

Synthesis and Study of Novel Nanostructured Membranes Incorporating N-doped CNTs for Water Treatment

S.D. Mhlanga^{a,b,*}, N. Phao^b, E.N. Nxumalo^a and B.B. Mamba^a

^aDepartment of Applied Chemistry, University of Johannesburg, P.O. Box 17011, Doornfontein, 2028, Johannesburg, South Africa

^bMolecular Science Institute, School of Chemistry, and the DST/NRF CoE in Strong Materials, University of the Witwatersrand, Private Bag 3, Wits, 2050, Johannesburg, South Africa

ABSTRACT

This paper presents the synthesis and evaluation of blend membranes of polyethersulfone (PES) containing Ag nanoparticles dispersed on N-doped carbon nanotubes (N-CNTs). The blend membranes were checked for any improved properties and tested for their efficacy in rejecting polyethylene glycol (PEG). The mechanical stability of the blend membranes increased from 3.7 to 4.4 MPa with a small addition of N-CNTs. Furthermore, the performance studies using a cross-flow system showed a 46% increase in pure water flux and a 13% increase in rejections for N-CNT blend PES membranes as compared to the pristine PES membrane. Characterization of the Ag/N-CNTs and the blend membranes was performed by SEM, TEM, FTIR, AFM and contact angle measurements. A study of the fouling capacity of the membranes was studied using humic acid.

Keywords: Nanocomposite membranes, polyethersulphone, nitrogen-doped carbon nanotubes, permeability, fouling

1 INTRODUCTION

Environmental pollution alleviation and the increasing demand for clean safe water are amongst some of the most critical challenges faced by nations worldwide [1]. Besides water supply shortages, pollution caused by waterborne diseases and hazardous chemicals poses a great health threat to millions of people. In general, water quality in South Africa and around the world is deteriorating due to contamination by organic, inorganic and microbial substances [2]. Although, conventional drinking water disinfection methods employed can be effective they have their own setbacks.

Membrane-based separations are potentially more economical and easier to implement than competing conventional separation technologies e.g. activated carbon. Also, their low energy and space requirement, as well as simplicity of operation renders them suitable for use in separation processes [3]. This technology has to date been widely used in pure and wastewater treatment for re-use. Also, membrane technologies have been employed in the treatment of municipal wastewater and oil spillages [3].

Membrane fouling is however still a serious factor limiting the use of membrane technologies [3]. In an attempt to solve the problems caused by fouling, many research groups have utilised carbon nanotubes (CNTs) as additives to improve the properties of the membranes. Previous studies by Shawky *et al.* have shown that multi walled carbon nanotubes (MWCNTs) blended polyamide membranes can improve mechanical and rejection properties [4]. Celik *et al.* have shown that MWCNT blended polyethersulphone membranes show increased roughness, hydrophilicity, porosity and water flux, which subsequently enhances the resistance of the membranes to fouling [5]

It is clear that drinking water contamination has reached unavoidable levels in terms of the population size and economy affected. Challenges relating to drinking water quality cannot be alleviated with one solution. Methods involving advanced techniques at the nanoscale still have to be probed and smart solutions with high performance must be developed. From this point of view, this study sought to synthesize advanced membranes incorporating silver (Ag) metal nanoparticles dispersed on nitrogen doped carbon nanotubes (N-CNTs) for use in water purification.

2 EXPERIMENTAL

2.1. Synthesis and functionalization of N-CNTs

N-CNTs were synthesized by a modified chemical vapour deposition (CVD) method [6]. The produced N-CNTs were then functionalized by adding them to a solution of 35% HNO₃, and stirred under reflux for 4 h at 110 °C. The CNTs were then dried in an oven at 120 °C for 12 h. The functionalized N-CNTs were then denoted as fN-CNTs.

2.2. Characterization of N-CNTs

The structural morphology and size distribution of the fN-CNTs were determined by transmission electron microscopy (TEM) using a FEI Tecnai G2 Spirit electron

microscope at 120 kV. To quantify the nitrogen content in the N-CNTs, carbon and nitrogen (C% and N%) analysis was done using a Carlo Erba NA 1500 C/N/S analyzer, which uses gas chromatographic (GC) separation of the gases produced on total combustion of the sample.

2.3. Membrane synthesis and characterization

The N-CNT/PES blend membranes were synthesized using a phase inversion method. PES was supplied by Solvay Advanced Polymer (South Africa). The fN-CNT/PES blend membranes were prepared by first dispersing the fN-CNTs in NMP to form a homogenous mixture. After dispersing the fN-CNTs in solvent, PES was dissolved in the fN-CNT/NMP solution by continuous stirring and heating at 80 °C for 3 h. The resultant solution was then left overnight to allow the product to settle and remove air-bubbles. The polymer solution was cast on a glass plate using a 200 µm thick casting knife. The glass plate, coated with a wet polymer solution was left to air-dry for 40 s. This was followed by dipping the glass plate into a water bath (deionised water). The formed membranes were subsequently stored in deionised water until use.

