# Polysulfone/Carbon Nanotubes Asymmetric Nanocomposite Membranes: Effect of Nanotubes Surface Modification on Morphology and Water Permeability

**S. Khoshrou[1], M. R. Moghbeli[1]\*, E. Ghasemi[2]**

[1]*School of Chemical Engineering, Iran University of Science and Technology (IUST), Tehran, Iran*
[2]*Iran Polymer and Petrochemical Institute, Tehran, Iran*

## Abstract

*Polysulfone/carbon nanotubes (PSF/CNTs) nanocomposite membrane was prepared via phase inversion induced by immersion precipitation technique. In addition, the surface of the CNTs was functionalized by polar carboxylic and amine groups to improve the interaction between the CNTs and the polymer matrix. For this purpose, the neat CNTs were chemically treated using sulfuric acid/nitric acid ($H_2SO_4/HNO_3$) mixture and an aromatic amine agent, i.e. 1-4-diamino benzene (DABZ), to produce the functional groups on the CNTs surface. The Fourier transform infrared (FTIR) spectra indicated the presence of carboxylic- and amine-functional groups on the nanotubes surface. Asymmetric PSF composite membrane with various levels of the functionalized CNTs were prepared to investigate the effect of functional group type on the morphology and water flux rate of the resulting membranes. The results showed that the incorporation of the functionalized CNTs up to 0.5 wt% increased the pore size and surface roughness of the sheet membranes, while further addition decreased porosity and roughness. Higher water flux rate was observed for the amine-functionalized CNTs (af-CNTs) reinforced PSF membrane when compared with the membranes reinforced with the carboxyl-functionalized CNTs (cf-CNTs). The stronger compatibility between af-CNTs and the PSF matrix caused higher water permeability. The salt rejection performance of these microfiltration composite membranes was evaluated.*

**Keywords:** *Asymmetric Membrane, CNTs, Polysulfone, Functionalization, Morphology*

---

\* Corresponding author: mr_moghbeli@iust.ac.ir

## 1. Introduction

In recent years, organic and inorganic membranes have been prepared for various industrial separation processes. Among these membranes the polymeric ones due to their inherent characteristics are the most important membranes. These features include their low cost, high efficiency, ease of use, proper mechanical properties, flexibility to shape, and low environmental impacts. Polysulfone (PSF) due to its excellent solubility in a large range of aprotic polar solvents, high thermal resistance and chemical resistance on the wide pH range, resistance in oxidative medium, high mechanical resistance of the films, and high separating power, is mainly used to prepare gas or liquid industrial membranes. Some reinforcements such as zeolite, silica, and carbon nanotubes (CNTs) can improve the mechanical and hydrophilicity of PSF membranes [1-7]. The reason for using CNTs in the PSF matrix is its extraordinary electrical and thermal features and also its exceptional mechanical properties [8-14]. However, the performance of CNTs in improvement of polymer properties depends on the dispersion state of CNTs inside polymer matrix. Van der Waals attraction forces between CNTs causes the nanotubes to be agglomerated [15-19]. Various suitable surfactants, such as cetyl trimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and dodecyldimethyl ammonium bromide Terry (DTAB), and chemical surface functionalization method were utilized to overcome this drawback through increasing the interfacial adhesion between CNTs and polymer matrix [20-23]. Zhang *et al*. [24] studied the fictionalization of CNTs by using hyper-branched polyurethane. They functionalized CNTs with hyper-branched polyurethane and prepared the polyamide/functionalized CNTs nanocomposites via melt mixing process. Dudchenko *et al*. [25] investigated the fouling potential of CNT/polyvinyl alcohol composite microfiltration membrane. Kara *et al*. [26] investigated the electrical and optical percolations of polystyrene/CNT composites by using different mass fractions of CNTs.

The goal of this research work is preparing PSF/CNTs asymmetric membranes via phase inversion technique [27,28]. To improve the compatibility between the CNTs and the polymer matrix in the resultant microfiltration membranes, the surface of the neat CNTs was functionalized by carboxylic and amino groups. Influence of the amount and type of functionality groups of the CNTs on the morphology and water flux of the membrane was investigated. Although some researchers functionalized the CNTs using various aliphatic amino reagents [29,31], less attention has been paid to the utilization of aromatic amines to functionalize the CNTs. In this research work, an aromatic amine agent, i.e. 1-4-diamino benzene (DABZ), as well as the strong acid mixture ($H_2SO_4/HNO_3$) were used to functionalize the CNTs with amine and carboxylic groups, respectively. The presence of aromatic ring in the structure of both the agent and PSF chains seems to

*S. Khoshrou, M. R. Moghbeli, E. Ghasemi*

improve the interaction between the CNTs and the polymer matrix and, consequently, the performance of resulting composite membrane for increasing water flux.

## 2. Experimental
### 2-1. Materials
All chemical reagents were prepared from Merck Co. (Darmstadt, Germany), unless otherwise stated. Polysulfone (MW: 58000 g/mole, density: 1.37 g/cm$^3$) [32], polyvinyl pyrrolidone (PVDF) and CNTs (C-100) were all purchased from Arkema Co. (France). To functionalize the CNTs, nitric acid (65%) and sulfuric acid (98%) were used. Dimethylformamide (DMF), 1-4-diaminobenzene (DABZ), triethylamine (TEA), tetrahydrofuran (THF), and dimethylacetamide (DMA) were used without any further purification. In all experiments, twice-distilled water was used to dilute the acids.

