalized MWCNTs were added to the PSF and (DMF; CHCL₃ and THF) solution during the stirring stage and membranes were then prepared using the phase inversion method detailed above.

2.4. Pre-Treatment of Oil Water Mixture (Coagulation)

Raw MWCNTs were used to pre-treat oil water before using the membrane filtration process; Solid particles in the emulsion had to be removed since they can damage the membrane or contribute to fouling during ultrafiltration process. The solid particles were too thin to be removed using certain other physical methods. Coagulation of oil droplets was one alternative identified for destabilization of emulsion in order to remove solid particles. An experimental investigation was then performed to find out which MWCNTs-mixture ratio will optimise the coagulation process. 15 ml of Oil water mixture was added in six different sample tubes. 0.0 g, 0.2 g, 0.3056 g, 0.4054 g, 0.4056 g and 0.5043 g of Raw MWCNTs were added in each respective tube. The sample tubes were then left for 21 days.

2.5. Filtration Tests

The cross flow model shown in Figure 1 was used for the filtration tests. A 45 cm² membrane was used at room temperature. The membranes were first compacted by flushing water through the system. The oil water emulsions were then passed through the pump at different pressures (2, 2.5, 3,

3.5, 4, 4.5 and 5 bar) and the time required to measure the collected permeate was recorded. The flux through the membrane (F) was then calculated using equation 1 [9, 27, 28]:

$$F = \frac{V}{At} \quad (1)$$

where F is the flux, A is the effective membrane area and v is the volume of permeate through the membrane during the

time t. The equation that describes solute retention (or rejection) by a membrane is given by:

$$R(\%) = \left[1 - \frac{C_p}{C_f} \right] \times 100 \quad (2)$$

where R is the rejection, and C_f and C_p are the feed and permeate concentrations, respectively [9, 27].

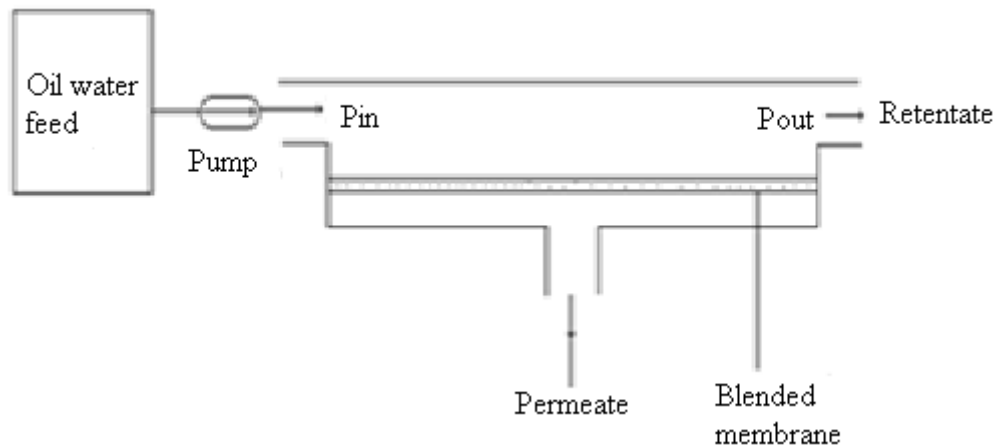


Figure 1. Schematic of the filtration module design.

3. RESULTS AND DISCUSSION

3.1 MWCNTs Characterization

3.1.1 Scanning Electron Microscope (SEM) Observation of MWCNTs

A SEM with high resolution was used for MWCNTs observation and morphological analysis. SEM Sigma series FE-SE in – lens was used at a 15KV and 17 KV accelerating voltage. This method gives information mainly about the surface morphology of the sample. The SEM image from Figure 2 shows MWCNTs of diameters less than 100 nm. From the scale of the images, the calculation of the outer diameter of the MWCNT is determined to be approximately 50 nm, which falls within the literature ranges for MWCNTs of between 2.4 nm and 100 nm. The morphology of MWCNTs is very similar to that of carbon nano-fibres (CNFs). The difference however between the two is the lack of a hollow tube in carbon nano-fibres. Figure 2 confirms that MWCNTs

were functionalized because the tubes appear to be hollow. A closer inspection of the image reveals one tube with a blocked end, a characteristic of MWCNTs and not CNFs 35. A Raman spectroscopy was used to characterize the functionalized MWCNTs. SEM gives valuable information on the morphology of MWCNTs, it is not sufficient to establish the ultimate nature of the MWCNTs. It is easy to confuse only on the basis of SEM observations carbon nanotubes from nanofibres. Thus, one proceeds to TEM analysis of the samples to have deeper information on obtained MWCNTs.

3.1.2 Transmission Electron Microscope (TEM) Observation of MWCNTs

Transmission electron microscope FEI Tecnai T12 was used to observe the internal structure of the sample. The microscope had accelerating voltage from 80 to 200 kV.

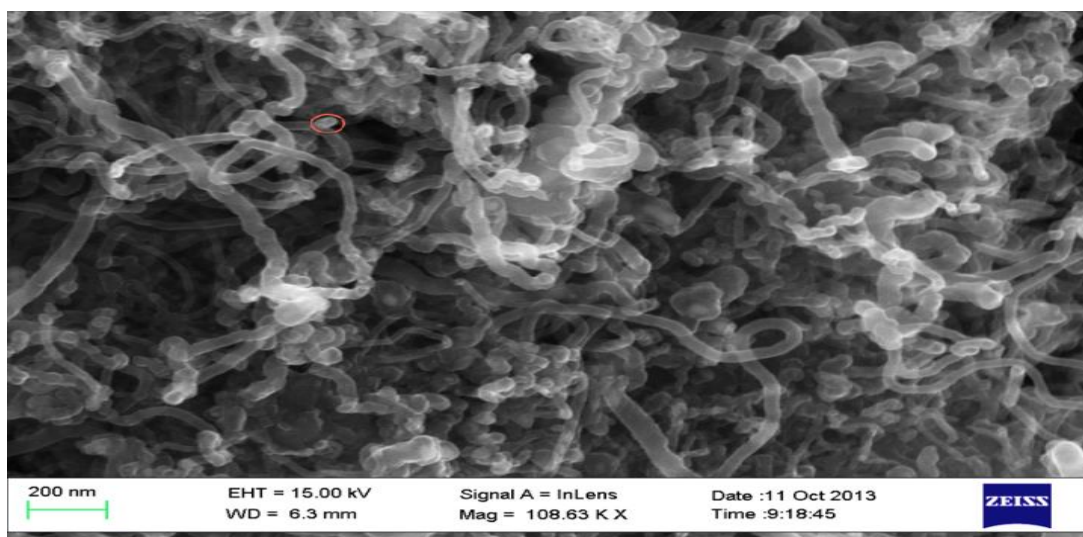


Figure 2. SEM image of functionalized MWCNTs.