The surface morphology of the membranes was studied using the Nova nano scanning electron microscopy (SEM) 200 and a Dimension 3100 Veeco atomic force microscopy (AFM). The performances of the fN-CNT/PES blend membranes were studied by measuring the pure water flux and rejections of 500 ppm Polyethylene glycol (PEG) (10 000). Experiments were carried out using the cross-flow filtration system (Sterlitech, USA) with a membrane area of 14.6 cm² at room temperature. The membranes were preconditioned by compacting with deionised water at an applied pressure until steady fluxes were obtained.

3. RESULTS AND DISCUSSION

3.1 TEM and SEM analysis of fN-CNTs and blend membranes

TEM images of the fN-CNTs without and with Ag NPs are shown in Figure 1. The fN-CNTs were found to have outer diameters ranging between 30 – 45 nm and they were characterized with bamboo compartments in their inner walls, which is typical of CVD synthesized N-CNTs. Indeed CN analysis revealed that these fN-CNTs contained 2 % nitrogen. The Ag NPs loaded onto the fN-CNTs could be identified as small dark spots on the outer walls of the CNTs. The AgNPs were uniformly dispersed on the N-CNTs, exhibiting diameters ranging from 2-10 nm with a mean size of 6.4 nm. The dispersion of the Ag NPs on the fN-CNTs was done in an attempt to reduce any fouling of the membranes incorporating the N-CNTs while the N-

CNTs themselves improved the mechanical strength of the membranes.

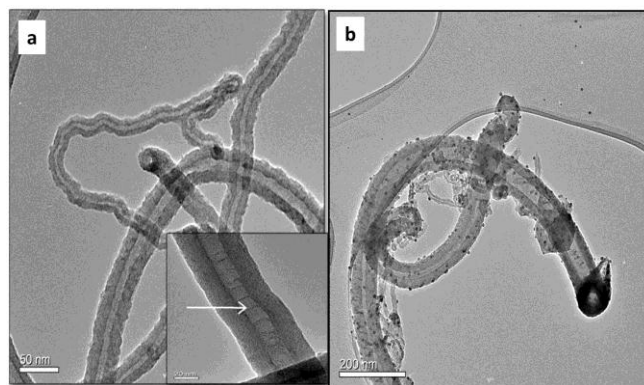


Figure 1: TEM images of fN-CNTs without (a) and with Ag NPs dispersed on their surface (b).

The materials above were the added to PES to form thin film blend membranes. Figure 2 shows a cross-sectional view of the fN-CNT/PES blend membranes. All membranes exhibited a similar asymmetric structure which is defined by a dense top layer and a highly porous sub-layer. No distinct difference was observed in structure between pristine PES and the fN-CNT/PES blend membranes. However, the average widths of pores immediately beneath the surface structure were slightly different. The widths were found to be 1.95, 1.63, 1.46 and 1.29 µm for PES, 0.02% N-CNT/PES, 0.04% N-CNT/PES and 0.08% N-CNT/PES respectively.

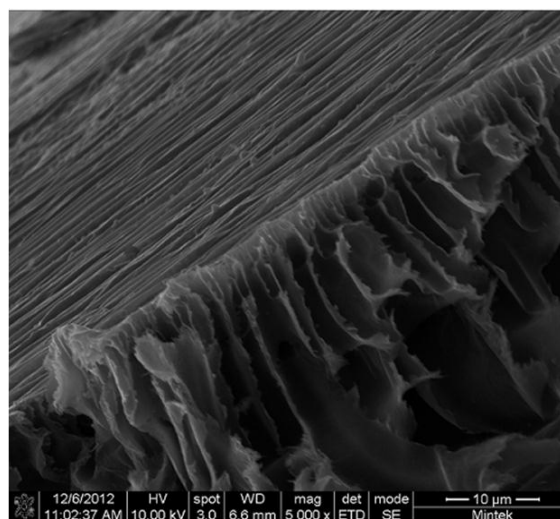


Figure 2: A typical cross-sectional view of fN-CNT/PES blend membranes synthesized using the phase inversion method.