### 2-2. Preparation of cf-CNTs
First, 0.5 g of pure CNTs was poured inside a 200 mL glass balloon. Then, 70 mL nitric acid (65%) and 10 mL sulfuric acid (98%) were added to the CNTs dispersion. The CNTs relative to nitric/sulfuric acid mixture was 0.4 wt%. A magnetic stirrer stirred the dispersion at 200 rpm and 80°C for 5 h. After complete reaction, a black mixture was obtained and separated from the solution using 0.2 μm filter. The CNTs were washed and deionized with water several times to remove any trace of unreacted acids until the pH of rinse water reached close to

neutral level. After this stage, the functionalized sample was dried in a vacuum oven at 100°C for 1 h before use.

### 2-3. Preparation of af-CNTs
0.4 g cf-CNTs prepared in the previous stage was soaked using 0.4 g DABZ and after that, the resulted mixture was added to 20 mL DMF. In order to better solve DABZ in DMF, 2 mL TEA was added to the dispersion. Thereafter, the dispersion was stirred at 200 rpm by magnetic stirrer. Temperature of resulting dispersion was increased to 90°C using a heater and the dispersion was refluxed for 96 h at that temperature. At the end, a black mixture was achieved and filtered with a paper filter. In order to remove the excess DABZ, the resultant black powder was washed three times by THF and then dried for 24 h under vacuum to obtain the dried af-CNTs.

### 2-4. Preparation of the composite membranes
Preparation of the PSF/CNTs microfiltration membrane was carried out via phase inversion method through immersion of the dispersion in a non-solvent (water) bath. Solutions of PSF (15 wt%) in a good solvent (DMF) along with various amounts of the functionalized CNTs (0, 0.05, 0.5, 1 wt% based on total polymer) were prepared. In addition, PVDF (4 wt%) was also added to the dispersion to facilitate the formation of more cavities in the membrane structure [33]. These percentages of the above ingredients

were achieved after doing some tests, because they exhibited more porosity in comparison with other concentrations. For the neat PSF membrane, 0.27 g of PVDF and 1.02 g of PSF were carefully weighed and dissolved in 5.5 g DMA to obtain a clear solution. Thereafter, the solution was stirred at 200 rpm at room temperature for 24 h. Finally, the solution was homogenized using an ultrasonic homogenizer for 10 min, and then held under immovable condition for 24 h to remove the entrapped air bubbles [34]. Then the resulting solutions or dispersions were poured into glass planes to form films with 100 μm thickness using a film applicator. The resultant films were immediately immersed in a distilled water bath and held for a further 24 h to complete the separation phase process. Subsequently, the resulting membranes were placed between two filter papers for 24 h and dried for a further 10 h in a vacuum oven.

For preparation of the PSF/CNTs composite membranes, various amounts of CNTs were added to the prepared polymer solutions. For instance, 0.0035 g of the neat or modified CNTs was dispersed in 5.5 g DMA to prepare 0.05 wt% CNT reinforced membrane. The dispersion was exposed to ultrasound waves for 30 min. Then, 1.02 g PSF and 0.27 g PVDF were added to the dispersion and stirred for 24 h at 200 rpm. The resulting dispersions were again homogenized for 10 min by ultrasonic waves. In order to remove the entrapped air bubbles, the dispersions were kept in stasis condition for 24 h at room temperature. Other stages

for preparing the membrane are like the aforementioned method. The recipes for the preparation of microfiltration membranes using various amounts of CNTs are shown in Table 1.

**Table 1**
Recipes for the preparation of the neat and CNT reinforced PSF membranes.

| Component | Amount (g) |
|---|---|
| Dimethylacetamide | 5.50 |
| Polysulfone | 1.02 |
| Polyvinyl pyrrolidone | 0.27 |
| CNTs | 0.070 , 0.035 , 0.0035* |

*Amount of CNTs in the casting membrane solution: 0.05 , 0.5 and 1 wt%

## 3. Membrane characterization
The bond chemical structure of the neat CNTs, cf-CNTs and cf-CNTs was studied using FTIR spectrometry (IR solution 8400S, Shimadzu, Japan). Morphology of the neat and CNTs-reinforced membranes was studied by means of SEM (Vega, Tescan). AFM device (Dual Scope 95-200E, DME Co.) was used to study the topography of the membrane surface. An experimental set-up was designed and used to evaluate the water permeability through the prepared membranes. The salt rejection performance of the prepared membranes was studied using conductivity test. Conductivity, as a desirable detection method, is a universal property of ions in solution and can be simply connected to ion concentration. However, experimental errors in the conductivity measurements are probable.

*S. Khoshrou, M. R. Moghbeli, E. Ghasemi*

## 4. Results and discussion
### 4-1. CNT functionalization

In order to improve the dispersion of the CNTs in the PSF membrane matrix, carboxylic and amine functional groups were chemically bonded on the CNT surface. Figure 1 indicates the FTIR spectrums of the pure and functionalized CNTs. For the neat CNTs, the peak at wave number 1641 cm$^{-1}$ is related to the C=C bonds. A peak at 3475 cm$^{-1}$ corresponds to hydroxyl groups (OH) of water vapor absorbed by the CNTs. The appearance of a peak at wave number of 1753 cm$^{-1}$ is due to the presence of carbonyl group (C=O) in the cf-CNTs. By comparing the results, it is observed that the intensity of peak at 3470 cm$^{-1}$ in the cf-CNTs is higher than that of the neat CNTs. This behavior shows higher tendency of the functionalized CNTs in absorbing the moisture.

