



# A nitrogen-doped carbon nanotube enhanced polyethersulfone membrane system for water treatment



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## ABSTRACT

Water quality in South Africa and around the world continues to deteriorate due to contamination by organic, inorganic and microbial substances. While many efforts have been done to address water quality problems, current drinking water treatment technologies remain costly and do not effectively remove pollutants to acceptable levels. In this work nitrogen doped carbon nanotubes/polyethersulfone (N-CNT/PES) blend membranes were synthesized via a modified phase inversion method and assessed for suitability in drinking water treatment. The N-CNTs with outer diameters of 30–45 nm and 3% N content were prepared using a conventional chemical vapour deposition method and functionalized by refluxing in HNO<sub>3</sub>. The confirmation and degree of functionalization with –OH and –COOH groups was determined using Fourier-transform infrared (FTIR) spectroscopy and zeta potential analysis. FTIR studies confirmed the successful incorporation of functionalized N-CNTs (N-CNTs) in the membrane matrix. Atomic force microscopy (AFM) analysis revealed that the addition of N-CNTs leads to reduced surface roughness, suggesting a good dispersion of the N-CNTs in the matrix. Permeability studies revealed that the addition of N-CNTs to the polyethersulfone (PES) solution increased the water flux of the blend membrane by up to 70%. N-CNT loadings of 0.04 wt% in the blend membranes gave low surface contact angle of 55° and high fluxes. In addition, inclusion of N-CNTs enhanced the mechanical properties of the N-CNT/PES blend membranes. The use of N-CNTs in mixed matrix PES membranes is reported for the first time here. The result already suggests superior compatibility of the N-CNTs with PES compared to undoped CNTs, due to the high surface reactivity of the N-CNTs.

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## 1. Introduction

The state of drinking water quality is a serious problem for rural based communities in South Africa and globally. Drinking water sources such as rivers and boreholes are increasingly deteriorating as a result of natural processes and anthropogenic activities. Consequently studies have shown that water quality differs from place to place depending on the activities occurring there. In most cases human activities which include agricultural and industrial activities, mining and recreation, are widely known to contribute significantly to the water quality problem (Pradeep and Anshup, 2009; Likodimos et al., 2010).

The presence of harmful substances in drinking water (e.g. bacteria, organics, and heavy metals) still remains a global challenge. These pollutants can be extremely disastrous to consumers and

have led to increased treatment costs of potable and drinking water. Water that is supplied for human consumption goes through various stages of purification and filtration to get rid of harmful dissolved and suspended substances. In almost all countries, drinking water treatment before distribution is mandatory. However in many of the developing countries such as South Africa, not everyone has access to treated water and where the water is treated, it still contains small amounts of pollutants which may be acceptable but they bio-accumulate with time and become deadly. This problem requires combined knowledge to develop integrated solutions such as nanotechnology enabled membrane systems for water purification at the point-of-use.

Membrane-based separations are potentially more economical and easier to use than competing conventional separation technologies (e.g. physical separation, chemical oxidation, etc. (Jirage et al., 1997)). Their low energy and space requirement, as well as simplicity of operation render them suitable for use in separation processes (Celik et al., 2011). The main constraint of conventional membranes is that they can be easily fouled after use. According

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to Kim and Van der Bruggen (2010), membrane fouling caused by chemical and biological substances requires great attention because it can result in an inherent trade-off between selectivity and permeability, higher energy demand, costly clean up and the eventual replacement of membranes (Kim and Van der Bruggen, 2010; American Water Works Association, 2005; Sae-Khow and Mitra, 2009; Freeman, 1999, Robeson, 1991; Ismail et al., 2009).

As such, the current outlook is towards a different class of membranes known as mixed matrix membranes (MMMs). MMMs are composed of inorganic nanomaterials (additives) embedded in a polymer matrix (membrane) (Ismail et al., 2009). Recent studies have shown that MMMs are a convenient way of avoiding limitations associated with conventional membranes (Ismail et al., 2009; Vatanpour et al., 2011). For example, inorganic nanomaterials such as zeolites, graphite and metal oxides have been used to improve the properties, performance and fouling resistance of membranes (Razmjou et al., 2011; Van der Bruggen, 2012; Kim and Van der Bruggen, 2010).

Amongst the different nanomaterials, carbon nanostructures have received great attention (Sahoo et al., 2010; Li et al., 2011; Li et al., 2008). A study conducted by Hinds et al., showed that aligned carbon nanotubes (CNTs) could be incorporated into a polymer film to form well-ordered nanoporous membrane structures. It was observed elevated performances for the modified membranes as compared to conventional membranes (Hinds et al., 2004). However, the experiments employed were cumbersome, costly and difficult to upscale. Consequently, researchers have settled with randomly dispersing the CNTs in the various polymer matrices such as, polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PANi), cellulose acetate (CA), polyamide (PA), and polyimide (PI) and more. Evidently, many of them have also received positive results. For example, Choi et al., 2006 studied the modification of PES blend membranes with CNTs by a phase inversion process and obtained a composite membrane with improved hydrophilicity. PES membranes modified with 4.0% of MWNTs showed higher flux and rejection compared to bare PES membrane. Narayan et al. (2005) also studied fabrication of PES with CNT to produce membranes with enhanced antimicrobial activity. Choi et al. (2007) synthesized CNT/PVA UF membranes with good micro-morphology and well distribution of CNTs and used them in the pervaporation of water out of ethanol solution. See Table 1 below for other work done on CNT membranes.

