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ABSTRACT

This study aims to improve the boron rejection of polyamide thin film composite membranes by embedding properly functionalized carbon nanotubes (CNTs) into the polyamide layer. In order to identify appropriate functional groups molecular simulation methods are used for screening. For this purpose, the possibility of creating a steric effect and hence employing gate keeper mechanism for boron rejection by the introduction of the functional group(s) on single walled carbon nanotubes is explored. This work focuses on one of the possible functional groups, namely biotin, which is chosen based on a literature review on CNT functionalization studies. SWCNTs without and with one and two biotin molecules has been constructed by using Materials Accelrys Studio software. After geometry optimization of the cell, the system has been equilibrated with molecular dynamics (MD) method by applying NVT-MD first for 100 ps and then for 1 ns. The SWCNT is then exposed to water-boric acid solution and the motion and behavior of the functional group and water-boric acid molecules has been investigated. The results indicate that more than one biotin molecule is needed to create a steric effect. Biotin seems to be a good candidate to reject boric acid molecules due to their steric hindrance effect by folding at the entrance of the CNT.

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LIST OF ACRONYMS/ABBREVIATIONS

B-SWCNT	: Biotinylated Single Walled Carbon Nanotube
CNTs	: Carbon nanotubes
COOH	: Carboxyl Group
IP	: Interfacial Polymerization
MD	: Molecular Dynamics
MED	: Multiple-Effect Distillation
MF	: Microfiltration
MMM	: Mixed Matrix Membrane
MSF	: Multi-Stage Flash Distillation
MWCNTs	: Multi Walled Carbon Nanotubes
NF	: Nano Filtration
PA	: Polyamide
RO	: Reverse Osmosis
SWNTs	: Single Walled Carbon Nanotubes
TFC	: Thin Film Composite
TFN	: Thin Film Nanocomposite
UF	: Ultrafiltration (UF)
WHO	: World Health Organization

1. INTRODUCTION

Although a significant part of the earth is covered with water, the greater part of water resources is either excessively salty for human consumption and agribusiness or available as ice and snow (Rodda, and Shiklomanov, 2003). As a result, around 700 million people living on earth do not have access to reliable drinking water and presently about one in eight need access to clean water supply (WHO/UNICEF, 2015). The growing world population and escalating levels of agriculture and industry increase the demand for fresh water. Moreover, the worldwide climate change affected the redistribution of rainfall causing progressively dry conditions in numerous territories (Solomon et al., 2007). The climatic changes are predicted to alter the natural availability of non-saline water and the location of available water, and create uncertainty in fresh water resources and supplies. (World Development Report, 2010).

Desalination, a technique that converts salty water to potable water, is one of the most important solutions for water scarcity. Total global desalination capacity is exponentially increasing over the last decade and is expected to be over 100 million cubic meters per day in 2016 (New Desalination Capacity, 2009). Reverse Osmosis (RO) is the most popular method of desalinating sea water into clean water. Other methods, such as multi-stage flash (MSF) distillation and multiple-effect distillation (MED) are energy intensive and is expected to leave the market eventually. As shown in Figure 1.1, the global fresh water capacity with different desalination processes and RO fulfills more than half of the supply. Contemporary new desalination plants are working with the principle of RO membrane technology and recently large plants have been built in Singapore, Israel, and Spain (largest in terms of desalination capacity in the Mediterranean region). These regions produce potable water that can cover 20 to 30% of total demand.

RO technology uses semi-permeable membranes to separate salt ions from water at the molecular level. This process has been improved greatly since first commercial RO membranes were produced in 1959. Using advanced membrane materials, module design, process design and energy recovery, remarkable reductions of cost have been succeeded. However, most RO membranes are made from synthetic polymers that

show a trade-off between water permeability and water/salt selectivity. This basically limits the performance of salt intake because higher water production rates cause to lower salt rejection and water quality. Larger scale desalination plants and higher energy consumption will be necessary to ensure that sufficient amount of clean water can be supplied for the incremental demand. In fact, energy consumption constitutes a significant fraction of the cost of total desalination (~ 45% of the total cost). Further technology is needed in the synthesis of next generation RO membranes (Chan, 2015).

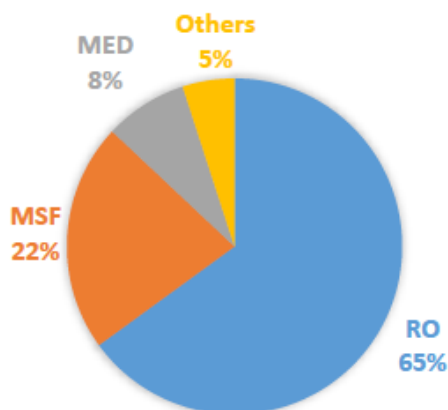


Figure 1.1. Total global desalination capacity by technology in 2013 (Chan, 2015).

In RO membranes, the diffusivity and permeability of water molecules in the polymer matrix should be kept at the top level while these properties should be minimum for salt ions. Even if the free volume and pore size of the membranes can enhance the permeability of water, they could also diminish salt rejection and resistance to salt transportation. In the last few decades, a new type of hybrid membrane comprised of inorganic materials distributed in a continuous organic polymer phase called as “mixed matrix membranes” (MMM) have appeared. Some nanoscale additives such as zeolites and carbon nanotubes have been recently incorporated into polymers to manufacture hybrid RO membranes yielding outstanding selectivity and transport rates. Research studies related to hybrid RO membranes demonstrate promising results that the nanomaterials improve not only the permeability of water but also salt rejection. Therefore, trade off relationship between permeability and selectivity is changed for nanocomposite polymeric membranes.

When it comes to inorganic nanomaterials, carbon nanotubes (CNTs) have shined out and attracted many researchers’ attention in water purification due to the high transport rates through them. Carbon nanotubes have exceptional transport

properties because of the unique smoothness of the potential energy surface inside them. Molecular dynamics (MD) simulations (Corry et al., 2008) have shown that carbon nanotubes with pore diameters less than 0.9 nm are able to completely block ions while allowing transport of water. In addition, recent experimental and computational studies both suggest that electrostatic interactions between the ions and fixed charges on the carbon nanotubes can control ion rejection.

In spite of its popularity, there are several challenges associated with the RO based desalination technology. Low flux, low chlorine resistance, fouling, and inability to reject low molecular weight trace solutes such as boron and arsenic are the most important limitations of RO. There is an increasing concern to remove boron from desalinated water to be used for drinking and irrigation purposes. Boron overdose in humans may lead to acute boron toxicity leading to nausea, headache, diarrhea, kidney damage, and even death. In addition, most harvest can be affected by excessive boron levels in irrigation water. Boron in small amounts is required for plants but becomes toxic at concentrations between 0.5–10 ppm for many agricultural crops (Jiang and Xu, 2008). The World Health Organization recommends boron concentrations in potable water and irrigation water for some crops such as orange, avocado, walnut, and apricot, be less than 2.4 ppm and 0.5 ppm, respectively.

Seawater can contain 10 ppm or more of boron. Since boron is present in seawater as boric acid whose effective diameter is nearly the same as that of a hydrogen-bonded cluster of water molecules, its concentration cannot be reduced adequately by conventional single-stage reverse osmosis. However, it can be done by using several RO stages in series at the cost of reduced water recovery. Increased water recovery is possible by raising the pH that causes boric acid to dissociate into hydrated borate ions for which currently available RO membranes have an adequate rejection. However, this requires use of chemicals and additional processes to reduce the pH again. Desalination followed by ion exchange, adsorption, or dialysis can also reduce the boron concentration at the cost of increased process complexity. None of these processes can achieve desalination and boron removal with a high water recovery using just membranes.

Incorporating materials such as zeolites and functionalized carbon nanotubes into the selective thin layer of RO membranes offer the potential for improving the boron rejection as well as the flux and anti-fouling properties. The aim of this study is

to improve the boron rejection of polyamide thin film composite membranes by embedding properly functionalized CNTs into the polyamide layer. It is hypothesized that a suitable functional group attached to the CNT can block its entrance and hinder boric acid transport through the membrane. This is called the “gate keeper” mechanism and has been shown to increase the salt rejection of polyamide RO membranes (Hinds, 2006). However, this concept has not been tested for boron removal.

The testing of the above hypothesis requires selection of a suitable functional group. Molecular dynamics methods can be used to screen candidate functional groups to identify the promising ones for further experimental studies. Candidate functional groups has been determined based on a detailed literature review. One of the candidate functional groups is 5-[(3a*S*,4*S*,6a*R*)-2-oxo-1,3,3a,4,6,6a-hexahydro-thieno[3,4-*d*]imidazol-4-yl]pentanoic acid (C₁₀H₁₆N₂O₃S), also known as biotin. In this study, we have studied the steric effect of one or more biotin groups attached to a CNT by molecular simulation. For this purpose, one end of a single walled CNT has been functionalized with one biotin molecule and then exposed to boric acid solution in water to investigate the steric behavior of the molecule. The same procedure has been repeated with two biotin molecules in order to observe how the number of functional groups attached to SWNT affects the boron rejection.