Images were acquired using the peltier-cooled CCD camera Kewen Vie. The CCD chip in this camera provides maximum resolution of 1376x1032 pixels with a 12 bit dynamic range (4096 gray values). The

KeenView supports frame rates of more than 20 images per second at 2x binning and of 10 10 images per second at full resolution.

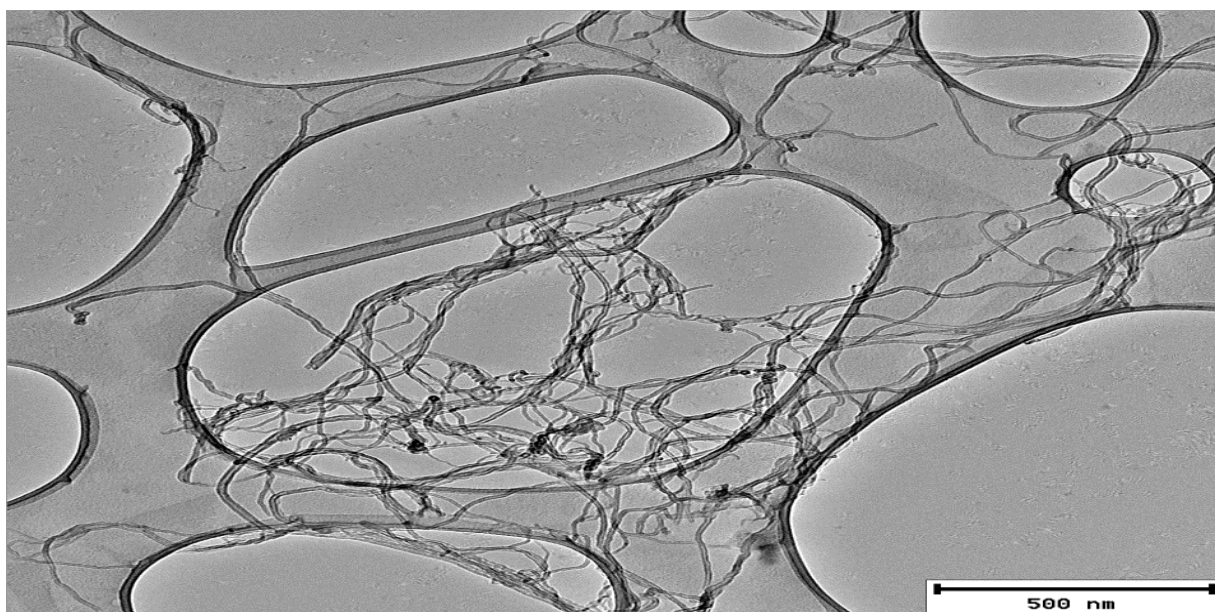


Figure 3. TEM images of MWCNTs.

Accelerating voltage 120 kV and magnification 100000 – 400000 times were used in this work. TEM was used due to its ability to measure nanotubes diameter in the bundle. From the TEM images (Figure 3) it is possible to determine directly the diameter of one nanotube and bundle diameter. Due to this

information, the number of nanotubes in the bundle can be found. Mostly, nanotubes in the sample are not in bundle, so they are alone (Figure 3). TEM micrographs clearly illustrate that nanotubes obtained display widely different morphologies according to some variable parameters. It is possible to

control the morphology. Within the medium value of the plasma power, as shown with SEM study, carbon nanotubes are already grown. These samples however display different mutual orientations. The highly oriented films are obtained under optimized conditions and poorly and medium oriented films are also obtained, showing more defects. Although the high resolution of the transmission electron microscope can be used to observe even atomic resolution, the TEM images could not provide the opportunity to determine the exact number of walls of the sample of MWCNTs. This deficiency may be the result of defects. In this way, mutually aligned tubes of different densities are obtained, depending on the nature the reactive gas mixture. TEM images of MWCNTs show that the mean diameter is around 25 nm. From the TEM image it could be observed that MWCNTs are very

thin. The TEM image of MWCNTs and CNFs are clearly distinct; however it is quite difficult to know the exact number of walls.

3.1.3 Raman Spectroscopy of Functionalized and Unfunctionalized MWCNTs

Prior to functionalization, it is important to achieve a well dispersed mixture of MWCNTs in the solvents (DMF) during the phase inversion method. Figure 4 shows the Raman spectroscopy of the functionalized and unfunctionalized MWCNTs. The deviation in the graph confirms an intensification of the defects in the wall matrix of the functionalized MWCNTs. The fact that the graphs have the same shape shows that the functionalization process does not change the material made.

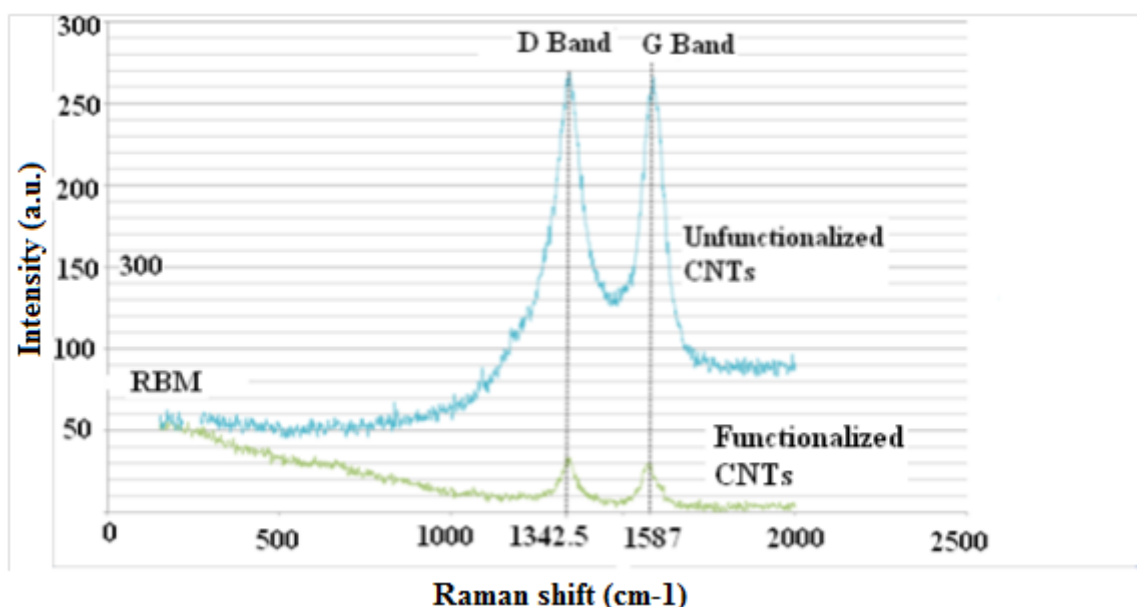


Figure 4. Raman spectroscopy for functionalized and unfunctionalized MWCNTs.

