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Selectivity-permeability optimization of functionalised CNT–polymer membranes for water treatment: A modeling study

Federica Bisignano [a], Davide Mattia [b], Giorgio De Luca [a,*]

[a] Research Institute on Membrane Technology (ITM-CNR), University of Calabria, Via P. Bucci, I-87036 Arcavacata di Rende (CS), Italy
[b] Department of Chemical Engineering, University of Bath, Bath BA27AY, UK

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ABSTRACT

Polymer membranes incorporating carbon nanotubes (CNT) belong to two broad categories: Vertically aligned (VA-CNT) membranes, where the polymer acts solely as a matrix embedding an aligned forest of nanotubes, and thin film composite (CNT-TFC) membranes which incorporate randomly aligned nanotubes in their selective layer. The former can achieve orders-of-magnitude higher permeability than many commercial membranes but cannot be scaled up industrially. The latter are based on commercial technology but provide only modest flux increases. Furthermore, filtration in VA-CNT is based on steric hindrance determined by the tubes' diameter, whereas in CNT-TFCs, the tubes are embedded in the polymer with selectivity given by the polymer alone.

In this work, a novel computational method to optimize the selectivity-permeability of an ideal CNT membrane encompassing the advantages of VA-CNTs and CNT-TFCs is presented. In analogy to the former, the tubes are all aligned with the membrane selectivity provided by their diameter; to the latter, the polymer matrix also contributed to the total membrane permeability. As nanotubes with larger internal diameter would provide higher flow, *ab-initio* modeling was used to improve their selectivity by functionalizing the tips of large multiwall nanotubes with PIM-1 monomers, achieving simultaneously an increase in selectivity toward small molecules (e.g. rac-fluoxetine, glucose, ethanol and water) and an increase in permeability (due to the large diameter). Results show up to 3 orders of magnitude increase in water permeability compared to a CNT-TFC membrane in the literature with randomly oriented tubes of comparable size and an increase in rejection of a factor of 2.5 and 2, for rac-fluoxetine and glucose, respectively, compared to water. The proposed methodology is of general use and requires no fitting parameters, only the chemical structure of the solutes to test and the tubes' geometry.

1. Introduction

In membrane-based filtration processes, permeability and selectivity are considered key performance parameters and, in general, the increase of the former comes at the expense of the latter. Mixed-matrix membranes, where a second phase is added to a polymer matrix to enhance either characteristic, emerged as the most promising technology to further reduce the energy cost and improve performance of membrane-based filtration processes. Among the many materials considered as potential additives, carbon nanotubes (CNT) have attracted the most interest due to promise of ultra-low transport resistance. The first published molecular dynamics simulation of water flow inside a single-wall carbon nanotube (SWNT) with a diameter of 1 nm or less showed very high flow rates [1], initially described in terms of ballistic transport [2] and attributed to the hydrophobicity of the nanotube's wall in respect to water [3]. As further modeling and experimental results have confirmed initial observations, interest shifted to measuring the performance of carbon nanotube membranes rather than flow in individual nanotubes [4]. A recent analysis by the authors shows that the orders-of-magnitude water high flow rates observed in single tubes do not automatically translate in orders-of-magnitude higher membrane permeability but rather smaller, yet still significant, increases [5]. This difference can be attributed primarily to the geometrical and structural characteristics of the CNT membranes, which, in turn, are a result of the fabrication methods available.

The first carbon nanotube membranes produced were all so-called vertically aligned carbon nanotube (VA-CNT) membranes: These were manufactured using an aligned array of CNTs produced

* Corresponding author. Tel.: +39 (0984) 492080.
E-mail address: g.deluca@itm.cnr.it (G. De Luca).
URL: http://www.itm.cnr.it (G. De Luca).

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via catalytic chemical vapor deposition on silicon/silicon oxide substrates. The array was then infiltrated with polymer [6–8] (or embedded within an inorganic matrix [9]) to provide mechanical stability and prevent leaks, detached from the substrate and the tube ends opened. These membranes usually have a filtration area of 1 cm^2 or less [10]. These membranes also tend to have low tube density (equivalent to porosity), which decreases performance. A molecular dynamics study of highly-packed and aligned SWNTs in a periodic cell has shown theoretical permeability increases of over 3 orders of magnitude compared to a commercial RO membrane with salt rejection close to 100% [11]. When the tube density was reduced to what can be currently achieved experimentally, a much smaller permeability was observed. An alternative technique deposited turbostratic carbon in the pores of alumina nanoporous templates, creating what have been called nanopipe structures [12]. Unfortunately, none of these techniques can actually be scaled economically to a level where they can supply the wastewater membrane market [4].

A more practical route has emerged, incorporating randomly oriented multi-wall carbon nanotubes (MWNTs) dispersions in the active layer of thin film composite (TFC) polymer membranes or polymeric matrices [13]. A large number of nanotube–polymer membranes have now been fabricated with varying performance: A 4-fold increase in permeability with no loss in salt rejection was observed in polyamide TFC membranes with 20 wt% MWNTs loading [14] compared to the virgin one. Another MWNT/PA TFC membrane saw a 6% decrease in flux compared to the reference without tubes but an increase in rejection for salt and humic acid (MWNT loading ~1 wt%) [15]. A 4-fold increase in flux was also observed for a 10 wt% MWNT/chitosan membrane [16], whereas a 2-fold increase was observed for randomly aligned MWNT/polyester TFCs [17]. A negligible increase in permeability, on the other hand, was observed for a MWNT/polysulfone (MWNT loading varying from 1 to 4 wt%) [18].