For the af-CNTs, the disappearance of the peak at 1753 cm$^{-1}$ and formation of a new peak at 1639 cm$^{-1}$ is probably due to the overlap of C=O and C=C peaks, which led to the formation of a broad peak in shorter wavelengths. Moreover, the peak observed at wavelength of 1577 cm$^{-1}$ corresponds to flexural vibration of N-H bond of amine groups. Higher intensity in the peak at 3419 cm$^{-1}$ is probably due to the stretching vibration of NH$_2$ groups.
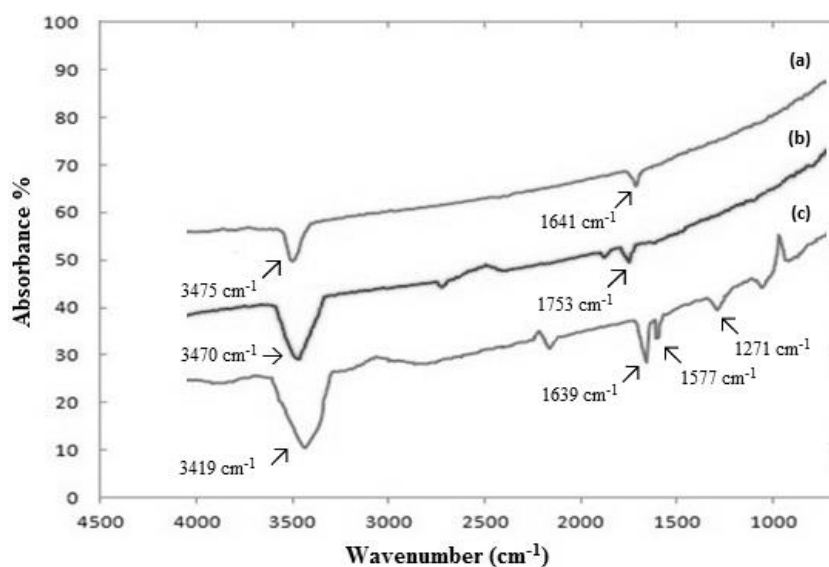


**Figure 1.** FTIR spectrum of: (a) the neat CNTs, (b) cf-CNTs and (c) af-CNTs.

## 5. Membrane morphology

SEM micrographs (Fig. 2) show the cross-section morphology of the microfiltration membranes containing various amounts of cf-CNTs. As shown, a typical asymmetric structure with a dense top layer, porous sub-layer, and fully developed macropores at the bottom were observed for all the prepared membranes. As shown, the pores at the base membranes. As shown, the pores at the base layer are quite large and further extended. A very large channel was observed at the bottom of the neat PSF membrane without any reinforcement (Fig. 2a). However, the incorporation of cf-CNTs in the membrane caused narrower finger pores and a dense top layer is observed (Figs. 2b-c). This behavior can be attributed to increasing the membrane solution viscosity by adding the nanotubes. The

increase in viscosity lowers the solvent-non-solvent exchange rate during the phase separation phenomenon. Figure 3 indicates the morphology of the neat membrane and its composites with 1 wt% CNCs, cf-CNTs and af-CNTs for comparison purposes. The SEM micrograph of the neat membrane (Fig. 3a) shows no lattice pores on the membrane surface. Nevertheless, the porosity of the un-functionalized CNTs reinforced membrane was slightly increased (Fig. 3b).
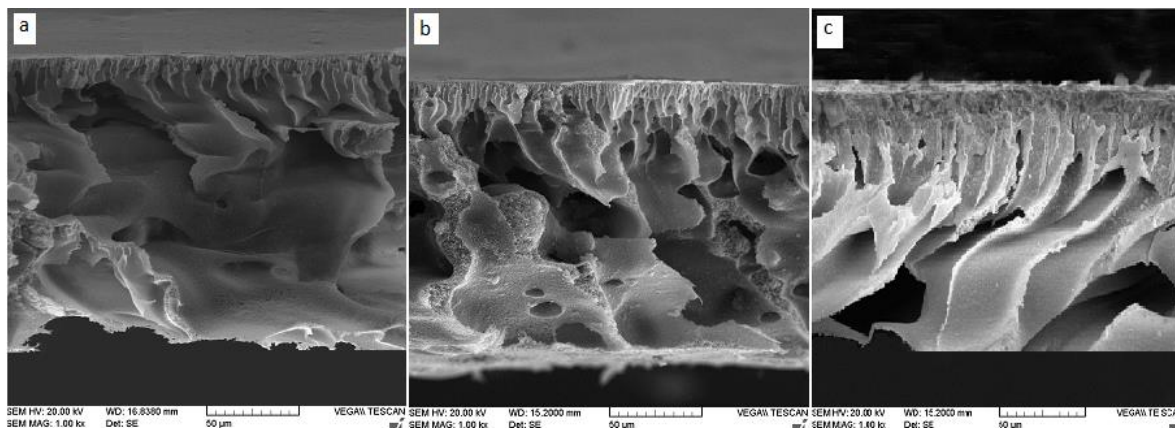