2. LITERATURE REVIEW

2.1. Reverse Osmosis Process

Reverse osmosis (RO) is a water purification process using a membrane which enables water to permeate but is fundamentally impermeable to dissolved salts. The salt solution is pressurized and fed to one side of the membrane. Water is withdrawn from the feed solution and permeate through the membrane, leaving as a low-pressure permeate, while the depleted salts/impurity stay in feed stream and become a concentrated brine as shown in Figure 2.1.

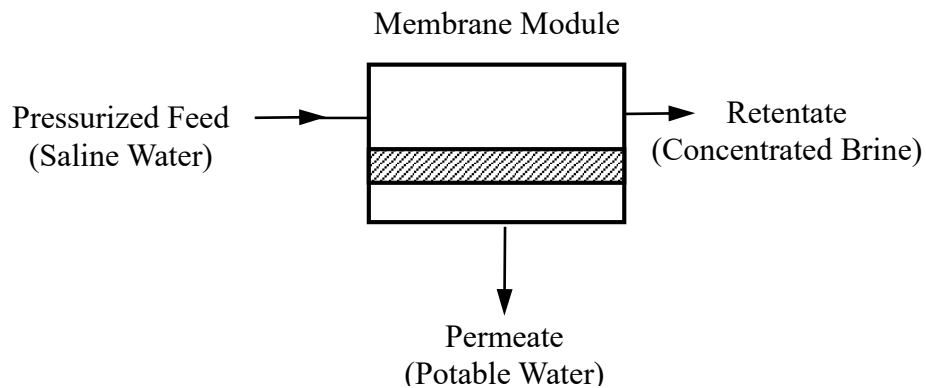


Figure 2.1. Schematic of membrane desalination process.

When a semipermeable membrane is placed between a salt solution and pure water, normal osmosis occurs spontaneously to even out the solute concentrations on both sides. Water permeates the membrane from the pure water side into the salty side to dilute the concentration of salt. If an external hydrostatic pressure is applied to the salt side of the membrane, the flow of water can be retarded and, when the applied pressure becomes equivalent to the osmotic pressure, the water terminates to flow across the membrane. The hydrostatic pressure required to stop the water flow is called the osmotic pressure (Π). If pressures greater than the osmotic pressure are applied to the salt side of the membrane as shown in Figure 2.2, then the water flow can be reversed, and happens from the salty solution side to pure water side. This process is called reverse osmosis.

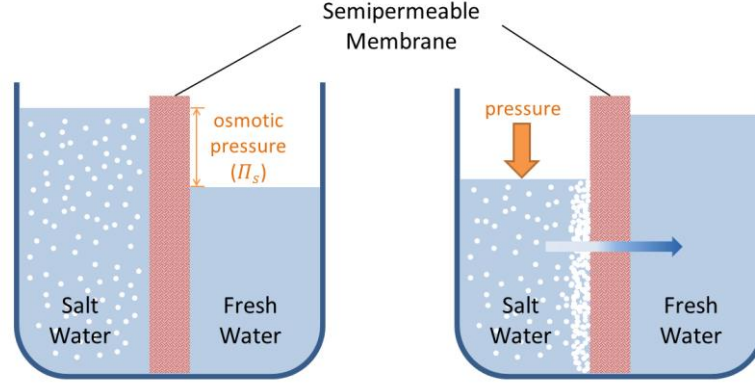


Figure 2.2. Schematic of reverse osmosis process (Chan, 2015).

The ideal desalination process for seawater is equivalent to the reversed thermodynamic process of mixing salt with water. Therefore, the minimum energy for the separation of dissolved salts from pure water and the free energy of mixing is equal as an absolute value but the signs are opposite:

$$-d(\Delta G_{\text{mix}}) = -RT \ln a_w dn_w = \Pi V_w dn_w \quad (2.1)$$

where ΔG_{mix} is the free energy of mixing, R is the ideal gas constant, T is the absolute temperature, a_w is the activity of water, n_w is the number of moles of water, and V_w is the molar volume of water.

The Van't Hoff equation gives

$$w_{\text{th0}} \cong \Pi V_w \quad (2.2)$$

where w_{th0} is the theoretical work of separation per unit water product for infinitesimal recoveries, Π is the osmotic pressure, and V_w is the infinitesimally small volume of desalted water across a semipermeable membrane. This is consistent with our understanding of reverse osmosis, that the minimum applied pressure to drive infinitesimally small volume of water across the membrane must be equal to the osmotic pressure of seawater.

The theoretical minimum energy for desalination is a function of the percent recovery of fresh water.

$$\text{recovery rate} = \frac{\text{product flow rate}}{\text{feed flow rate}} = \frac{Q_P}{Q_F} \quad (2.3)$$

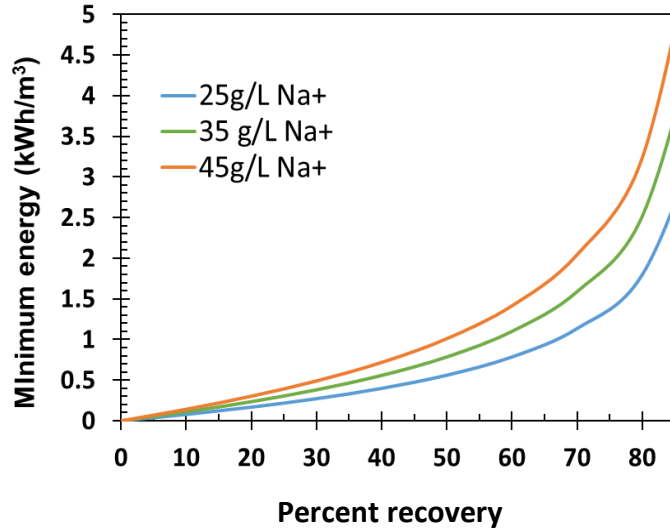


Figure 2.3. Theoretical minimum energy for desalination as a function of recovery rate of common seawaters of different salinity (Chan, 2015).

2.2. Solution-Diffusion Model

Reverse osmosis membranes have a dense polymer layer with no visible pores, in which the separation occurs. These membranes show different transport rates for molecules as small as 2–5 Å in diameter. The fluxes of permeants through these membranes are also much lower than through the microporous membranes. Transport is best described by the solution-diffusion model. According to this model, once dissolved in the membrane, individual permeating molecules move by the same random process of molecular diffusion. The spaces between the polymer chains in these membranes are less than 5 Å in diameter and so are within the normal range of thermal motion of the polymer chains that make up the membrane matrix. Molecules permeate the membrane through free volume elements between the polymer chains that are transient on the timescale of the diffusion processes occurring (Baker, 2008). The opening and closing of transient gaps govern the diffusion, as shown in Figure 2.4, to allow penetrants to do diffusional jumps within the matrix.

At steady state, the diffusive permeability of a penetrant i , P_i , can be written in terms of a sorption, or partition, coefficient, K_i , and an effective, concentration averaged diffusion coefficient, D_i .

$$P_i = K_i \times D_i \quad (2.4)$$

This relationship describes both water and ion transport through polymers.

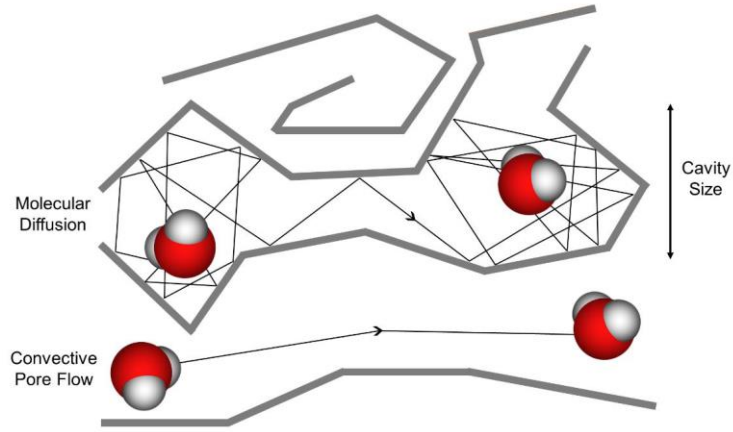


Figure 2.4. Illustration of the motion of a water molecule in a polymer matrix (Chan, 2015).

Using solution-diffusion model, water flux through the membrane is described as below

$$J_w = \frac{D_w K_w c_{w0} v_w (\Delta p - \Delta \Pi)}{\ell RT} \quad (2.5)$$

where J_w is the steady state volumetric flux of water, D_w is the diffusion coefficient of water, K_w is the sorption coefficient at the interface c_{w0} is the water concentration in the feed solution, v_w is the molar volume, Δp is the applied hydrostatic pressure, ℓ is the membrane thickness.