Despite the aforementioned studies, there are still significant challenges in preparing CNT MMMs e.g. the agglomeration of the carbon nanomaterials in the membrane matrix. The agglomeration can lead not only to the uneven distribution of CNTs, but also the potential compromise of the mechanical strength and formation of non-selective voids in the membrane (Shawky et al., 2011; Wu et al., 2010). Thus, the need for good interfacial adhesion between the CNTs and the membrane matrix for good uniform dispersion is necessary (Shawky et al., 2011; Razmjou et al., 2011; Ismail et al., 2009). For this reason, two main approaches have been employed to address these challenges: (1) mechanical modification, which involves sonicating and/or grinding the CNTs before being embedded into the membrane matrix, (2) chemical modification, which

involves acid functionalization and/or the use of surfactants to alter the surface properties of the CNTs (Razmjou et al., 2011). Nevertheless, most researchers use the latter approach due to its ability to improve the hydrophilicity, flux and fouling resistance of the membrane (Ismail et al., 2009; Vatanpour et al., 2011).

According to Van der Bruggen (2012), the preparation of multi-phase materials (e.g. MMMs) with high performances and reproducible structures are a common challenge. Mainly because, up till now, only a limited number of CNT features have been explored (Van der Bruggen, 2012). For this reason, we looked at further modifying the CNTs by introducing a heteroatom in the material structure. Doping of heteroatoms (e.g. boron, nitrogen) offers a route to tailor the physico-chemical properties of the CNTs (Mabena et al., 2011). Moreover, improve their reactivity with other components.

As such, this study looked at using heteroatom modified CNTs. In particular, the use of functionalized N-CNTs (N-CNTs) to improve the mechanical strength, hydrophilicity, permeability, and rejections of PES based membranes. N-CNTs have been found to exhibit enhanced electronic and mechanical properties, high surface area and improved chemical reactivity (Nyamori et al., 2008; Nxumalo and Coville, 2010). As a result, they are much easier to functionalize, thus making them ideal additives to use in membrane composites.

To our knowledge, N-CNTs have not yet been used as fillers in MMMs. Based on this and previous work, the objective of this study was to synthesize N-CNT/PES blend membranes and their efficacy in rejecting model pollutants. Characterization of the N-CNTs and the N-CNT/PES blend membrane matrix was performed by transmission electron microscopy (TEM), scanning electron microscopy (SEM), zeta potential measurements, thermogravimetric analysis (TGA), Fourier transform infra-red spectroscopy (FTIR), atomic force microscopy (AFM) and contact angle measurements. Further, filtration tests were carried out to determine the flux and the ability of the new membranes to reject polyethyleneglycol (PEG) from water using a cross-flow system.

## 2. Experimental

### 2.1. Synthesis and functionalization of N-CNTs

N-CNTs were synthesized by a modified chemical vapour deposition (CVD) method (Mhlanga et al., 2009; Tetana et al., 2012). Typically, a 10 wt% Fe-Co/CaCO<sub>3</sub> catalysts was uniformly spread in a quartz boat and placed in the central position in a quartz tube, which was inserted in a furnace. Nitrogen gas (N<sub>2</sub>) was introduced through the quartz tube at a flow rate of 50 ml/min while the furnace was heated up to the desired synthesis temperature (700 °C), wherein acetylene gas was passed over the catalyst (by bubbling through acetonitrile) together with N<sub>2</sub> (flow rate 240 ml/min) for 1 h. The furnace was then cooled to room temperature by passing N<sub>2</sub> gas through the reactor. The boat was removed from the reactor and weighed to establish the amount of N-CNTs produced. The produced N-CNTs were then functionalized by adding them to a

**Table 1**  
Previous work on polymer blend CNT membranes.

| Type of membrane           | Materials used                               | Separation conditions                        | Reference                 |
|----------------------------|--|--|---------------------------|
| Polymeric                  | Polyamide/MWCNTs                             | Removal of salt                              | Thostenson et al. (2001)  |
| Polymeric                  | Polysulphone/MWCNTs                          | Separation of PVP at 25 °C                   | Choi et al. (2006)        |
| Polymeric                  | Polypropylene/Polyvinylidene fluoride/MWCNTs | Separation of polar and non-polar solutes    | Sae-Khow and Mitra (2009) |
| Polymeric                  | Polysulphone/MWNTs                           | Protein adsorption at various pHs            | Sung et al. (2004)        |
| Polymeric                  | PVA/PVA-SWCNTs                               | Functionalized CNTs for polymeric composites | Lin et al. (2007)         |
| Polymer/Ceramic composites | N/A  | Review of CNT composites                     | Thostenson et al. (2001)  |

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