The D and G band from Figure 4 are 1342.5 cm^{-1} and 1587 cm^{-1} respectively. This is a 0.94% and 0.44% deviation from the literature values of 1330 cm^{-1} and 1580 cm^{-1} . These values confirm that graphene sheets were formed and that defects were introduced into the Walls of the MWCNTs. Figure 4 shows an RBM

for the lower frequencies of the functionalized MWCNTs but no evident RBM for the unfunctionalized MWCNTs. The lack of RBM for the unfunctionalized indicates that the average diameter of the MWCNTs is greater than 3 nm, which agrees with the diameter of 66 nm calculated above. 54 The ratio at ID/IG is

the intensity of the D band to the G band and indicates the degree to which defects have been introduced into the MWCNTs wall matrix. The values are summarized in Table 1, which shows that ID/G increased

by 9.98%, confirming the presence of defects in the wall matrix of the MWCNTs. Therefore, it can be concluded that the MWCNTs were successfully functionalized.

Table 1. Intensity ratio for functionalized and unfunctionalized MWCNTs.

	Unfunctionalized CNTs		Functionalized CNTs	
	D Band	G Band	D Band	G Band
Raman Shift cm-1	1342.5	1587	1340.50	1572.50
Intensity (a.u.)	268.752	265.692	33.670	30.258
I D/G	1.012		1.113	

3.2 Membrane Characterization

3.2.1 SEM Images of the Membranes

The membrane surface morphologies were further studied using SEM characterization. The images of the top surface and the cross sectional view of the membrane were taken as shown in Figure 5 (a, b). The pores on top surface of the membrane are clearly observable at the moderate magnification.

A closer look shows that the pores on the surface of this membrane are not equal, i.e., they are asymmetric. This is a typical behaviour for the polysulfone membranes synthesized using the phase inversion method. Larger pores serve as pre-filters to the smaller ones. Figure 5 (b) however, shows small pores running across the membrane at a scale of 12 microns.

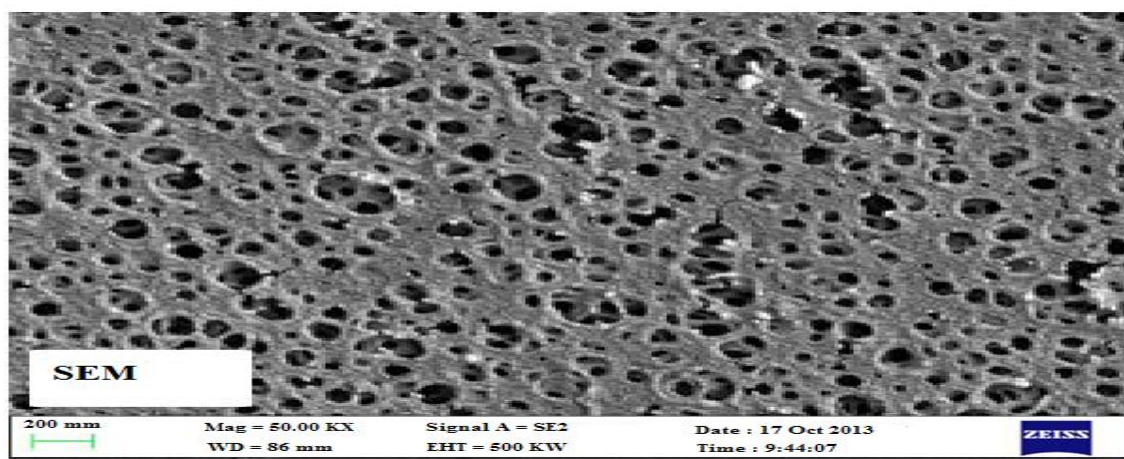


Figure 5(a). Top surface view of the MWCNTs / PSF membrane.

Functionalized (and characterized) MWCNTs were blended in to the PSF membrane in varying concentrations from

0.1 to 0.6 wt%. Figure 6 (a, b, c, d, e, f) show the membranes produced with different concentrations of MWCNTs.