**Figure 2.** SEM micrographs show the cross-section morphology of the PSF membranes containing various cf-CNT levels: (a) 0, (b) 0.5 and (c) 1 wt%.
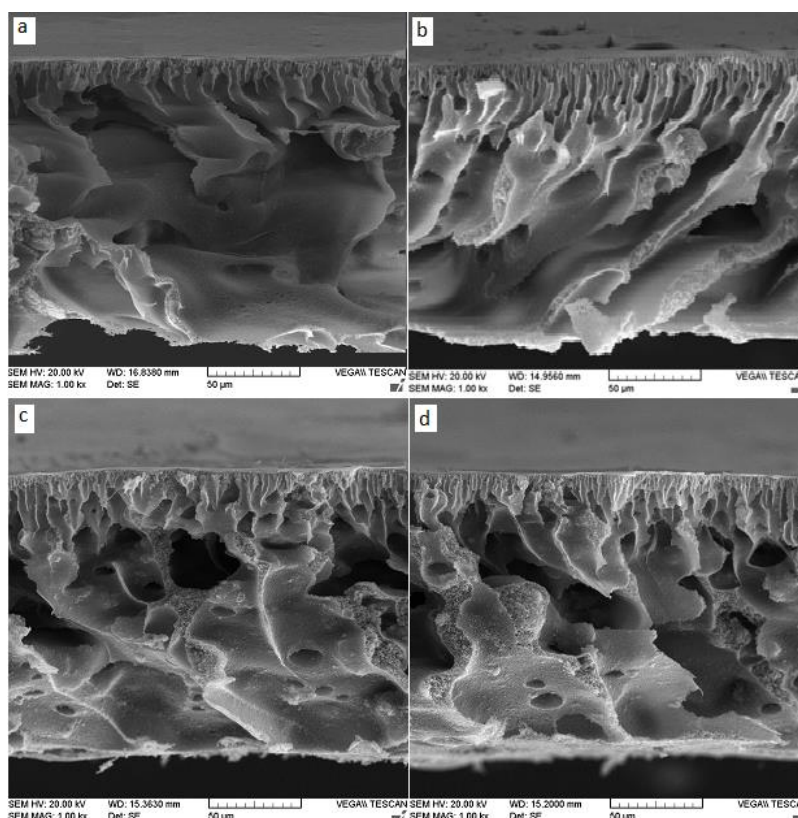


**Figure 3.** SEM micrographs exhibit the cross-section morphology of the PSF membranes containing: a) 0% CNTs, b) 1 wt% neat CNTs, c) 1 wt% cf-CNTs, and d) 1 wt% af-CNTs.

SEM micrograph of the cf-CNTs reinforced membrane (Fig. 3c) indicates a uniform distribution of the holes because the functionalized nanotubes have greater consistency with the membrane matrix to be dispersed. The incorporation of af-CNTs exhibits a denser top layer and formation of larger pores in the bottom layer (Fig. 3d). It should be mentioned that the thickness of top layer in af-CNTs reinforced membrane is significantly higher than that of the cf-CNTs reinforced one. This behavior can be attributed to a stronger interaction between the amine group of the DABZ with the polar groups in the PSF chains. Furthermore, Van der Waals interactions and π-π stacking between the aromatic rings in the DABZ and polymer chains increased the interfacial interaction, which may improve the dispersion state of the functionalized CNTs and enhance the viscosity of the membrane casting solution. In fact, the increase of viscosity could delay the phase separation occurrence and enhance the thickness of the membrane top layer due to formation of narrower longer finger pores. AFM images exhibit the surface topography of the composite membranes containing various amounts of the functionalized CNTs. As seen, the dispersion of the CNTs on the surface was observed through three-dimensional images (Fig. 4). In these images, the bright regions represent the highest points of the membrane surface and dark regions indicate the lowest points, valleys or holes, on the surface. Adding the functionalized CNTs to the casting membrane solution affected the membrane surface topology significantly. It seems that the porosity and pore size of the membrane increased when the amount of the CNTs increased up to 0.5 wt% in the membrane solution. Therefore, the polymer membrane containing 0.5 wt% of CNTs exhibited the larger pore size and higher surface roughness. However, further increase in the amount of functionalized CNTs resulted in smooth surface and decreased the mean pore size. Additionally, surface parameters of the membranes were calculated by SPM DME software and summarized in Table 2. The results indicate that increasing the CNT level up to 0.5 wt% increased the average surface roughness (Sa) of the neat membrane from 16.9 to 28.2 nm, while further increase to 1 wt% CNTs lowered the roughness to some extent.
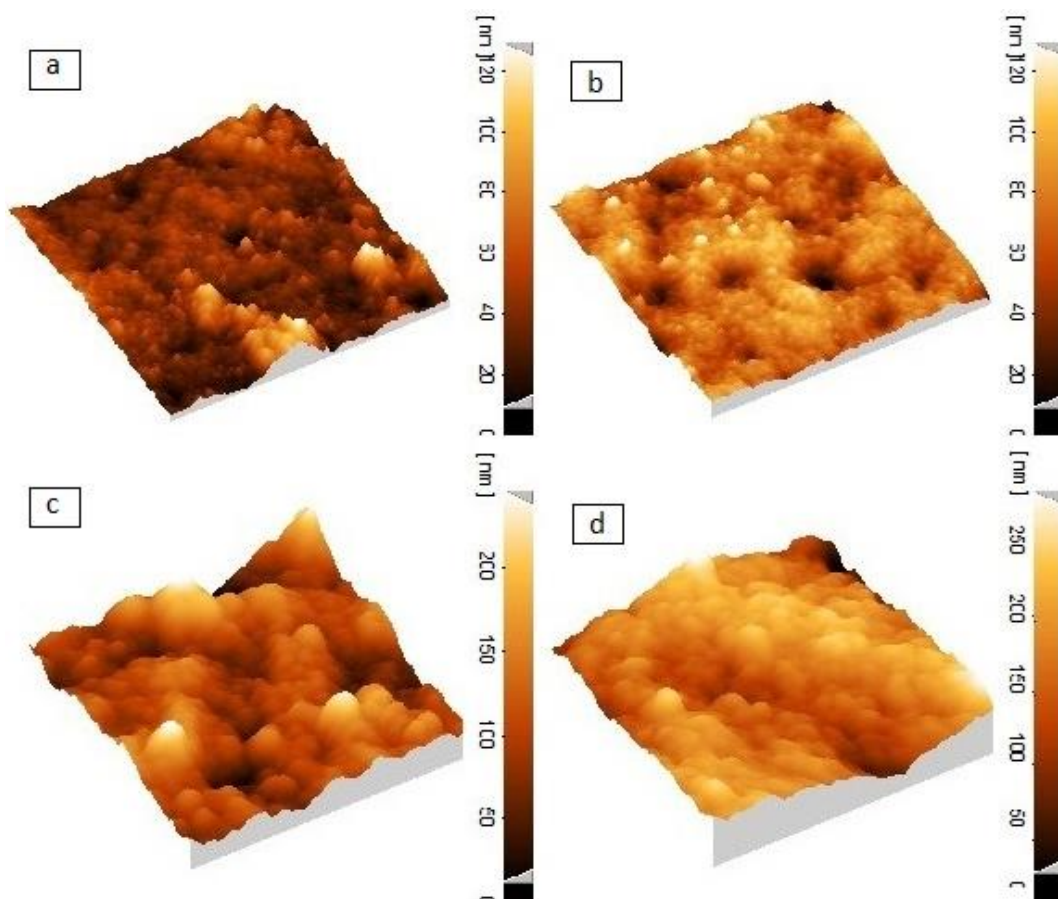
**Figure 4.** AFM images of the PSF membranes containing various levels of cf-CNTs: (a) 0, (b) 0.05, (c) 0.5, and (d) 1 wt%.