3.2 Mechanical properties of the fN-CNT/PES blend membranes

The mean modulus, ultimate tensile strength (UTS), and tensile strain of the blend membranes as a function of fN-

CNT content are provided in Table 1. For both the modulus and the UTS increases in membrane stability are evident at low fN-CNT fractions. The increase in fN-CNT loadings from 0 to 0.04 wt% in the PES membrane increased the modulus from 114 to 138 MPa and the UTS from 3.8 to 4.5 MPa. Also, an increase in tensile stress at tensile strength from 3.7 to 4.4 MPa was observed. These improvements are attributed to the strong interaction (hydrogen bonding) between the PES matrix and the N-CNTs at low N-CNT fractions. A decrease in modulus, tensile strength and tensile strain was observed at N-CNT loadings above 0.04 wt%. This is consistent with increase in rigidity of the membrane structure, thus, leading to a decrease in mechanical stability.

Table 1: Mechanical properties of pristine PES and fN-CNT/PES blend membranes.

Sample Name	Modulus (MPa)	Tensile stress at strength (MPa)	UTS (MPa)	Elongation at break (%)
PES	114	3.7	3.8	22
0.02 N-CNT/PES	138	4.0	4.1	14.5
0.04 N-CNT/PES	135	4.4	4.5	18.2
0.08 N-CNT/PES	100	2.6	2.7	7.8
0.5 N-CNT/PES	123	3.2	3.2	6.6

3.3 Membrane performance: flux, and rejection studies

To investigate the influence of the fN-CNTs on the membrane performance, the contact angle, cross-flow system and the Instron tensile strength tester were used. A plot of pure water flux vs. pressure is given in Figure 3. The highest flux was obtained at a fN-CNT loading of 0.04 wt% and pressure of 120 psi, beyond which, further loading of fN-CNTs lead to a decrease in flux. Furthermore, the fluxes for 0.02 and 0.04 wt% fN-CNT membranes were larger than that of the pristine PES despite the low loadings.

Two factors are known to influence the permeation properties of the CNT blend membranes: (1) hydrophilicity and (2) pore influence. The high flux for 0.02 and 0.04 wt% blend membranes can be explained by the hydrophilic nature of functionalised N-CNTs on the membrane at lower carbon contents. However, when the fN-CNTs exceeded

0.04 wt%, their density increased. Moreover, the viscosity of the dope solution increased, thus producing denser membrane structures with narrower pores. Consequently lower fluxes and higher contact angles were observed for membranes with 0.08 and 0.5 wt% loading.

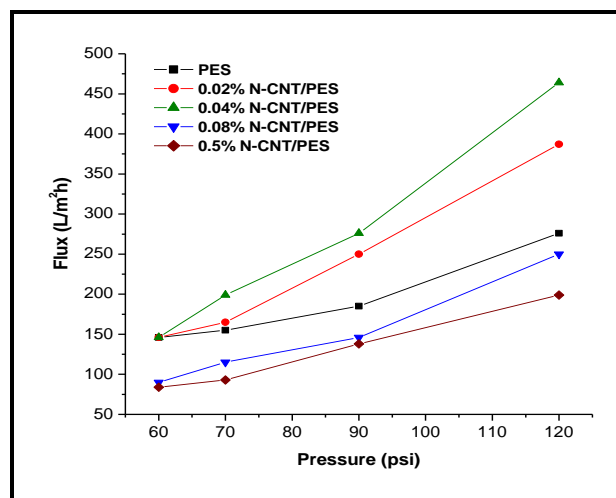


Figure 3: Pure water flux as a function of pressure for the fN-CNT/PES membranes and the pristine membrane.

The rejection properties of the fN-CNT/PES blend membranes were observed using 500 ppm aqueous solution of PEG 10.000 as the feed. Figure 4 shows the rejections relative to the membranes under study. The order of rejections is as follows: 0.04 < 0.08 < 0.02 < PES < 0.5. This trend is inverse to what was obtained with water flux studies, with the exception of the membrane with 0.08 wt% fN-CNTs. The membrane with the highest flux (0.04 wt% fN-CNT/PES) showed the lowest rejection, whereas the membrane with the lowest flux showed the highest rejections. The behaviour can be explained by the presence of pore structures of the membranes, which are related to the amounts of fN-CNTs in the membrane matrix. At higher fN-CNT loadings a denser membrane structure is obtained with smaller pores. This then leads to increased rejections (up 77% rejection of PEG obtained with 0.5% N-CNTs/PES) and reduced water fluxes.

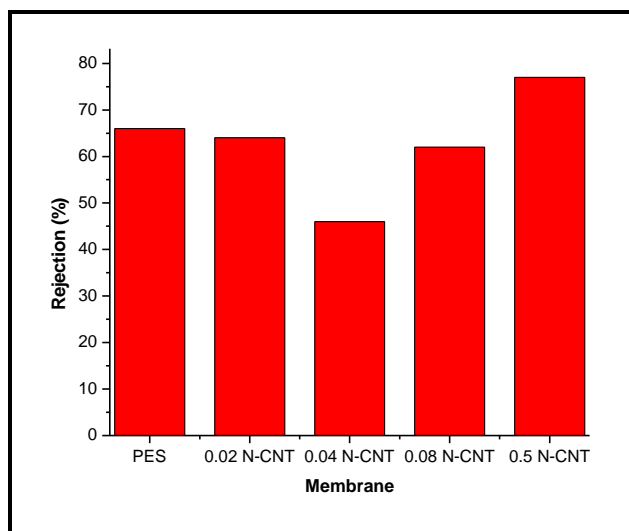


Figure 4: Rejection of a 500 ppm PEG in aqueous solution using the fN-CNT/PES blend membranes.