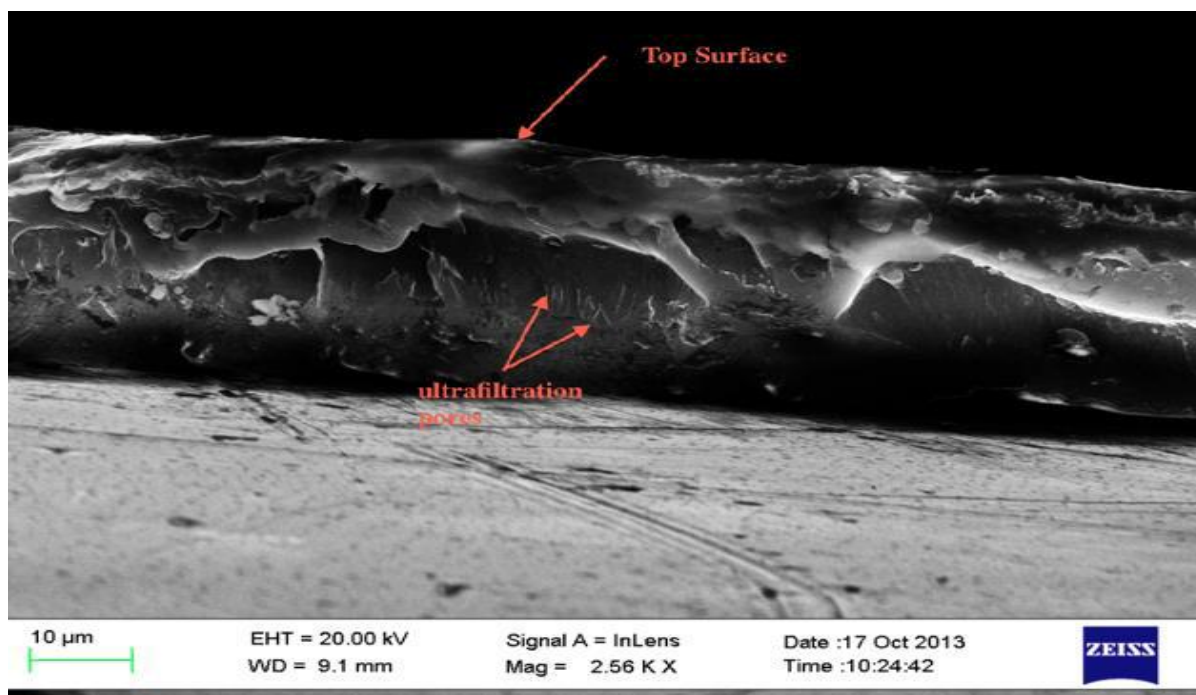
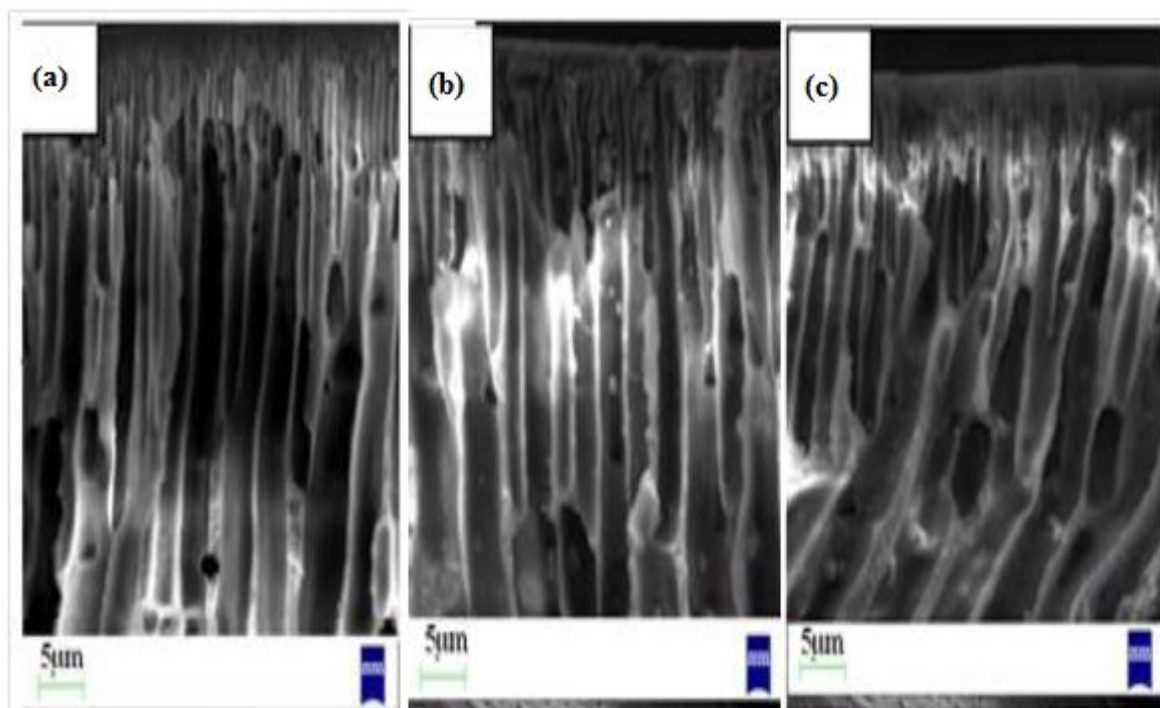


Figure 5(b). Cross section view of the CNTs/PSF membrane.

To investigate the influence of weight fraction of MWCNTs on the PSF membrane performance, the MWCNTs/PSF membranes containing 0.1 wt% to 0.6 wt% MWCNTs were prepared using the DMF solvent. The SEM images of the cross-

sections of MWCNTs/PSF membranes with different amounts of MWCNTs are shown in Figure 6. It has been found that there is not a pronounced difference in the structures of the cross-sections of the different MWCNTs/ membranes.



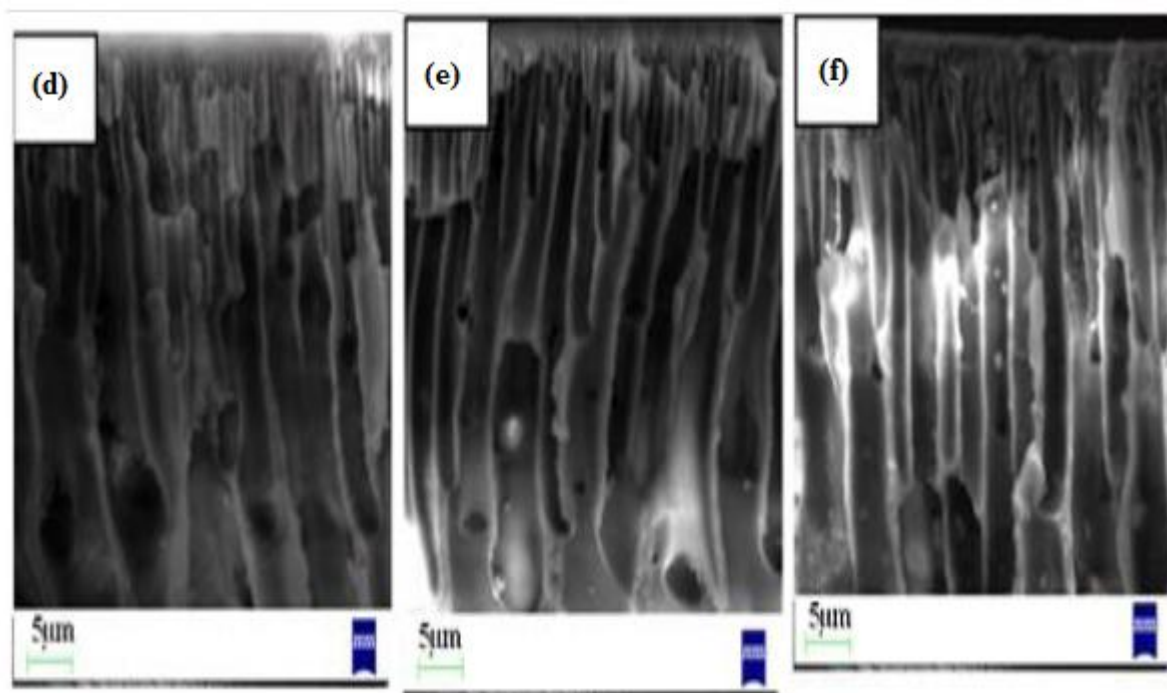


Figure 6. SEM images of the (a, b, c, d, e, f) cross-sections of MWCNTs/PSF membrane produced with different concentration of MWCNTs (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 wt %).