**Table 2**
Surface roughness parameters of the composite membranes with various CNT levels.
$s_a$: average roughness, $s_z$: average difference between the highest peak and the lowest point, $s_q$: root mean squares of Z parameter.

| Code | Concentration of CNTs | Sz (nm) | Sa (nm) | Sq (nm) |
|------|----------------------|---------|---------|---------|
| M1   | 0                    | 153     | 16.9    | 21.1    |
| M2   | 0.05                 | 172     | 19.9    | 23.4    |
| M3   | 0.5                  | 253     | 28.2    | 33.5    |
| M4   | 1                    | 216     | 22.4    | 30.1    |

For the membranes prepared using various cf-CNT levels below 1 wt%, the hydrophilicity effect of the casting solution can overcome the viscosity enhancement to improve the solvent/non-solvent exchange rate during the phase inversion process, hence membranes with coarser surface morphology and larger pore size were observed. On the contrary, further increase in the CNT level to 1 wt% enhanced the casting solution viscosity and reduced the solvent/non-solvent exchange rate, which led

to the formation of solid membrane with lower surface roughness.

## 6. Pure water permeability
### 6-1. Effect of CNT level
In order to study the water permeability performance of the prepared membranes, pure water flux test was carried out at room temperature. In this case, the performance of the neat PSF and its composites with various amounts of cf-CNTs (0, 0.05, 0.5 and 1 wt%) was evaluated. Figure 5 indicates the effect of the functionalized CNT level on the pure water flux of the resulting membranes. As shown, the incorporation of cf-CNTs up to 0.5 wt% CNTs significantly increased the water flux of PSF membrane from 8 to 30 $l/m^2h$, while further increase decreased the flux to some extent. This behavior can be related to the morphology and hydrophilicity of the composite membranes prepared using different CNT levels.
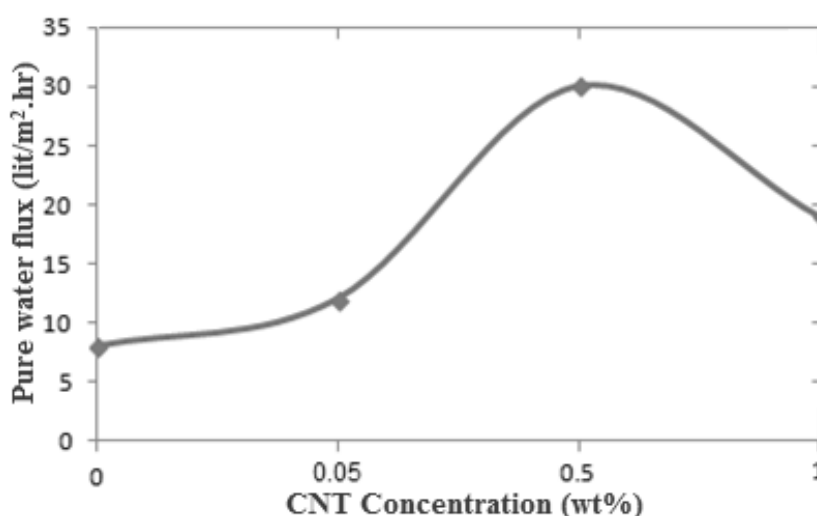


**Figure 5.** Pure water flux rate passing through the PSF membranes containing different amounts of the cf-CNTs.

In fact, water flux through the membranes was influenced by both hydrophilicity and porosity factors. The introduction of cf-CNTs reinforced membranes below 0.5 wt% increased the hydrophilicity due to the presence of carboxylic group of the nanotubes which could enhance the solvent/non-solvent exchange rate during the phase inversion process. Therefore, larger pores in the membrane structure and, consequently, higher water flux rate were obtained. However, increasing the amount of CNTs above 0.5 wt% increased the viscosity of membrane casting solution and decreased the solvent/non-solvent exchange rate. This viscosity enhancement resulted in composite membranes with less porosity and lower pure water flux rate. Figure 5 indicates that the increase in cf-CNT level from 0.5 to 1 wt% lowered the water flux rate from 30 to 19 $l/m^2h$.