This equation can be simplified to

$$J_w = A(\Delta p - \Delta \Pi) \quad (2.6)$$

where A is a constant which is usually called the water permeability constant.

For salt ions in solution, the effect of the pressure gradient on their transport is very small. Therefore, the salt flux is essentially independent of pressure:

$$J_s = \frac{D_s K_s (c_{s0} - c_{s1})}{\ell} \quad (2.7)$$

where c_{s0} is the salt concentration in the feed solution side and c_{s1} is the salt concentration in the permeation side. This equation can be simplified to

$$J_s = B(c_{so} - c_{sl}) \quad (2.8)$$

where B is usually called the salt permeability constant.

The rejection coefficient, R , is generally used in quantifying the overall performance of the RO membrane. It can be defined as

$$R = \left(1 - \frac{c_{so}}{c_{sl}}\right) \times 100\% \quad (2.9)$$

2.3. Limitations of RO Desalination Processes

Although RO desalination processes have many advantages, they also have some disadvantages such as low permeation flux, insufficient selectivity for trace molecules, inadequate membrane chemical stability, membrane fouling, high operating and equipment cost (Michaels, 1990).

Fouling is the fundamental handicap in membrane technology, which affects capital investment and operating and maintenance costs (Guo et al., 2012). To avoid and handle fouling, capital investment requires additional pretreatment units, energy, material and chemicals (Alhseinat, and Sheikholeslami, 2012). Fouling problem also increase the mass transfer resistance and therefore raise of trans-membrane pressure is needed that leads to much more energy consumption to keep flux at the same level. In addition, operational cost become higher because of chemical cleaning step for cleaning the membranes (Sheikholeslami, 1999). Microfiltration (MF)/Ultrafiltration (UF) procedures have been used to lessen fouling of RO membranes rather than traditional pretreatment (Yu and Zhao, 2015). UF is the most aggressive pre-treatment, particularly for high fouling bolster water source, for example, surface water, wastewater, or an open-consumption seawater. Innovative methods such as granular media filtration, use of additional chemicals, effective downstream protection of RO membranes, basic chemical disinfection cure and solid design of hardware are necessary (Wenten et al., 2014). Membrane adjustment is also a useful way in order to diminish the fouling bias of RO membranes by tailoring surface hydrophilicity, roughness, zeta potential, and functional groups (Yu and Zhao, 2015). Use of nanostructured materials to modify membranes provide relatively better performance and efficiency to RO system. Diminishing energy, membrane maintain cost and

required area, vulgarizing pre-treatment process, accomplishing single pass desalination and increasing capacity are the essential target for nanomaterials integrated system (Lee et al., 2011). Low boron rejection is another trouble for RO membranes desalination process to supply fresh water in appropriate quality. Boron is available in seawater at the about concentration of 4.6 mg/L. According to World Health Organization (WHO), the maximum allowable concentration of boron for drinkable water is 0.5 mg in one liter (Park et al., 2012). To gain more than 90% boron removal is the difficult operation for ordinary RO membrane (Kezia et al., 2013).

2.4. Thin Film Composite (TFC) Membranes

Thin-film composite membranes (TFC) are semipermeable membranes manufactured principally for use in water purification or water desalination systems. They also have use in chemical applications such as batteries and fuel cells. A TFC membrane can be considered as a molecular sieve constructed in the form of a film from two or more layered materials.

TFC membranes are commonly classified as nanofiltration (NF) and reverse osmosis (RO) membranes. Both types are typically made out of a thin polyamide layer (<200 nm) deposited on top of a polyethersulfone or polysulfone porous layer (about 50 microns) on top of a non-woven fabric support sheet (Figure 2.5). The three-layer configuration gives the desired properties of high rejection of undesired materials (like salts), high filtration rate, and good mechanical strength. The polyamide top layer is responsible for the high rejection and is chosen primarily for its permeability to water and relative impermeability to various dissolved impurities including salt ions and other small, unfilterable molecules. As is suggested by the name, TFC membranes are composed of multiple layers. Membranes designed for desalination use an active thin-film layer of polyamide layered with polysulfone as a porous support layer.

Polyamide TFC membranes are produced by “interfacial polymerization” method. Reverse osmosis membranes produced by this technique have very high salt rejections and water fluxes, and almost all reverse osmosis membranes are now made by interfacial polymerization process. In this method, an aqueous solution of a reactive prepolymer, such as a polyamine, is first deposited in the pores of a microporous support membrane, typically a polysulfone ultrafiltration membrane. The amine-loaded support is then immersed in a water-immiscible solvent solution containing a

reactant, such as a diacid chloride in hexane. The amine and acid chloride react at the interface to form a densely crosslinked, extremely thin (less than 1 micrometer) membrane layer (Baker, 2008).

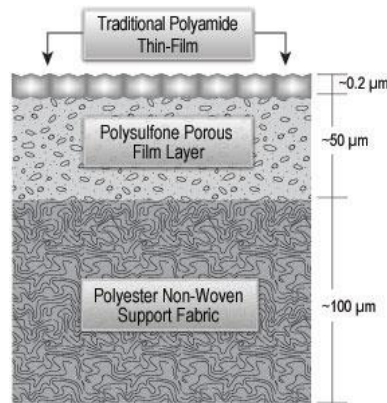


Figure 2.5. A typical polyamide thin film composite membrane (Mattia et al., 2014).

Current research on RO membrane technology tries to solve three primary challenges: (1) low permselectivity for seawater and brackish water desalination; (2) surface biofouling; and (3) poor resistance to chemical attack such as that of chlorine used for disinfection. Thin-film composite membranes synthesized by interfacial polymerization (IP) process forms polyamide (PA) barrier layer which has a thickness of 100 to 200 nm atop of porous substrate. It provides fast water flux, and have control over the design of most of the RO membranes, even though it was a technique developed over four decades ago. The dominant effect also limits the possibility of further development to resolve the major challenges because the performance is seriously relied on the physiochemical aspects of the PA layer. Chlorine radicals may attack the amide bonding on the backbone of PA chain and cause to break down to short chains. Regular PA membrane can start to dissolve only after 12 hours of exposure in solution with chlorine concentration at 2 g/L and experience significant diminishment in salt rejection. Furthermore, the surface of PA is negatively-charged at normal pH because of the carboxylic functional groups present on the polymer backbone, which is formed from the hydrolysis of unreacted acid chloride group on the crosslinking agent during IP. This charged surface is prompt to protein and bacteria adsorption, and subsequently increase the chance of biofouling.

To resolve these challenges, recent development in the RO industries have approached each problem singly and commercialized different types of membrane modules, such as seawater RO membranes with high boron removal, low surface fouling, or energy saving membrane that runs at ultra-low pressure. Table 2.1 summarizes the performance of some of the commercial membranes available in the market.

Table 2.1. Comparison of membrane performance between different manufacturers in terms of the permeation flux and rejection. (Chan, 2015)

Name	RO Membrane Type	Solution Concentration (NaCl ppm)	Applied Pressure (bar)	Permeance (L/(m ² h)/bar)	Rejection (%)
⁴ DOW FILMTEC™					
SW30HR-380	Seawater	32,000	55	0.50	99.7
SW30XHR-400i	Seawater + Boron Removal	32,000	83	0.31	99.8
BW30HR-440i	Brackish Water	2,000	15.5	2.82	99.7
⁵ Hydranautics™					
SWC@-5-LD	Seawater + Low Fouling	32,000	55.2	0.69	99.8
ESPA@-1	Ultra-Low Pressure	1,500	10.3	4.95	99.3
⁶ TORAY™					
TM840M-1760	Seawater	32,000	55.2	0.53	99.8
TM740-1760	Brackish Water	2,000	15.5	2.77	99.7
⁷ FLUID SYSTEM™					
SW 8	Seawater	32,800	55.2	0.55	99.8
FR 8	Fouling Resistant	2,000	15.5	3.01	99.6
⁸ LG NanoH2O™					
SW 400 ES	Seawater	32,000	55	1.06	99.7
BW 400 ES	Brackish Water	2,000	10.3	4.34	99.6

2.5. Thin Film Nanocomposite (TFN) Membranes

Polymer composite membranes have been extensively studied in recent years. Manufacture of low cost, small energy production and compact module design with high flexibility have led to mega-scale desalination plants in the Middle East and Europe. The design of the membranes has been limited to various difficulties, such as low resistance to biological pollution, as well as disrupting the balance between water permeability and water / salt selectivity. For this reason, new generation membranes should be developed with high chemical selectivity, good contaminating properties and chemical attack resistance in terms of energy efficiency and cost effectiveness.