3.4 Fouling studies of the fN-CNT/PES membranes

The flux performances for PES and fN-CNT/PES blend membranes using humic acid spiked DI water as feed at room temperature and at a pressure of 100 psi are shown in Figure 5. The plots show the permeate flux over time during fouling of the blend membranes with humic acid. Although membrane fouling was not observed in the absence of humic acid (data not shown), fouling was quite prominent for solution containing 20 mg/L humic acid. The greatest fraction of flux decline was observed after the first few minutes of introducing the feed solution. This initial decline can be attributed to the adsorption of the humic acid on the surface of the membrane upon initial introduction of the solution. Previous studies have shown that membrane fouling can be observed by the reduction in permeate flux with time.

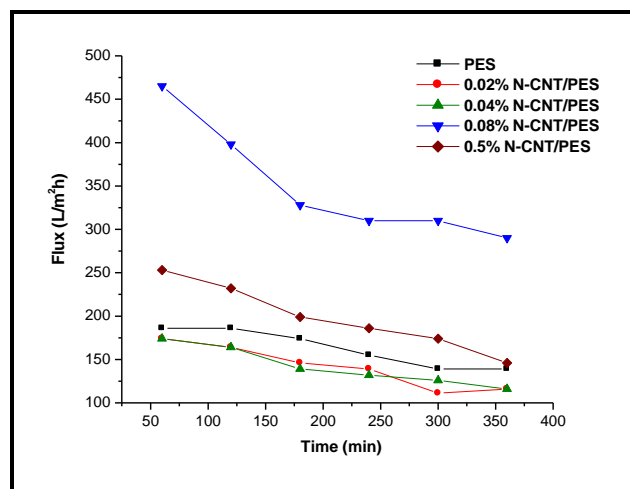


Figure 5: Flux decline behaviour of membranes during fouling studies with humic acid.

4 CONCLUSION

In this study fN-CNTs and Ag/fN-CNTs were uniformly dispersed into polyethersulphone (PES) membranes to form fN-CNT/PES and Ag/fN-CNT/PES blend membranes respectively. The blend membranes were checked for any improved properties and tested for their efficacy in rejecting PEG from water. AFM results revealed a reduction in surface roughness from 23.9 to 12.7 nm in the fN-CNT/PES blend membranes. The mechanical stability increased from 3.7 to 4.4 MPa with a small addition of fN-CNTs. Furthermore, the performance studies showed a 46% increase in pure water flux and a 13% increase in rejections for fN-CNT/PES membranes as compared to the pristine PES membrane. Antibacterial studies were also performed wherein Ag/fN-CNTs were found to destroy bacteria by almost 2-fold in the bacterial suspensions. Finally, having examined Ag/fN-CNTs for their antibacterial activity, they were immersed into PES membranes. The Ag/N-CNT/PES blend membranes were tested for their activity towards bacteria. Conversely, they were found not to exhibit any antibacterial properties. This lack of activity was due to the entrapment of the Ag/N-CNTs in the membrane matrix. Studies are on-going to address this problem.

REFERENCES

- [1] V. Likodimos, D.D. Dionysiou, and P. Falaras, *Rev. Environ. Sci. Biotechnol.* 9, 87-94, 2010.
- [2] S.D. Mhlanga, B.B. Mamba, R.W. Krause, and T.J. Malefetse, *J. Chem. Technol. Biotechnol.* 82, 382-388, 2007.
- [3] J.P. Chen, H. Mou, L.K. Wang, T. Matsuura, and Y. Wei, *Membrane separation: Basics and applications membrane and desalination technologies*, Humana Press. 271-332, 2008.
- [4] H.A. Shawky, S.-R. Chae, S. Lin, and M.R. Wiesner, *Desalination* 272, 46-50, 2011.
- [5] E. Celik, H. Park, H. Choi, and H. Choi, *Water Research* 45, 274-282, 2011.
- [6] S.D. Mhlanga, K.C. Mondal, R. Carter, M.J. Witcomb and N.J. Coville, *S. Afr. J. Chem.* 62, 67-76, 2009.

*Corresponding author email: sdmhlanga@uj.ac.za, Tel: (+2711) 559 6187, Fax: (+2711) 559 6425.