### 6-2. Effect of functional group type
Additionally, the influence of the functionality CNT group on the water flux rate was investigated (Fig. 6). As shown, the

pure water flux rate of the neat PSF membrane is higher than the un-functionalized CNTs membrane. This is probably due to the presence of hydrophobic un-functionalized CNTs in the polymer matrix which resulted in CNT agglomeration, which clogged the membrane pores. On the contrary, the water flux of membrane containing cf-CNTs is higher than the aforementioned membranes because of the presence of the hydrophilic CNTs in the membrane structure. These cf-CNTs with probable good dispersion in the membrane improved the hydrophilicity and increased the water flow rate. The S=O bonds in the neat PSF membrane absorb water molecules and prevent them from passing through the membrane. However, bonding the carboxylic groups with sulfur atoms of PSF chains may decrease the sulfur's ability to absorb water molecules and, consequently, increase the water permeability. PSF/af-CNTs composite membrane showed the highest pure water flux rate in comparison with the other above-mentioned membranes. A proper interaction between the aromatic rings both in the amine modifier and the polymer chains as well as the Van der Waals interactions and $\pi$-$\pi$ stacking, provides better CNT dispersion in the membrane matrix. In addition, the increase of the interaction between the nitrogen of the af-CNTs and the sulfur atoms of PSF chains decreased the ability of sulfur atoms in adsorption of water molecules.
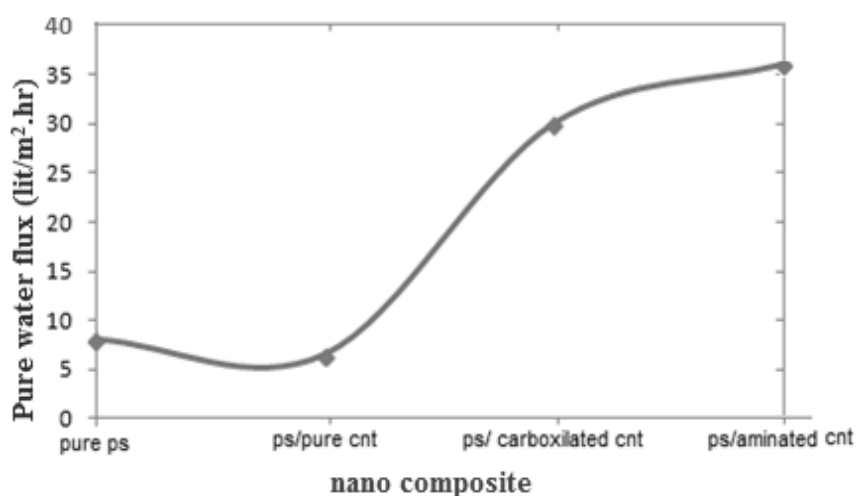


**Figure 6.** Pure water flux passing through the PSF membranes with different types of the functionalized CNTs.

## 7. Salt rejection performance

A separation test was carried out to evaluate the salt rejection potential of the resulting neat and composite membranes. These asymmetric reinforced membranes can be used as a support for manufacturing reverse osmosis (RO) membranes. Therefore, salt-rejection performance of both support and active top layer in RO membranes is an important parameter to prepare water-treatment apparatuses. For this purpose, an aqueous NaCl solution (200 ppm) in 3 bar applied pressure was used to evaluate the performance of PSF

membranes with different amounts of cf-CNTs (0, 0.05, 0.5 and 1 wt%). In order to investigate the performance of membranes, researchers use different salts, such as NaCl and MgCl₂. Because of easy availability and valid results of NaCl in membrane tests, in this work NaCl was used for salt rejection test. The separation process for all the reinforced membranes was carried out under unique conditions, i.e. the same process temperature and pressure parameters. After separation, the permeate portion was collected to determine the salt rejection efficiency using conductivity apparatus. The reinforced membranes with various levels of cf-CNTs were used for salt rejection test. Figure 7 shows the results of the electrical conductivity of permeates passed through the reinforced membranes with the various levels of the functionalized CNCs. It is clear that the lower conductivity in the permeate means lower concentration of NaCl. The electrical conductivity of the solution feed was 1.09 s/m. It is observed that the membrane containing 0.5 wt% cf-CNTs has the lowest conductivity in comparison with the other membranes. The presence of the charged CNTs on the membrane surface creates repulsive force between ions in the solution and ions on the nanotubes surface, which prevents the penetration of the salt ions through the membrane. Generally, membrane behavior in passing the ions is influenced by Donnan mechanism. Ionization of the carboxylic functional groups of the CNTs on the