All the cross-section images have finger-like structures with various pore sizes. Furthermore, as the amount of MWCNTs increases, the surface of the MWCNTs/PSF membrane becomes rougher and the pores of the cross-section become larger. The MWCNTs/PSF membrane with 0.4 wt% MWCNTs (Figure 6, d) has the roughest surface and the largest pore size. For membranes containing more than 0.4 wt% MWCNTs, the surfaces become smoother and the pore sizes of the cross-section are smaller. This is due to agglomeration of MWCNTs inside the matrix of the polymeric membrane.

3.2.2 Hydrophilicity (Contact angle) Test of the Membranes

A Sessile drop experiment was performed using a Goniometer to determine the water contact angles on the membrane surface. Figures 7 (a, b, c) describe the three different contact angle experiments performed to assess the impact of MWCNTs on the hydrophilicity of the PSF membrane. The three different graphs revealed that all the polymeric

membranes have a contact angle of less than 90° , confirming that they are hydrophilic [30]. It shows an initial decrease in the contact angle from 75° for the pure polymeric membrane to 45° , Figure 7(a). This indicates an increase in the hydrophilicity of the membrane with increasing the concentration of functionalized MWCNTs; however a decrease it observed in hydrophilicity of the membrane was observed for the MWCNTs concentration more than 0.4 wt. % due to the agglomeration of MWCNTs inside the PSF membrane matrix. A decrease in contact angle from 81° to 49° was observed for Figure 7(b) and from 83° to 52° for Figure 7(c). This indicates an increase in hydrophilicity of the membranes with increasing concentration of MWCNTs. Contaminants on the surface of the membrane significantly increase the measured contact angles [31]. The 0.4wt% MWCNTs membranes show the best contact angles for each type of membranes produced. These results suggest that the addition of MWCNTs to the membrane did modify its hydrophilicity.

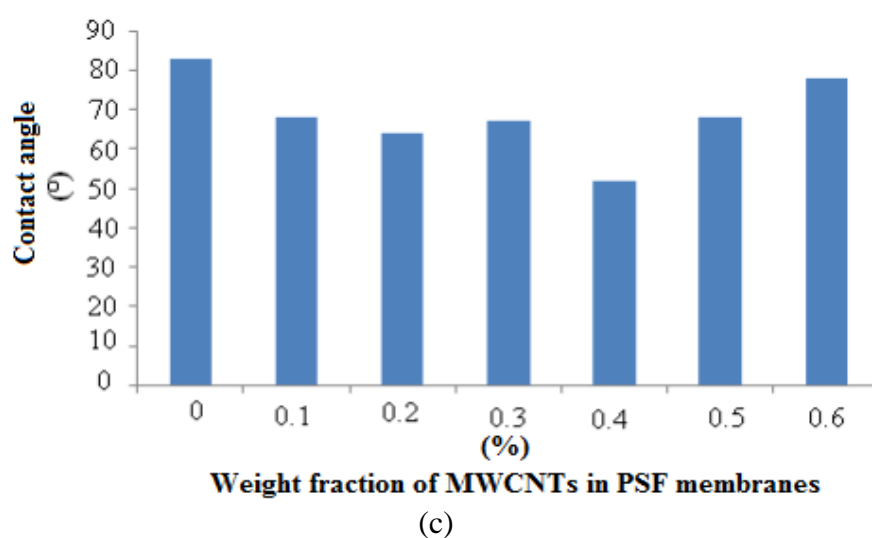
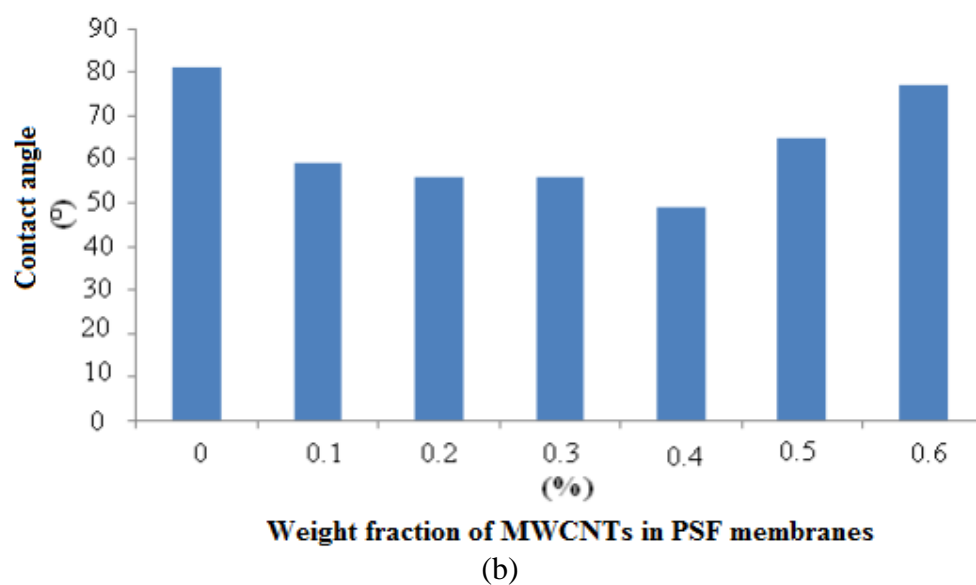
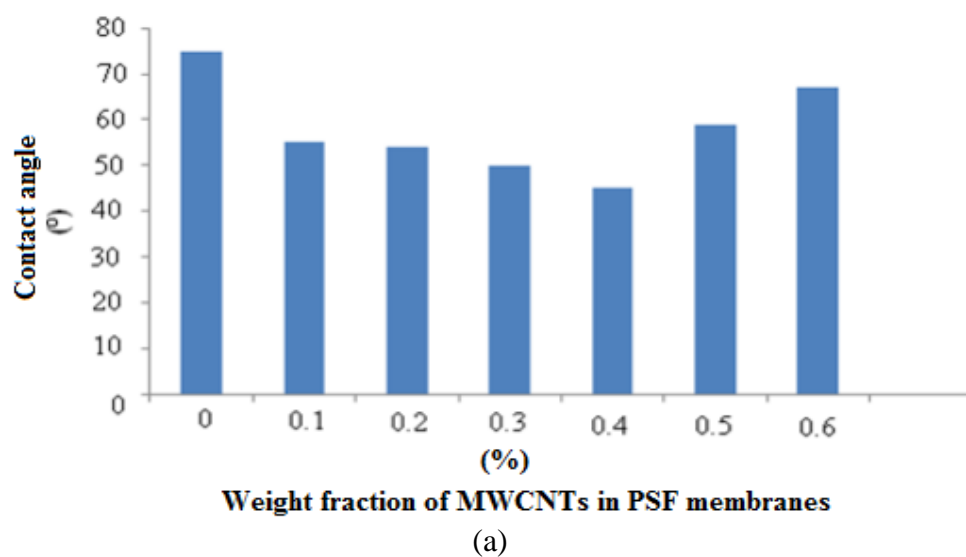


Figure 7(a, b, c). Contact angle of the MWCNTs/PSF membranes produced with DMF as solvent and different MWCNTs concentrations.