The successful use of nanomaterials in thin film operations such as, sensors, batteries and fuel cells has motivated the separation industry to utilize the concept of nanocomposite membranes (Jia et al., 1991). In order to exceed the Robeson

upperbound limit in the area of gas separation (Robeson, 1991; Robeson, 2008), Jia et al (1991). incorporated a zeolite into polydimethylsiloxane (PDMS) to advance membrane permeability and selectivity. Today, mixed matrix membranes (MMM) containing nanomaterials dispersed in a polymer matrix is being utilized for applications of gas-gas, liquid-liquid and liquid-solid separations.

For conventional composite membranes, nanomaterials can be deposited in three different locations on the membranes: (1) the membrane surface (i.e. nanoparticles grafted-on); (2) bulk phase of polymer matrix, or so-called thin-film nanocomposite (TFN); and (3) the substrate on which thin-film composite (TFC) membrane is formed. Nanoparticles (NP) in various sizes and shapes, as well as nanotubes, nanofibers and nanosheets have recently been investigated with promising results. Nanomaterials used in the manufacture of TFN membranes include zeolites, CNTs, silica, Ag, and TiO₂. TFN membranes are also fabricated by the common fabrication method of interfacial polymerization (IP) process between aqueous m-phenylenediamine (MPD) and trimesoyl chloride (TMC) organic solution as depicted in Figure 2.6. The nanofillers can be dispersed either in the aqueous or organic phase (Chan, 2015).

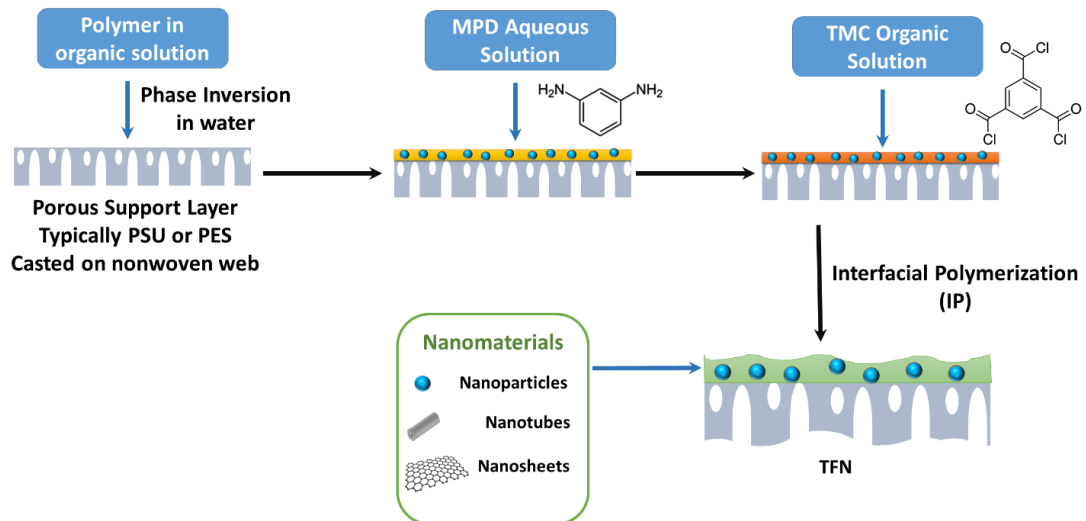


Figure 2.6. Schematic of the thin-film nanocomposite membrane fabrication (Chan, 2015).

The advantage of adjusting the TFC membrane surface is that the cost of materials is fractional in comparison with the entire process and can be easily enhanced the capacity for industrial applications. However, in situ grafting to the membrane surface or hydrogen bonding polymers reduces the independence to regulate the

features of the membrane. As previously noted, the majority of surface coatings could provide higher hydrophilicity to the membrane for better fouling resistance, while sacrificing water permeability performance. A unique area for developing water treatment using nanotechnology has recently been concentrated. The specific idea is separating the solute from the solvent at the molecular level by using either the nanoscaled particle which is embedded in TFC membranes or internal nanostructure (i.e. nanopores) of the membrane. Membranes having nanomaterials, such as zeolite membranes and aligned carbon nanotube membranes, have been studied both theoretically and experimentally. In 2007, Hoek et al. introduced first thin film nanocomposite (TFN) RO membranes and obtained excellent results in increasing membrane performance. The goal is to insert nanoparticles along the thin film layer of the polycondensation polymer, and the most outstanding nanoparticles examined are other nanofillers such as zeolites, carbon nanotubes (CNTs), silver, TiO₂, silica particles and metal organic frameworks. Most TFN membranes testified higher water flux without reducing salt rejection. The recommended mechanisms for improved desalination performance of TFN membranes include (i) faster water transport in porous nanomaterials; (ii) aqua membrane affinity increase; (iii) PA structure change. Nanomaterials can also change positively some physical film properties, such as thermal stability, mechanical strength or resistance to contamination. The Table 2.2. shows some of the recent developments in TFN membranes using different nanomaterials, along with the performance of the resulting membranes and the advantages offered by nanofillers (Chan et al., 2015).

2.6. Carbon Nanotubes (CNTs)

CNTs consist of a sheet of graphene that are rolled into hollow smooth cylindrical tubes, and inner diameter of tube can be less than 1 nm, on the other hand length of tube can reach up to micro scales. Therefore, this feature is able to offer significant phantom proportion (Chan, 2015). CNTs have extraordinary properties in terms of structure and function such as mechanical, tensile, and electrical distinctiveness. They, consequently, provide considerable advantages for assorted technological applications (Daer et al., 2015). In fact, carbon nanotubes can be classified into two main group based on the quantity of cylindrical arrays rounded and hollowed by empty nanotube center: single walled carbon nanotubes and multi walled

carbon nanotubes (Figure 2.7). In nanomaterials selection, CNTs are remarkable choice and preference for water desalination and purification applications thanks to their channels likewise aquaporin biological channels (Chan, 2015). Molecular dynamics simulation has been used to emerge behavior of water molecules when they are in motion (Kalra et al., 2003), (Corry, 2008). Hydrogen-bonded water molecules form chain-like structure within the CNT not only makes water molecules easy to enter but also enables fast antifriction transmission through the tubes according to simulation study of Hummer et al (2001). Table 2.3 shows most of the recent CNT-TFN membranes with CNTs functionalized with various functional groups.

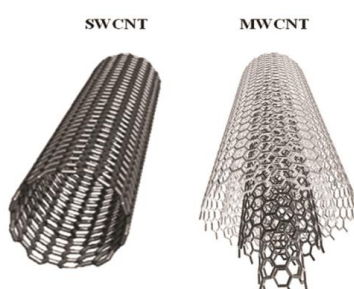


Figure 2.7. Single and Multi-Walled Carbon Nanotubes (Choudhary and Gupta, 2011).

Table 2.2. Nanomaterials used for TFN Desalination Membranes (Chan, 2015).

Nanoparticles	Aqueous Phase	Salts in Feed	Applied Pressure (Psi)	Permeation Flux (L/(m ² h))	Rejection (%)	Advantages
Multi-walled CNT; <8nm in diameter, 10-30µm length	MPD [2wt%]	NaCl 1000ppm	100	22.0 ± 2.8	92.1 ± 1.3	Applied potential significantly increases anti-biofouling property. 1 min-flushing can recover almost 92% of flux.
Halogen reactive nitrogen from amines, imides, sulfonamides, and more	MPD [4wt%]	N/A	N/A	54	>99	Chloramines was formed on the surface when chlorinated water comes in contact with reactive nitrogen. It protects the surface from Chlorine attack and biofouling.
Zeolite A nanoparticles [0.4 % w/v] (in organic phase)	MPD [2wt%]	NaCl 2000 ppm	180	16.5 ± 1.3	91.2 ± 0.5	Zeolite A increases surface hydrophilicity which improves water permeability, solute rejection and fouling resistance.
Linde type A (LTA) zeolite nanocrystals	MPD [2-3% w/v] TEACSA [6% w/v] SLS [0.02% w/v] IPA [0-20% w/v]	NaCl 2000 ppm	224.8	20.4 to 108.8	90 to 95	Microporous defects were observed in nanocomposite membranes, indicating that nanoparticles change bulk polyamide structure and reducing cross-linking
TiO ₂ (in organic phase)	MPD [2 wt%] NaOH [0.05 wt%]	MgSO ₄ 2000 ppm	87	9.1	95	TiO ₂ nanoparticles in PA produced the increase of water flux due to the enhanced hydrophilicity in the membranes
Silver Nanoparticles	MPD [2 wt%] NaOH	MgSO ₄ 2000 ppm	125 to 250	~90	96 to 97	With Ag nanoparticles on the membranes colonies of Pseudomonas were almost all dead
Polyhedral Oligomeric Silsequioxane (POSS) (in organic phase)	MPD [2 wt%]	NaCl 2000 ppm	225	22 to 33	>98	POSS acts as cross-linkers and increases free volume of the PA film, which thus increases permeation.