membrane surface provides negative electrical charges over the surface and causes high negative zeta potential in neutral pH. The negative potential can create a strong electrostatic repulsive force with the same charged ions in the aqueous salt solution. This repulsion depends on membrane charge, ionic strength, and ions capacity. When a charged membrane is in contact with an electrolyte solution, the charged surface adsorbs counter ions. This adsorption results in decrease in concentration of the counter ions in the solution, Therefore, the concentration of the same ions in the solution would increase. Because of this difference in ions concentration, a potential difference in both interface of membranes and solution was developed which led to an electrochemical balance between the membrane and solution. The reinforced membranes containing less than 1wt% cf-CNTs act based on Donnan mechanism to reject the salt ions. However, when the concentration of the CNTs in the membrane surface becomes 1 wt%, the ion concentration on the membrane surface considerably increased and caused the concentration of the counter ions to remarkably decrease in the aqueous salt solution. Due to decrease in ions concentration on the membrane surface, its ability to prevent the penetration ions would decrease and consequently the more ions can pass through the composite membrane and increase the conductivity (Fig. 7).
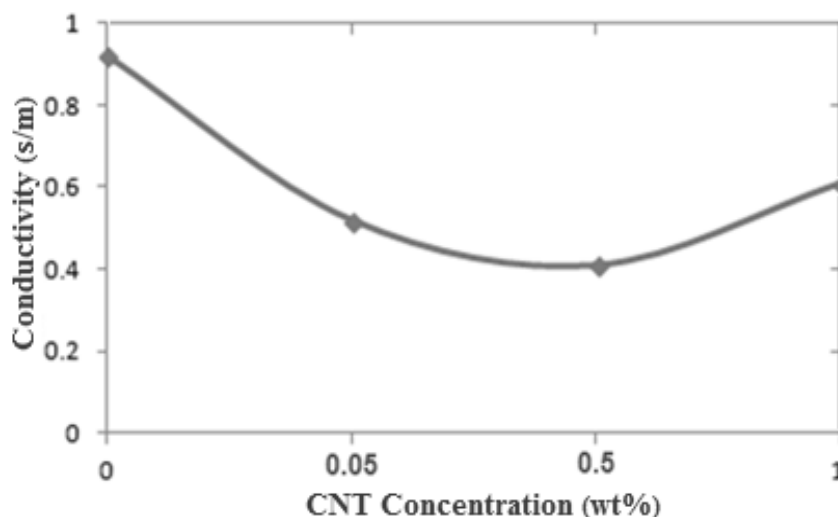
**Figure 7.** Electrical conductivity of the permeate passing through the PSF membranes reinforced with various amounts of cf-CNTs.

## 8. Conclusions

PSF membrane reinforced using various levels of CNTs were successfully prepared via phase inversion induced by immersion precipitation technique. The effect of amount and surface functionalization of the CNTs on morphology and pure water permeability of the resulting composite membrane were investigated. The SEM micrographs showed that using the cf-CNTs and af-CNTs resulted in a typical asymmetric membrane structure and probable proper CNT dispersion in the PSF matrix. In fact, the functionalized CNTs increased the porosity and hydrophilicity of the resulting composite membranes as compared with the neat membrane without any reinforcement. However, the presence of aromatic groups in both the selected amine agents, i.e. DABZ, further increased the compatibility between the nanotubes and polymer matrix and consequently the membrane porosity. The incorporation of the functionalized CNTs up to 0.5 wt% enhanced the porosity and pure water flux through the membrane, while further increase in the amount of functionalized CNTs decreased the mean pore size and pure water flux, to some extent. This behavior can be attributed to the CNT agglomeration in the polymer matrix. The results showed that the af-CNTs could increase the water flux more than the cf-CNTs because of the presence of nitrogen atoms and hydrogen bond formation between water molecules and amino groups in the reinforced membranes. On contrary the membrane reinforced with cf-CNTs and af-CNTs is more compatible with the polymer matrix and further increases the hydrophilicity and water flux of resulting composite membranes.

## Reference

[1] Ciobanu, M. Marin, L. Cozan, V. and Bruma, M., "Aromatic polysulfones used in sensor applications", *Rev. Adv. Mater. Sci.*, **22**, 89 (2009).

[2] Medina-Gonzalez, Y. and Remigy, J., "Sonication-assisted preparation of pristine MWCNT–polysulfone conductive

microporous membranes", *Mater. Lett.*, **65**, 229 (2011)

[3] Ulbricht, M., "Advanced functional polymer membranes", *Polymer*, **47**, 2217 (2006).

[4] Kim, S. Chen, L. Johnson, J. K. and Marand, E., "Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: theory and experiment", *J. Membrane Sci.*, **294**, 147 (2007).

[5] Sanchez, S. Pumera, M. and Fabregas, E., "Carbon nanotube/polysulfone screen-printed electrochemical immunosensor", *Biosens. Bioelectron.*, **23**, 332 (2007).

[6] Favvas, E. P. Nitodas, S. F. Stefopoulos, A. A. Papageorgiou, S. K. Stefanopoulos, K. L. and Mitropoulos, A. Ch., "High purity multi-walled carbon nanotubes: preparation, characterization and performance as filler materials in co-polyimide hollow fiber membranes", *Sep. Purif. Technol.*, **122**, 262 (2014).

[7] Khalid, A. Al-Juhani, A. A. Al-Hamouz, O. Ch. Laoui, T. Khan, Z. and Atieh, M. A., "Preparation and properties of nanocomposite polysulfone/multi-walled carbon nanotubes membranes for desalination", *Desalination*, **367**, 134 (2015).

[8] de Lannoy, Ch. Soyer, E. and Wiesner, M. R., "Optimizing carbon nanotube-reinforced polysulfone ultrafiltration membranes through carboxylic acid functionalization", *J. Membrane Sci.*, **447**, 395 (2013).

[9] Wang, J. Lang, W. Xu, H. Zhang, X. and Guo, Y., "Improved poly(vinyl butyral) hollow fiber membranes by embedding multi-walled carbon nanotube for the

ultrafiltrations of bovine serum albumin and humic acid", *Chem. Eng. J.*, **260**, 90 (2015).

[10] Stankova, L. Fraczek-Szczypta, A. Blazewicz, M. Filova, E. Blazewicz, S. Lisa, V. and Bacakova, L., "Human osteoblast-like MG 63 cells on polysulfone modified with carbon nanotubes or carbon nanohorns", *Carbon*, **67**, 578 (2014).

[11] Herrera-Herrera, A. V. Gonzalez-Curbelo, M. Hernandez-Borges, J. and Rodriguez-Delgado, M. A., "Carbon nanotubes application in separation science", *Anal. Chim. Acta*, **73**, 1 (2012).