3.2.3 Mechanical Test Results

The rigidity gradient, strain energy and percentage resilience is measured using the TAXT plus Texture Analyzer. The mechanical property shown in Figures 8, 9 and 10 strongly supports the suggestion of the improvement of resilience, rigidity gradient and tensile strength with addition of MWCNTs in the PSF membrane matrix. The hardness of the membrane increases with increasing MWCNTs composition up to 0.1 wt%. However, Figures 8 and 9 show flattening behavior from 0.4 to 0.6 and from 0 to 0.2 wt% MWCNTs respectively (due to the agglomeration of MWCNTs). The strength of the MWCNTs/PSF membrane increases with increasing volume fraction of MWCNTs, which is comparable to the results of variation of resilience and rigidity gradient with MWCNTs composition. It is concluded that the homogeneous distribution of MWCNTs within the PSF membrane matrix and the formation of strong interfaces between MWCNTs and PSF enhances the strength, rigidity

gradient and resilience of MWCNT/PSF nanocomposites [29].

In this study, it was proven that MWCNTs could improve could improve the mechanical properties of MWCNTs/PSF nanocomposites. However, some membranes show some irregularities due to the agglomeration of MWCNTs inside the PSF membrane matrix and the low dispersion of MWCNTs in the PSF matrix. Therefore, the majority of PSF/MWCNTs nanocomposites show a homogeneous distribution of MWCNTs in the PSF membrane matrix and strong interfacial bonding MWCNTs and the matrix, which are the main important factors in obtaining strengthening and toughening of MWCNTs/PSF membrane.

3.3 Membrane Filtration Test

3.3.1 Influence of MWCNTs on the Membrane Performance (Pure Water Flux)

To investigate the influence of the MWCNTs on the membrane performance, the cross-flow system was used at room temperature ($25\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$).

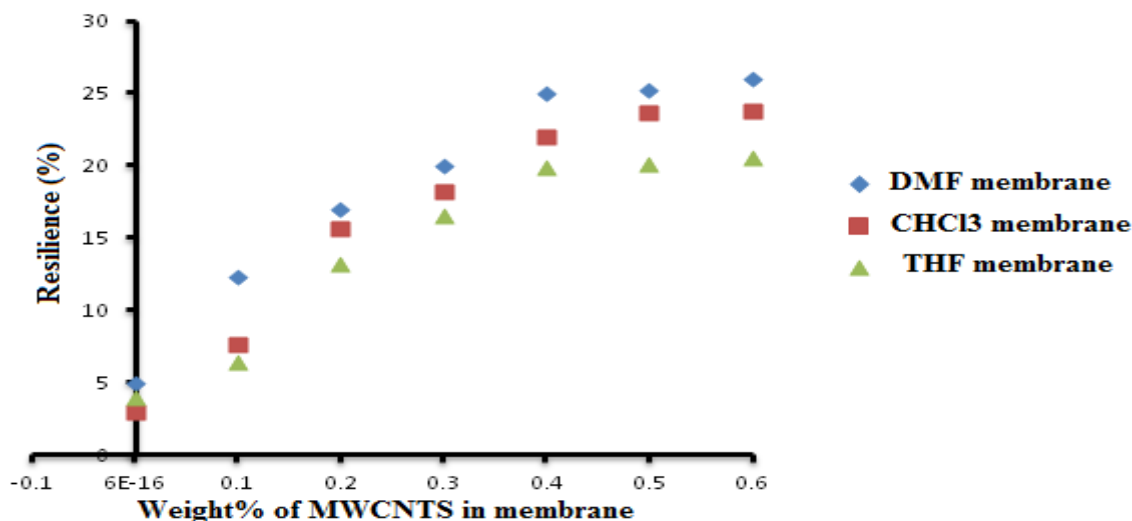


Figure 8. Variation of % resilience with MWCNTs composition.

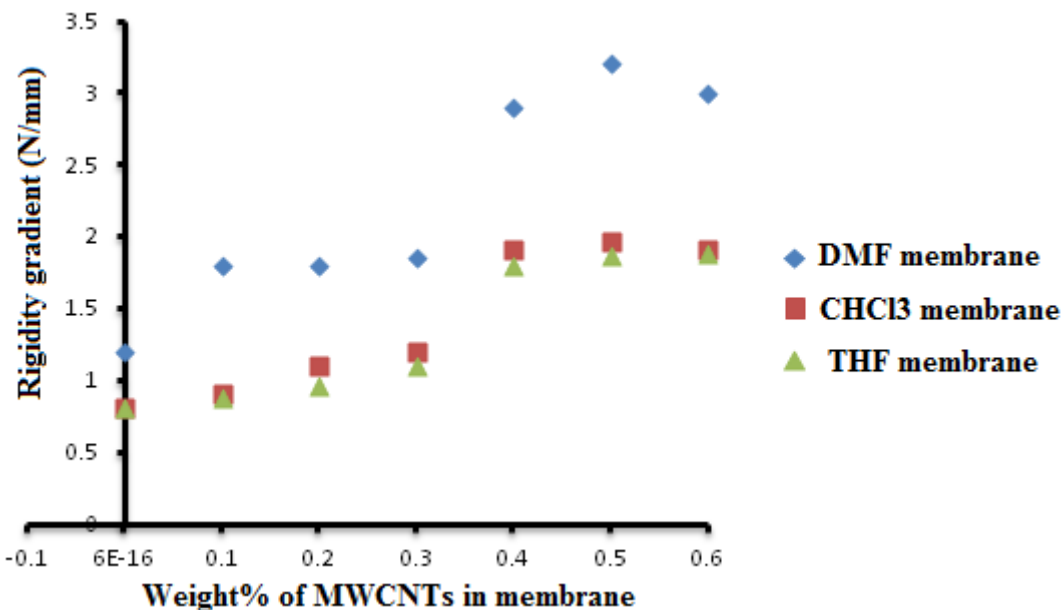


Figure 9. Variation of rigidity gradient with MWCNTs composition.