Table 2.3. The Use of Carbon Nanotubes in Thin-Film Nanocomposite Desalination Membranes (Chan, 2015)

Type	Loading	Dimension	Application	Salts in Feed	Applied Pressure (Psi)	Permeation Flux (L/(m ² h))	Rejection (%)
Oxidized MWNTs	<ul style="list-style-type: none"> ▪ 0-0.2% (w/v) in aqueous phase ▪ 0-5% in organic phase 	N/A	Reverse Osmosis	NaCl 2000 ppm	100	71	Obviously Decrease
Zwitterionic SWNTs	<ul style="list-style-type: none"> ▪ 20 wt%; Direct deposit onto membrane substrate 	OD = ~1.5nm L = ~1μm	Reverse Osmosis	NaCl 2500 ppm	530	48.8	98.6
Carboxylic MWNTs	<ul style="list-style-type: none"> ▪ 3 mg per membrane sample; Direct deposit onto substrate 	OD < 8nm L = 10–30μm	Reverse Osmosis	NaCl 1000 ppm	100	<i>Applied potential: 1.5V</i> 22.0 ± 2.8	92.1 ± 1.3
PMMA modified MWNTs	<ul style="list-style-type: none"> ▪ 0.67, 1.33, 2.0 g/L in organic phase 	OD = 20–30nm	Nanofiltration	Na ₂ SO ₄ 2000 ppm	145	69.7	99.0
Amine functionalized MWNTs	<ul style="list-style-type: none"> ▪ 0.01%, 0.05%, 0.1% in aqueous phase 	OD = ~5nm L = ~50μm	Forward Osmosis	NaCl 10mM feed 2M draw	N/A	95.7	89.3
Aminisilanized SWNTs	<ul style="list-style-type: none"> ▪ 0.05%, 0.1%, 0.2% (w/v) in organic phase 	OD = ~2.7nm L = ~150nm	Low pressure Reverse Osmosis	NaCl 34mM	232	~22	~96
Functionalized MWNTs	<ul style="list-style-type: none"> ▪ 0.01–0.06% in aqueous or organic phase 	OD = ~30nm L = 10–30μm	Nanofiltration	Brilliant blue	N/A	Increase	No Change

2.7. Functionalization of CNTs

In theory, it is possible to produce CNTs having greater than or equal to 0.4 nm (Liu et al., 2000) diameter that would reject ions based on size elimination (Cannon et al., 2012). When it comes to ion separation, MD simulation studies of Corry et al (2008). have analyzed that the CNTs can sift particles from water with their diameters changing from 0.6 nm to 1.1 nm. They reported practically entire particle rejection from pores up to 0.9 nm diameter because of particle desolvation energy barriers. In spite of this, water confronts moderately low energy barriers and can pass through these restricted nanotubes. Nevertheless, production of CNTs with diameter less than 0.9 nm is not economically right now, due to sifting nanotubes which have a very narrow diameter variance. Larger diameter CNTs have considerably higher water flux, yet are not be able to reject ions.

For instance, Yu et al. (2010) considered ion transport through CNT membranes utilizing huge diameter (3 nm) CNTs, and the outcomes demonstrated no particle exclusion features the length of a ceaseless water channel forms inside the CNTs. To improve the atomic selectivity of CNT past steric impacts, their surface chemistry can likewise be adjusted through functionalization. This option approach is to begin from a non-particle specific CNT with bigger diameter, and connect functional groups at the

CNT tip to decrease the effective pore sizes either by steric impediment or charge shocks.

Holt et al. (2008) studied the particle avoidance of CNTs by using nanotubes with pore diameter underneath 2 nm, and functionalized it with hydroxyl bunches to reject ions through charge-charge association between the tip functional groups and the dissolved salt particles, while permitting non-charge water molecules to go through the tubes with quick permeation flux.

Majumder et al. (2007) who studied voltage gated CNT membranes shaped by tying charged molecules to the finishes of large diameter CNTs. Their work has concentrated on examining transport of two distinctive size yet equivalently charged particles, ruthenium bipyridine and methyl viologen, through MWCNTs with 7 nm ostensible center diameters. They demonstrated that flux and selectivity could be changed by applying a voltage over the membrane; this outcome verifies the charged functional groups being drawn into the CNTs at positive predisposition, bringing about a regulation of the pore size.

Fornasiero et al. (2010) used hydroxyl (OH⁻), carbonyl (C=O) and carboxylic/carboxyl groups (COOH) to functionalize CNTs having pores under 2 nm in diameter and solution ionic strength, pH, and ion valence are variable parameters for their study. Their results propose that electrostatic interaction between the carboxylate (COO⁻) charges at the end of the CNTs and mobile ions dominate rejection mechanism called Donnan-type. On the other hand, this also shows that at higher electrolyte concentrations, the rejection proportions diminished dramatically. the CNT pore radius (~1.6 nm) were considerably bigger than the hydrated radii of the ions (~0.6 nm) and consequently, ions separation was impossible to occur.

Corry's atomistic simulations study (2008) anticipated that ion rejection can occur in CNTs which have 1.1 nm diameter if functional groups having charged part are added. Electrostatic repulsion of charged groups enables to prohibit like-charged ions from entering the tube. Corry found that CNTs having 1.1 nm diameter and 8 COO⁻ groups completely inhibit transportation of the both positive and negative ions.

Chen et al. (2011) used simulations in order to design an asymmetric tip functionalized CNT membrane to reject salt. Hydrophilic-hydrophobic ends in smaller tubes supply driving force (6,6) and (8,8) convince the transport of water but ions

always are rejected. Using larger diameter nanotubes enhanced the permeability of water over narrow CNTs, even though the water flux decreased by nearly a factor of 5, due to added large number of functional groups.

Simulation by Won et al. (2006) indicates that the free energy of both ions and water molecules inside the CNTs are influenced by charges on the walls of the CNTs. This is match up with the idea that free energy barrier for water and ions entering nanotubes is affected by charges. Joseph et al. (2008) used MD simulations when partial charges were presented on the rim atoms the nanotubes and external field was applied along the nanotubes axis, in order to discover the occupancy of ions in narrow CNT channels. The simulation outcomes demonstrated that the occupation of ions in a CNT which are solvated in an electrolyte was too for neutral nanotubes and enhanced considerably in the existence of charged functionalities.

According to study of Suk and Aluru (2009), the water flux under applied pressure for (6,6) CNTs is influenced by the electric fields. Thus, electric fields are generated by charged groups at the ends of the CNTs will also disturb the water flux (Aluru et al., 2003). Simulation studies on (10,10) boron nitride nanotubes versus (10,10) CNTs prove that selectivity of K and Cl ions are reversed because of variety of entry impacts that based on the variation in charges at the entrance of the nanotubes (Aluru and Won, 2009).

Hughes et al. (2012) compared water diffusion in (6,6) and (8,8) CNTs as a function of functional groups which are hydrogen, hydroxyl, carboxylic acid, and carboxylate. They found that polar functional groups act to slow water diffusion. These experimental and simulation studies explicitly show that the ion and water transport can be adjusted using functionalizing.

3. SIMULATION STUDY

3.1. Molecular Dynamics

Molecular dynamics (MD) is one of the simulation techniques used to study physical motion of molecules and atoms by using computer and it is kind of N-body simulation. The atoms and molecules are allowed to interact for a certain period of time, giving a perspective of the dynamics of the system. In the most well-known form, Newton's equation of motion adjusts the directions of molecules and atoms by solving numerically for an arrangement of collaborating particles, where forces between the particles and their potential energies are ascertained utilizing interatomic possibilities or molecular mechanics force fields. The technique was initially created inside the field of hypothetical physical science in the late 1950s, yet is connected to present applications of chemical physics, materials science, and modeling of biomolecules. Molecular dynamics simulations are in many respects very similar to real experiments. When a real experiment is performed, firstly, a sample of the material is prepared to study and then connected to a measuring instrument (e.g., a thermometer, manometer, or viscometer), and the property of interest is measured during a certain time interval. If measurements are subject to statistical noise as in the most measurements, then the longer average, the more accurate our measurement becomes. In a MD simulation, the same approach is exactly followed. First, a sample is prepared; i.e. a model system consisting of N particles are selected and solved by Newton's equations of motion for this system until the properties of the system no longer change with time (we equilibrate the system). After equilibration, the actual measurement is performed. In fact, some of the most common mistakes that can be made when performing a computer experiment are very similar to the mistakes that can be made in real experiments (e.g., the sample is not prepared correctly, the measurement is too short, the system undergoes an irreversible change during the experiment, or do not measure the correct variable).