Although most studies on CNT membranes have, so far, focused on maximizing permeability, some work has been done on CNT membrane selectivity, particularly salt rejection for RO applications. As steric-only rejection requires extremely small tubes with a negative effect on permeability – for example, to reject a 200 Da molecule a SWNT with diameter of 1 nm or less would be required – functionalization of the nanotube inlet has emerged as a more practical alternative [19]. Charge-based selectivity was significantly increased when the tips of a MWNT-polymer membrane were functionalized with alkanes and amines, attached to the tubes via carboxylic defects created on the tubes' tips [20]. MD studies on CNT functionalization for seawater desalination have shown that the addition of charges on the tip of a 1.1 nm SWNT can reduce the passage of ions but at the expense of water permeability [17]. Another MD study showed the effect on salt rejection and permeability of a SWNT membrane of several different functional groups grafted onto the tube tips [11]. Results showed that functionalization reduced flux in all cases, with the largest reductions occurring for the bulkiest functional groups and those with the strongest charge density. For the same reasons, ion rejection increased in the functionalized tubes compared to the pristine ones.

All these large variations can be attributed to two main factors:. First, carbon nanotubes are actually a family of materials, whose properties can vary significantly due to the synthesis process used, from geometrical characteristics (diameter and length) to the surface structure (from turbostratic to highly organized graphitic) to the surface chemistry (from hydrophobic to hydrophilic) [3,21]. MD studies have confirmed that the presence of defects [22], the structure of the tubes [23] and their length [24] all affect water flow through the tubes. A recent theoretical model by the authors has shown that these apparent discrepancies can be resolved by normalizing modeling and experimental flow rates for the tubes' geometrical characteristics and solid–liquid molecular interactions [23,25,26]. Second, as the tubes are randomly aligned (in TFCs), there is little to no control on the degree of orientation of the tubes, leading to varying performance [27].

In this publication, a novel computational methodology, free of adjustable and empirical parameters, to maximize both water permeability and selectivity for functionalized carbon nanotube-polymer membranes, is presented. The aim is to provide a computational strategy to design bespoke CNT-polymer membranes for specific filtration applications, maximizing both permeability and selectivity. As a demonstration of the proposed method, the functionalization of the tips of large multi-wall nanotubes with organic monomers to reject small solutes, difficult to separate from water, is presented.

2. Materials and modeling approach

An ideal MWNT-polymer membrane is considered in this modeling study where all the nanotubes are perpendicularly aligned to the membrane's surface in a polymeric matrix with no voids present between the polymeric matrix and the tubes (as in a VA-CNT membrane) but with the polymer matrix also contributing to permeability (as in a CNT-TFC). Two cases from the recent literature are used as reference, one a polyester TFC asymmetric membrane [17] and the second a chitosan porous membrane [16] both containing randomly aligned MWNTs embedded in the polymer with no direct access to the feed. For the first membrane, the thickness of the selective layer is approximately 500 nm with a total membrane area of 27 cm^2. The measured pure water flux was ~10.8 L m^{-2} h^{-1} (LMH) at 0.6 MPa and room temperature for the membrane containing no nanotubes. The flux increased to ~21.8 LMH under the same conditions, when 0.5 mg/ml of MWNTs (external diameter, D_{CNT} < 8 nm; internal diameter, d_{CNT} = 2–5 nm; L = 10–30 μm) was added to the aqueous phases during the phase inversion process. The chitosan membrane presents a mean thickness of the wet membrane of about 130–140 μm and a membrane area of 11.33 cm^2. The pure water flux was ~28 LMH at 0.1 MPa without MWNTs. The flux increased to ~120 LMH at 0.1 MPa with 10 wt% of MWNTs (D_{CNT} = 10–30 nm; L = 5–15 μm).

2.1. Permeability optimization

When considering MWNTs, the thickness of the tubes has to be considered in the calculation of the effective CNT permeable area:

$$A_{CNT,eff} = \sum_{i=1}^{n} \pi \frac{d_{CNT,i}^2}{4} \equiv n\pi \frac{d_{CNT}^2}{4} \quad (1)$$

where n the total number of tubes vertically trapped in the membrane while d_{CNT} is internal diameter of the MWNT. On the other hand, the membrane surface fraction occupied by the MWNTs is:

$$f = \frac{A_{CNT}}{A_{mem}} = \frac{1}{A_{mem}} \sum_{i=1}^{n} \pi \frac{D_{CNT,i}^2}{4} \equiv n\pi \frac{D_{CNT}^2}{4A_{mem}} \quad (2)$$

where A_{mem} is the total membrane area, A_{CNT} is the total area occupied by the MWNTs, and D_{CNT} is the 'external diameter' of the MWNTs. The above relationships assume no size distribution for the nanotubes, a constant cross-section throughout their length and tortuosity, τ = 1. With these assumptions, f is equivalent to a standard surface porosity and its maximum value is 0.74, following standard geometrical rules [11]. For the multi walled CNTs, $A_{CNT,eff}$ < A_{CNT}, whereas for a SWNT it is assumed that $D_{CNT} \equiv d_{CNT}$, with this value being the distance between the CNT carbon nuclei.