The effect of weight fraction of MWCNTs on the membrane performance was studied. The MWCNTs/PSF membranes

containing 0.1 to 0.6 wt% MWCNTs were prepared using the phase inversion method [32].

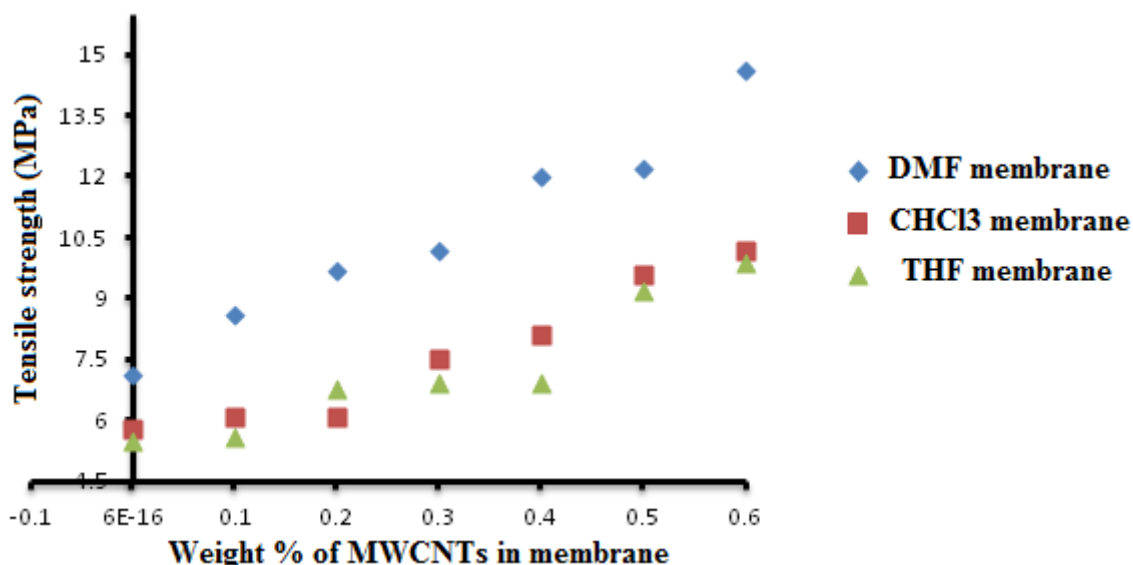


Figure 10. Variation of tensile strength with composition of MWCNTs.

The pure polymeric membrane without MWCNTs was also prepared using the same techniques [32]. Figure 11 shows the flux calculated using equation 1 for different % MWCNTs loadings (at constant pressure of 2 bar) using a cross flow filtration module at room temperature. It has been found that the water flux of the DMF, CHCl3 and THF

blended membranes increases with addition of functionalized MWCNTs. In the case of the DMF membrane incorporated with functionalized MWCNTs, the water flux reaches appreciable values especially, for the 0.4 wt% of MWCNTs which gives the highest water flux of 113 L/m².h. However, a 72 decrease of flux was observed for

concentration of MWCNTs above 0.4 wt% for the three different membranes due to the increasing density of functionalized MWCNTs; this causes the steric hindrance between the functionalized MWCNTs to agglomerate inside the polymer matrix during the phase inversion [32-35]. The increase in water flux is usually found with increase in surface pore size and increased hydrophilicity of the membranes. The higher water flux of the DMF blended membrane might be due to increased surface pore size and the right dispersion of MWCNTs in the PSF membrane matrix, which controls the pore size and alters the pore structure of the PSF layer allowing for greater flux across the membrane.

3.3.2 Influence of Pressure (Driving Force) on the Membrane Performance

The water fluxes of pure polymeric and blended membranes were measured at

room temperature ($25^{\circ}\text{C} \pm 5^{\circ}\text{C}$) and at different transmembrane pressure with a constant concentration of MWCNTs (0.4 wt. %) retained as the optimum MWCNTs concentration from the previous experiments. Figure 12 shows the flux calculation using Equation 1 for different pressures and constant % MWCNTs loading of 0.4 retained as the suitable concentration of MWCNTs in PSF membrane for ultrafiltration using a cross flow module at room temperature. The pure water flux through the membrane increases with the increase in pressure; however, flattening behavior has been observed between 2 and 4 bar for each blended membrane which might be due to fouling inside the pores or on the top surface of the membrane. This is called fouling or blockage inside the membrane pores.

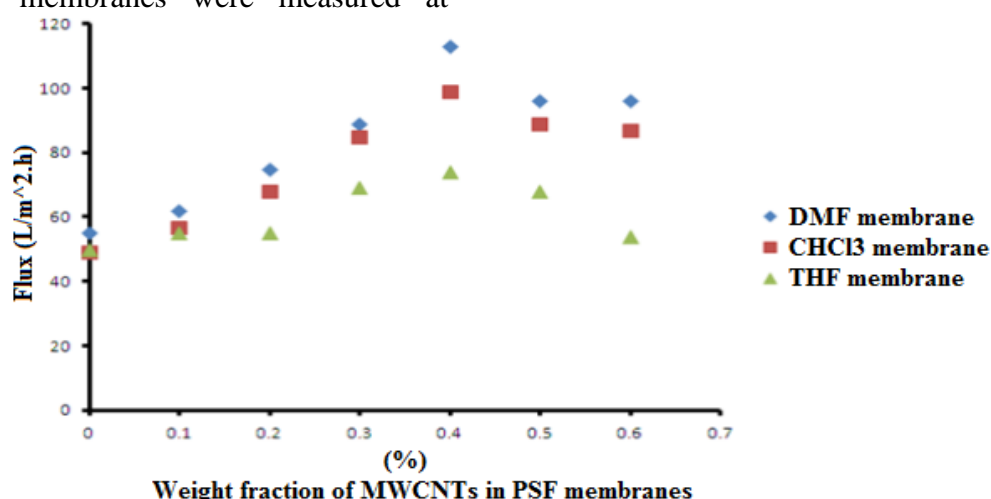


Figure 11. Variation of the pure water flux with MWCNTs composition at different membrane solvents.