3.2. Selection of Functional Group

Biotin, shown Figure 3.1, is a water-soluble B-vitamin, also called vitamin B₇ and formerly known as vitamin H or coenzyme R (Wikipedia, 2017). Hinds et al. (2004) demonstrated that biotin functionalized CNTs limit the transport of Ru(NH₃)₆⁺ particle. Fornasiero et al. (2008) demonstrated enhancement in particle rejection utilizing CNTs functionalized with hydroxyl, carbonyl and carboxylic groups. The pore diameter of CNTs was in sub-2 nm range (much bigger than the normal size of salt particles), however, result of CNT membrane has demonstrated higher salt rejection with fast water transport. Their outcomes propose a Donnan-type rejection mechanism, ruled by electrostatic interactions between the settled COO⁻ charges at the ends of the CNTs and mobile particles. However, this also means that the salt rejection decrease along with the increase of ion concentration in feed solution. When electrostatic repulsion is totally retarded by the strong ionic strength in the solution, CNTs alone did not enable any sorts of size exclusion and therefore rejection dropped considerably. For the particles with small hydrated size, their rejections achieved to zero.

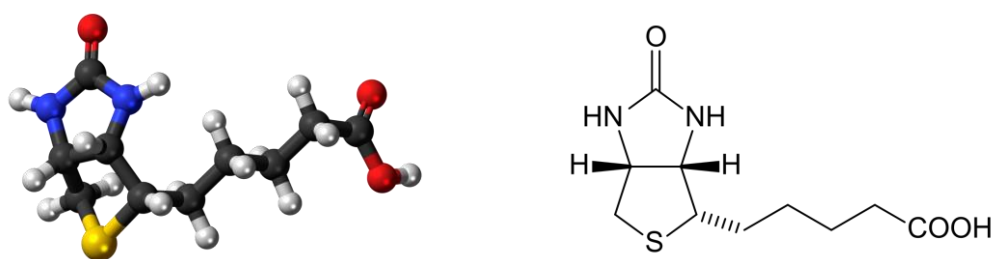


Figure 3.1. Molecular structure of biotin in 3D and schematic demonstration.

3.3. Molecular Simulation Procedure

The simulation procedure consists of several steps. Each step is described in this section briefly. In this study, Materials Accelerys Studio software has been used in order to construct and simulate whole system with its modules and tools.

▪ Constitution of Single Walled Carbon Nanotubes

First of all, before the binding operation of functional group, the basis system of structure has been prepared. Firstly, a single walled carbon nanotube (SWCNT) which

has (8, 8) chiral vector has been built by using “Build Nanostructure” module. Having 10 repeat units, non-periodic boundaries, bond length of 1.42 Å CNT has been selected. After selection of parameters, this SWCNT has resulted in a length of 24.60 Å and diameter of 10.85 Å. And then, the x and y coordinates of the system are fixed to be 30 x 30 Å.

▪ **Functionalization of The SWCNTs**

The commercial CNTs generally have carboxyl groups (COOH) at their ends. Therefore, one carboxyl group has been attached to one end of the SWCNT to bind biotin molecule to the tube. Firstly, OH⁻ ion has been cut off from COOH. Secondly, biotin has been bonded to carbon atom of carboxylate anion. As a result, CNT has been functionalized with biotin molecule and the last structure contains biotin-(C=O)-SWCNT composition or biotinylated SWCNT (B-SWCNT).

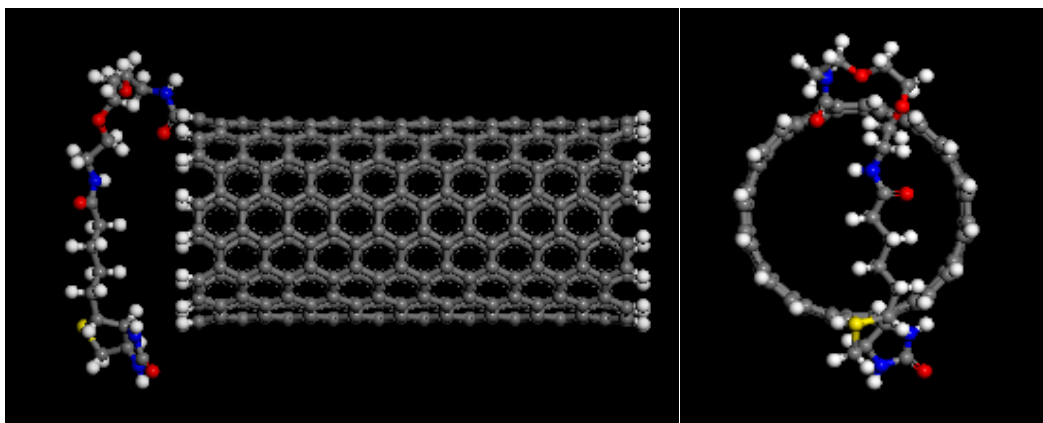


Figure 3.2. SWCNT functionalized with biotin.

▪ **Determination of Charge of Functional Groups & SWCNT**

After functionalization of SWCNT step, “DMol3” module has been applied on the structure containing biotin in order to calculate charges of atoms. In order to reduce running time, only the atoms of the biotin, C atom of the CNT and its adjacent C atoms within the first three rows have been included in the charge calculations. For this purpose, calculation has been implemented onto another SWCNT with 2 repeat units bound to biotin. After that, obtained data have been imported to the 10 repeat units’ SWCNT manually. In addition, charge distribution of entire system can be calculated using “smearing” method in Dmol3 module without manual import.

- **Inserting water molecules inside the SWCNT**

The channel of functionalized SWCNT has been packed with water molecules using “Amorphous Cell” module and water molecules located outside of SWCNT has been deleted. As a result, water molecules are only present inside the nanotube.

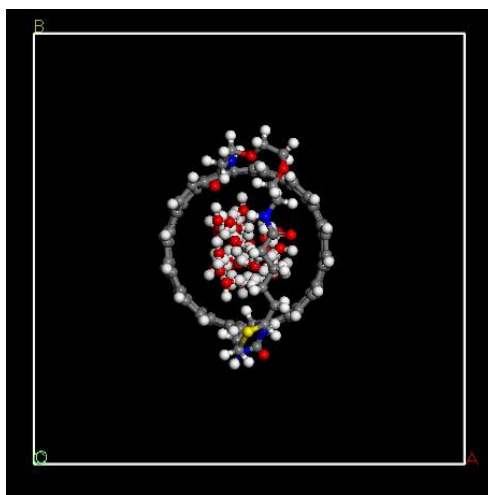


Figure 3.3. Water packing inside the SWCNT.

- **Construction of Repellent Wall**

In order to provide that the flow of water-boron mixture passes only through the SWCNT, a repellent wall has been created around the SWCNT that would physically serve as a barrier. For this purpose, Xenon crystal is preferred in the literature although there is no such a system in reality. Xenon has an inert character and is solid at 25°C. Consequently, it acts like a limiting surface.

- **Construction of Water Molecule**

Water molecule has been formed by using the most preferred model, TIP3P, in the literature for water mixtures. The parameters defined for the water molecule (r (OH), Å:0.9572; HOH, α : 104.52; $A \times 10^{-3}$, kcal Å¹² / mol: 582; B, kcal Å⁶ / Mol: 595; Q (O): -0.834; Q (H): +0.417). Dreiding force field is edited with "Forcite Forcefield Manager" module.

- **Construction of Boric Acid Molecule**

Boric acid parameters have been created by Otkidach and Pletnevsu (2001) by adapting to the CHARMM force field for different compounds containing boron in the

literature. For the boric acid molecule, the charge distribution ($q(\text{B})$: 0.562, $q(\text{O})$: -0.367 $q(\text{H})$: 0.179 and $q(\text{B})$ obtained with the B3LYP method and the aug-cc-pVTZ pressure set in "Computational Chemistry Comparison and Benchmark DataBase" was used. In the same way, the boric acid parameters are converted into appropriate forms for the Dreiding force field and edited by the "Forcite Forcefield Manager" module.

▪ **Construction of Water-Boric Acid Layer**

A water-boric acid layer was formed to model the interaction with the applied functional groups. For this purpose, 448 water molecules and 45 boric acid molecules were packed into a 30 Å x 30 Å x 20 Å triclinic unit cell with the aid of the "Amorphous Cell" module. In experimental conditions, the average number of boric acid residues at 4.5 ppm in seawater is very low for a 30 Å cubic unit cell in a molecular simulation. For quantity of boric acid, a concentration of 10 % was preferred in order to increase the interaction possibilities. Therefore, cell composition becomes that mole ratio for water is 1.0 with 0.744 weight fraction; mole ratio of boric acid is 0.1 with 0.256 weight fraction.

▪ **Construction of a Pure Water Layer**

A pure water layer was formed to be placed on the other end of the CNT to create the desired concentration difference. For this, water molecule was packed into 30 x 30 x 20 Å triclinic unit cell with "Amorphous Cell" module using packing method.

▪ **Building The SWCNT - Xenon Wall Layer**

A xenon panel has been combined with SWCNT with the help of "Build Layer" tool. Its coordinates have been fixed and it has been placed at the center of SWCNT. Since xenon atoms cannot be located inside the SWCNT and they can be only present around SWCNT the atoms which located inside the SWCNT have been erased.