[12] Kim, S. Fornasiero, F. Park, H. G. In, J. B. Meshot, E. Giraldo, G. Stadermann, M. Fireman, M. Shan, J. Grigoropoulos, C. P. and Bakajin, O., "Fabrication of flexible, aligned carbon nanotube/polymer composite membranes by in situ polymerization", *J. Membrane Sci.*, **460**, 91 (2014).

[13] Han, Zh. and Fina, A., "Thermal conductivity of carbon nanotubes and their polymer nanocomposite", *Prog. Polym. Sci.*, **36**, 914 (2011).

[14] Wong, K. C. Goh, P. S. and Ismail, A. F., "Gas separation performance of thin film nanocomposite membranes incorporated with polymethyl methacrylate grafted multi-walled carbon nanotubes", *Int. Biodeter. Biodegr.*, **102**, 339 (2015).

[15] Siddiqui, N. A. Khan, Sh. U. Ma, P. Ch. Li, Ch. Y. and Kim, J., "Manufacturing and characterization of carbon fibre/epoxy composite prepregs containing carbon nanotubes", *Compos. Part A Appl. S.*, **42**, 1412 (2011).

[16] Wei, F. Zhang, Q. Qian, W. Yu, H. Wang, Y. Luo, G. Xu, G. and Wang, D.,

"The mass production of carbon nanotubes using a nano-agglomerate fluidized bed reactor: A multiscale space–time analysis", *Powder Technol.*, **183**, 10 (2008).

[17] Siddiqui, N. A. Li, E. L. Sham, M. Tang, B. Zh. Gao, Sh. L. Mader, E. and Kim, J., "Tensile strength of glass fibres with carbon nanotube–epoxy nanocomposite coating: effects of CNT morphology and dispersion state", *Compos. Part A Appl. S.*, **41**, 539 (2010).

[18] Fiedler, B. Gojny, F. H. Wichmann, M. H. G. Nolte, M. C. M. and Schulte, K., "Fundamental aspects of nano-reinforced composites", *Compos. Sci. Technol.*, **66**, 3115 (2006).

[19] Ma, P. Siddiqu, N. Marom, G. and Kim, J., "Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites", *Compos. Part A Appl. S.*, **41**, 1345 (2010).

[20] Das, D. and Das, P. K., "Superior activity of structurally deprived enzyme-carbon nanotube hybrids in cationic reverse micelles", *Langmuir*, **25**, 4421 (2009).

[21] Yurekli, K. Mitchell, C. and Krishnamoorti, R., "Small-angle neutron scattering from surfactant-assisted aqueous dispersions of carbon nanotubes", *J. Am. Chem. Soc.*, **126**, 9902 (2004).

[22] Rausch, J. Zhuang, R. and Mader, E., "Surfactant assisted dispersion of functionalized multi-walled carbon nanotubes in aqueous media", *Compos. Part A Appl. S.*, **41**, 1038 (2010).

[23] Hilding, J. Grulke, E. Zhang, Z. G. and Lockwood, F., "Dispersion of carbon nanotubes in liquids", *J. Dispers. Sci. Technol.*, **24**, 1 (2003).

[24] Zhang, R. H. Yang, Y. K. Xie, X. L. and Li, R. K. Y., "Dispersion and crystallization studies of hyper-branched poly(urea-urethane)s-grafted CNTs filled polyamide-6 nanocomposites", *Compos. Part A Appl. S.*, **41**, 670 (2010).

[25] Dudchenko, A. Rolf, J. Russell, K. Duan, W. and Jassby, D., "Organic fouling inhibition on electrically conducting carbon nanotube–polyvinyl alcohol composite ultrafiltration membranes", *J. Membrane Sci.*, **468**, 1 (2014).

[26] Kara, S. Arda, E. Dolastir, F. and Pekcan, O., "Electrical and optical percolation of polystyrene latex-multiwalled carbon nanotube composite", *J. Colloid Interf. Sci.*, **344**, 395 (2010).

[27] Chen, Sh. Liou, R. Lin, Y. Lai, Ch. and Lai, J., "Preparation and characterizations of asymmetric sulfonated polysulfone membranes by wet phase inversion method", *Eur. Polym. J.*, **45**, 1293 (2009).

[28] Temtem, M. Casimiro, T. and Aguiar-Ricardo, A., "Solvent power and depressurization rate effects in the formation of polysulfone membranes with $CO_2$-assisted phase inversion method", *J. Membrane Sci.*, **283**, 244 (2006).

[29] Tasis, D. Tagmatarchis, N. Bianco, A. and Prato, M., "Chemistry of carbon nanotubes", *Chem. Rev.*, **106**, 1105 (2006).

[30] Sahooa, N. G. Rana, S. Cho, J. W. Li, L. and Chan, S. H., "Polymer nanocomposites based on functionalized CNTs", *Prog. Polym. Sci.*, **35**, 837 (2010).

[31] LaeeqKhan, A. Cano-Odena, A. Gutierrez, B. Minguillón, C. and Vankelecom, I., "Hydrogen separation and purification using polysulfone acrylate–zeolite mixed matrix membranes", *J. Membrane Sci.*, **350**, 340 (2010).

[32] Mark, J. E., Polymer Data Handbook, Oxford University Press, England, p. 480 (1999).

[33] Amirilargani, M., Saljoughi, E., Mohammadi, T. and Moghbeli, M. R., "Effects of coagulation bath temperature and polyvinylpyrrolidone content on flat sheet asymmetric polyethersulfone membranes", *Polym. Eng. Sci.*, **50**, 885 (2010).

[34] Medina-Gonzalez, Y. and Remigy, J., "Sonication-assisted preparation of pristine MWCNT–polysulfone conductive microporous membranes", *Mater. Lett.*, **65**, 229 (2011).