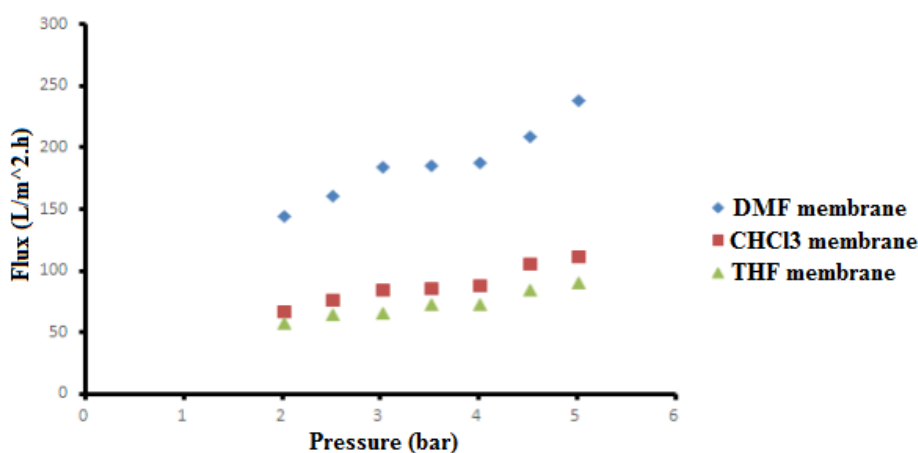


Figure 12. Variation of the pure water flux with pressure at a constant MWCNTs loading.

DMF membrane gives the best water flux which might be due to the hydrophilicity and porosity its mixed matrix membrane.

Blended membrane gives the best water flux which might be due to the hydrophilic since a better dispersion of MWCNTs in DMF solvent across the PSF matrix was observed. The pressure 5 bar gives appreciable results for each blended PSF membrane. The decrease in flux may be predicted after the pressure of 5.5 bar because of the fouling and concentration polarization. The permeate flux was found to increase with an increase of pressure, and flux declines during the initial stages of filtration for all the membranes and then increased continuously (the increase

ranging from 3 to 5 bar). The reason that the pressure and the between retentate and permeate played the role of an effective driving force (and the increased pressure) could overcome the resistance; hence compelling more solution to filter through the membrane and resulting in a higher permeate flux [32-35].

3.3.3 Influence of Filtration Time on Membrane Performance

The water fluxes of pure polymeric and blended membranes were measured at room temperature ($25\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$) and at different filtration time with a constant concentration of MWCNTs (0.4 wt. %) and pressure (4.5 bar) .

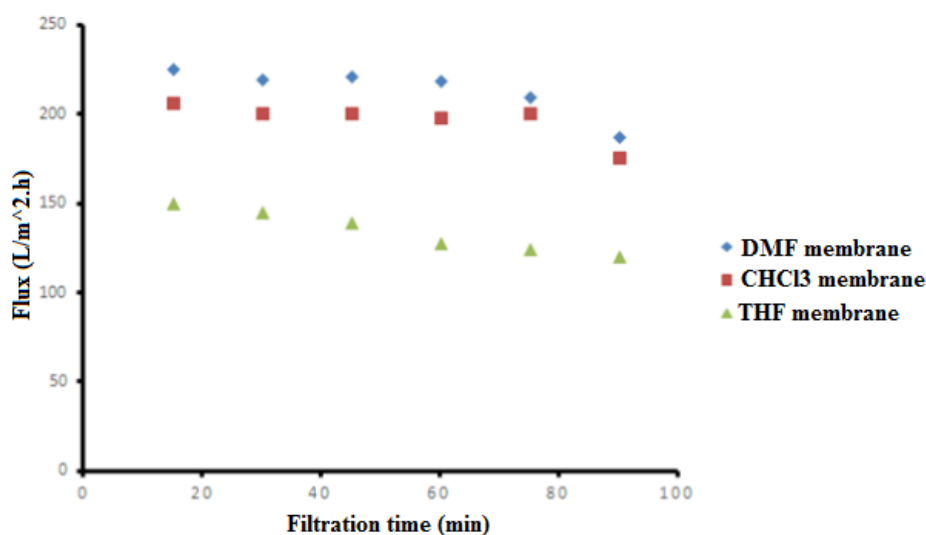


Figure 13. Graph showing the variation of the pure water flux with filtration time at a constant MWCNTs loading

Figures 13 shows the variation of the flux with filtration time at a constant % MWCNT loading of 0.4 and pressure of 4.5 bar (which were retained from the previous experiments) as optimum oil droplets. The different membranes give an appreciable flux for the filtration time from 15 min. The greatest fraction of flux decline was observed after the first 45 min of introducing the feed solution. This flux reduction can be attributed to the adsorption of oil droplets on the surface of

parameters for membrane ultra filtration using a cross flow module at room temperature. The plots show the permeate flux over time during fouling of the pure polymeric and blended membranes with the membranes upon initial introduction of the solution (concentration polarization) [32- 35].

4. CONCLUSION

The main aim of this study was to assess the effect of functionalized MWCNTs on a

PSF membrane and to characterize the system using TEM, SEM, tensile strength test, hydrophilicity (contact angle test) and the cross-flow filtration system. MWCNTs were synthesized using the CVD process at the temperature range: 800 °C - 900 °C.

The MWCNT/PES membranes performance was tested for any improvements in pure water flux. Improved performances were observed with addition of different fractions of MWCNTs on the polymeric membranes produced with different solvents (DMF, CHCl₃ and THF). An appreciable 48.6 % increase in water flux was observed with 0.4 wt% of MWCNTs to PES membrane produced with DMF as solvent. At values above 0.4 wt% MWCNTs the water flux decreased. The increase in permeability of the membrane was related to the hydrophilicity and adsorption effects of MWCNTs. However, increased viscosity of the casting solution at higher MWCNT loading (>0.4wt %), retarded the exchange between solvent and non-solvent during the phase inversion process, smoother membrane surfaces and smaller pores appearing. Hence, water flux was severely limited. At a relatively higher ratio, more MWCNT agglomeration resulted in the formation of gaps, which are large enough for water molecules to pass through. Eventually, water flux increased while the rejection decreased to some extent. Therefore, if a right amount of MWCNTs is added, the permeation flux of the MWCNTs/polymer membranes can be improved and the selectivity can be

simultaneously well maintained. It can be concluded that functionalized MWCNTs modified PSF membranes and improve the mechanical and chemical properties of the polymeric membrane. However, there is a certain amount of MWCNTs to use for blending. DMF has been retained as the best solvent compared to CHCl₃ and THF because it decreased the intertube interactions leading to a better dispersion of MWCNTs in the matrix of the PSF membrane.

5. RECOMMENDATIONS

The cross - flow filtration module used in this work contains a pump with limited range of pressure. For future work, it would be appropriate to use a large pump with large range of pressures to test the efficiency of the membrane.

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CONFLICT OF INTEREST

The authors certify that they have NO affiliation with or involvement in any organization or entity with any financial interest or non financial interest in the subject matter or materials discussed in this manuscript.

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