3.4. Simulation Cell Setup

Simulation cell consists of three layers. The first layer is boric acid – water layer including 10 % concentration of boron. The second layer or mid layer is the functionalized SWCNT with Xenon panel and the last/third layer is the pure water layer. These three layers have been combined using "Build Layer" tool. In addition, vacuum area has been added to left side of the boron – water layer as shown in Figure

3.4. The coordinates of the bulk structure of xenon atoms and SWCNT are fixed and their charge is set to zero. However, the carbon atoms to which functional groups are attached, 3 consecutive carbon atoms and all hydrogen atoms at the both ends of the tube are flexible and have a certain charge distribution. The "Geometry Optimization" tool in the "Forcite" module in the simulation program (Materials Studio) has been used for the system equilibrium. Then, in order to model the interaction of functional groups with water-boric acid molecules, the system was equilibrated with MD method by applying NVT-MD for 100 ps using Forcite Dynamics tool. Finally, 1 ns NVT-MD has been applied to the obtained structure. During this time, movements and behavior of functional groups and water-boric acid molecules has been examined. And the same procedure has been repeated and simulated for SWCNT functionalized with two biotin molecules.

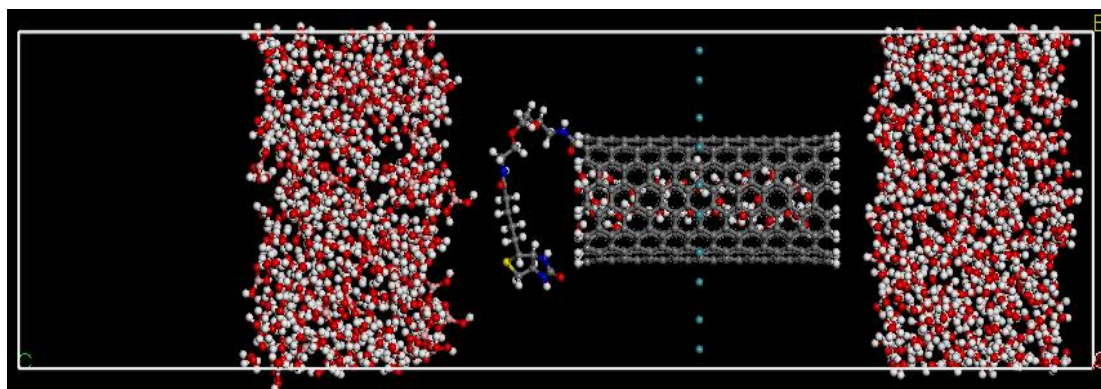


Figure 3.4 Simulation cell with three layers; vacuum, water-boric acid, B-SWCNT and pure water layer, from left to right.

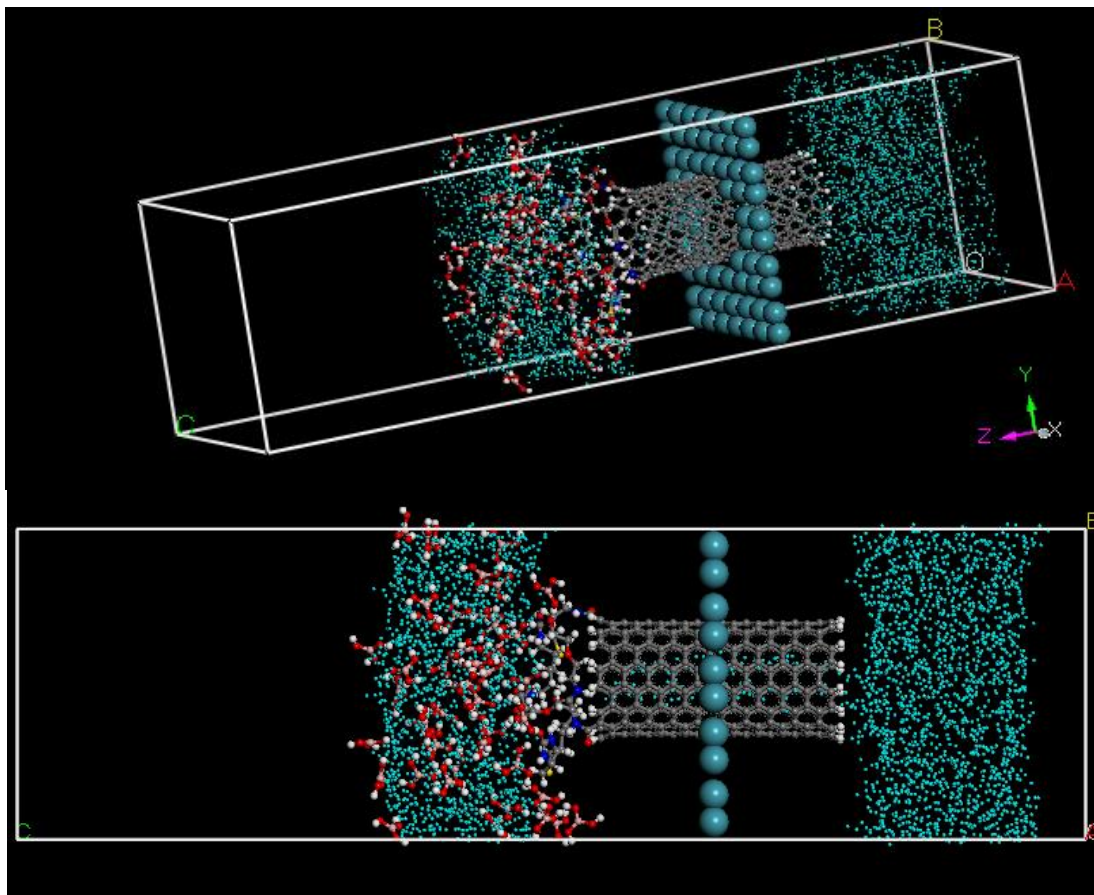


Figure 3.5. Simulation cell of SWCNT functionalized with two functional groups, blue dot represents water molecules.

4. RESULTS AND DISCUSSION

Firstly, one biotin molecule has been bonded to end of SWCNT both externally and internally before the simulation as shown in Figure 4.1. In order to observe final configuration of one biotin molecule, simulation has been done. At the end of the simulation, both initial configurations of biotin have been positioned as an external structure as shown in Figure 4.2.

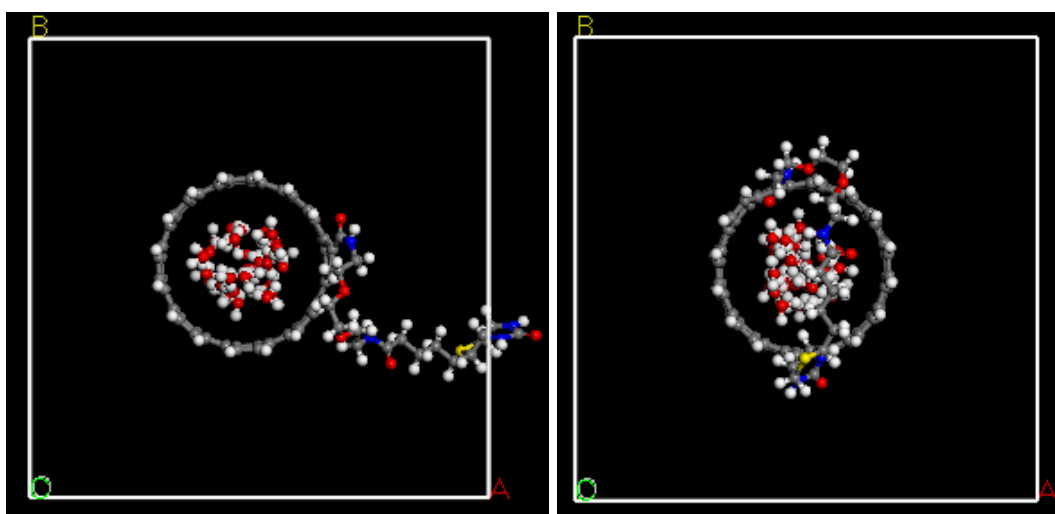


Figure 4.1 SWCNT with one biotin; externally at the left, internally at the right

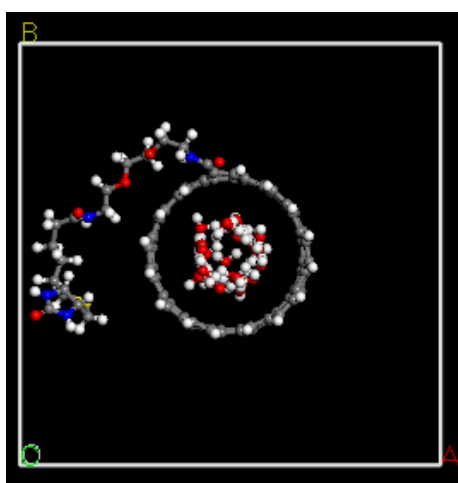


Figure 4.2 Unfolded final configuration (Unfavorable).

Result indicate that gatekeeper mechanism is not valid for one biotin molecule which has unfolded and positioned through outside which is an unfavorable structure. According to simulation result, independent of initial configuration, 2 biotin molecules fold inside and close the entrance of the tube when they attach to SWCNT due to interactions between each other. Therefore, the result has shown that more than one biotin molecule should be used in order to obtain steric hindrance as shown in Figure 5.3.

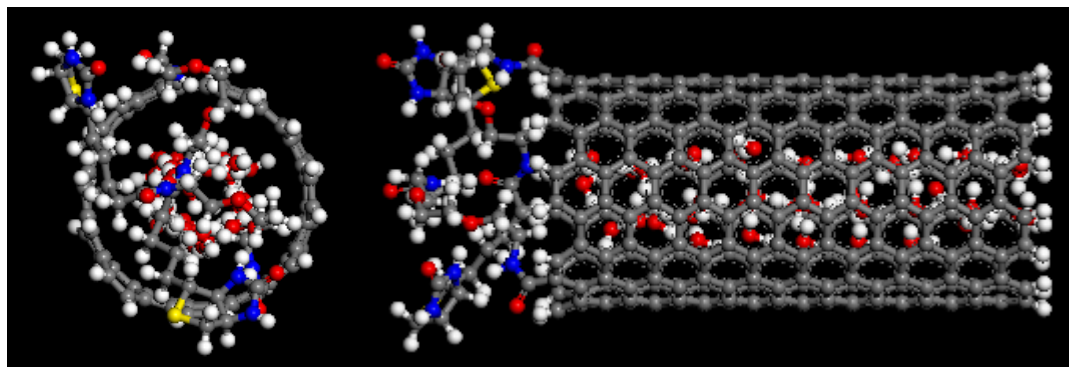


Figure 5.3. Final configuration of 2 biotin molecules at the end of the 1 ns.

In order to evaluate the likelihood of boric acid molecules entering the SWCNT, Radial Distribution Function (RDF) and atomic volume analyzes have been done for each case. For the RDF analysis, the boric acid molecules in the system and the carbon atoms closest to the boric acid-water layer on the surface of SWCNT (first 16 carbon atoms bound to the hydrogens or functional group/groups) have been selected and radial distribution graphs for the total MD period of 1 ns have been plotted using the "Forcite Analysis" module. These graphs indicate presence probability of boric acid molecule at a certain distance with respect to selected carbon atoms. For atomic volume analysis, snapshots have been taken at the beginning, middle, and end of the 1 ns simulation for each case, and the occupied volume and vacant volume of the SWCNT has been visualized with the aid of the "Atom volumes & surfaces" tool.

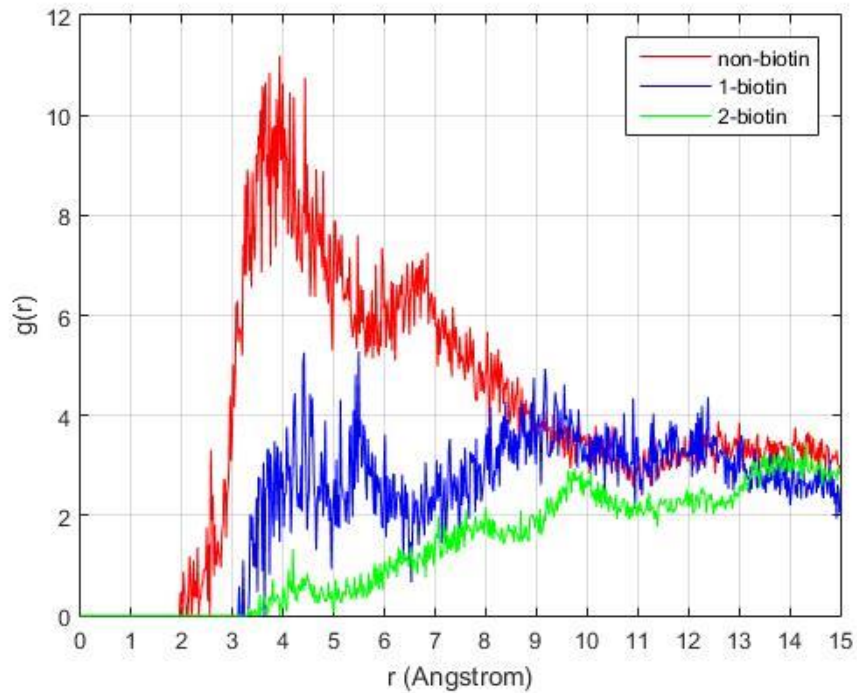


Figure 4.4 RDF graph of boric acid molecules-selected carbon atoms when SWCNT without biotin, with one biotin and with two biotin molecules.

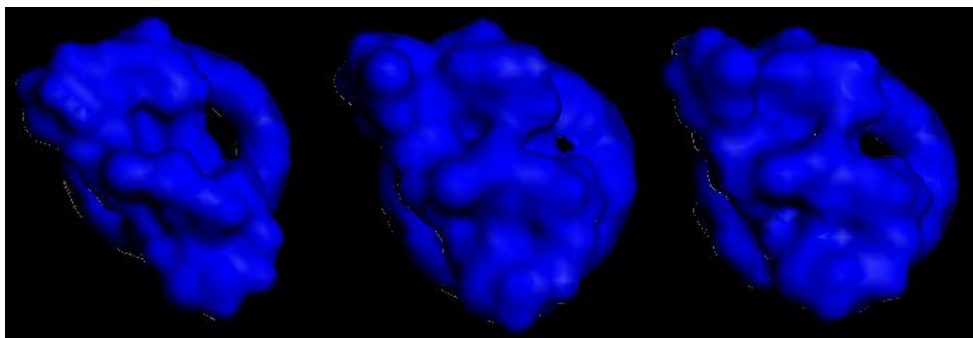


Figure 5.5. Atom volumes and surfaces analysis of SWCNT functionalized with two biotin molecules for 1 ns simulation, at the moment of 1st frame, mid frame and last frame from left to right, respectively.

When the RDF result (Figure 5.4) and atom volumes & surfaces analysis (Figure 5.5) are evaluated together, In the case;

- i) Where SWCNT without functional group, it is seen that the probability of boric acid to be located at a distance of about interval of 3 and 4 Å from the selected carbon atoms is high. That means that boric acid molecules have a high tendency to enter to the SWCNT.

- ii) Where SWCNT with one functional group, it is seen that the probability of boric acid to be located at a distance of about 4.5 and 5.5 Å from the selected carbon atoms is high. In this case, boric acid molecules still can enter to the SWCNT.
- iii) Where SWCNT with two functional group, it is seen that the probability of boric acid to be located at a distance of interval of about 10 and 14 Å from the selected carbon atoms is high. Boric acid molecules are considerably blocked by two biotin molecules due to gatekeeper mechanism and steric hindrance.

After all these observations, when the number of functional groups increases, the RDF graph shifts slightly to the right and boric acid molecules prefer to be located further from selected carbon atoms on the SWCNT. Moreover, two biotin molecules close down the mouth of SWCNT while one biotin cannot do that. Therefore, biotin can be preferred for boron removal as a functional group when more than one group is bound.

5. CONCLUSIONS

In this simulation study, the dynamic behavior of biotin attached to a SWCNT has been studied to determine the effect of this functional group on boric acid rejection potential of CNT filled polyamide TFN membranes. For this purpose, a CNT without functional group (control) and CNT functionalized with one and two biotin molecules has been built by using Materials Accelrys Studio software. After a biotin molecule is attached to the end of a SWCNT, the charge of each atom has been calculated using Dmol3 module. Then, the channel of functionalized SWCNT has been packed with water molecules using the “Amorphous Cell” module. In order to force the water and boric acid molecules to transport only through the CNT channels, a repellent Xenon wall has been created around the tube. After geometry optimization, the system has been equilibrated with NVT-MD for 100 ps. Then, 1 ns NVT-MD has been applied to the obtained structure. During this time, motion and behavior of the functional group and water-boric acid molecules has been observed.

The study has shown that if the SWCNT has no functional group, boric acid molecules are able to enter inside the tube. However, if the SWCNT is functionalized with only one biotin, the biotin is not able to fold and close the entrance of the tube but still has a slight effect on boron rejection. On the other hand, if two biotin molecules are attached to the end of the tube, it has been observed that the functional groups interact with each other. In this case, the entrance of the tube has been partially closed by functional groups which are folded. Consequently, two biotin molecules are able to increase boron rejection due to steric effect and gatekeeper mechanism. Therefore, it is concluded that biotin is an appropriate candidate for CNT functionalization and TFN fabrication for boron removal by RO process.

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