Carbon Nanotubes Membranes: Application in Water Treatment

Shyamal Kumar Roy[1], Suman Ghosh[2], Aveek Chattopadhyaya[3]
Madhumita Chakrabortyt[4]

[1,2,3,4] *Department of Electrical Engineering, Guru Nanak Institute of Technology, West Bengal, India*

Abstract - *This article serves as an explanation to the application of Carbon Nanotubes (CNTs) in water purification. The article is concerned with identifying the role that nanotechnology plays in water treatment and the specifics of water transport in CNT based membranes. The article analyzes the fabrication of CNT membranes and their effectiveness in water permeability, water desalination and other forms of water purifi- cation. Functionalized membranes were also analyzed by breaking down the process whereby PEG is added to carboxylic CNTs in a reaction catalyzed by sulphuric acid, with such structure being found to have increased mechanical properties. A comparison between CNT based membranes and other conventional membranes used in water purification were formed. This comparison was made by considering the efficiency of the membranes in water permeability, salt rejection, as well as the overall physical and mechanical properties of the membranes. CNT based membranes were found to perform better than the conventional membranes in most categories, making them the most cost effective and useful among the membranes with room for further improvement.*

Key Words: **Carbon nanotubes, Membranes, SWNT, PEG, CVD, Filtration**

1. INTRODUCTION

In the modern world, nanomaterials are manufactured and used for a variety of different purpose. Each purpose that a nanomaterial can serve depends on the structure and physical properties that the material may possess as a result of existing in the nanoscale. An important purpose for nanomaterials that has emerged in the past few years is water purification. This is a field that is a requirement considering the depletion of the availability of safe drinking water across the world. Due to the rise in sea level and evaporation caused by global warming and climate change, fresh water sources are facing rapid salination and increased forms of pollution. Without effective water purification technology, this is resulting in a larger number of people getting less access to potable water, especially in less economically developed countries where is most needed. Nanotechnology is being tested and developed in order to alleviate this problem. A wide range of nanomaterials that perform useful tasks such as adsorption, ultrafiltration, reverse osmosis, ion exchange and electrolysis have been developed. However, their cost of production and energy they require make them difficult to implement at a large scale and make them available to low income areas. Also some processes such as the adsorption techniques fail to desalinate water, and therefore cannot deal with the issue. Some of these processes, such as the membrane technologies, seem to be performing the task of desalination with increasing promise. Although they have not yet been made commercially viable, they utilize deionization in order to properly reduce the salt content in water. Scientists are looking to incorporate carbon nanotubes (CNTs) into the membrane technologies, using them as robust pores for water decontamination proper- ties. Since CNTs have self-cleaning properties, it makes them more useful and suitable for separating and rejecting salt ions and permitting water to flow through the interior of the nanotubes. The functionality of these CNTs will be examined, and their effectiveness will be compared to other conventional membranes. [2]

2. NANOTECHNOLOGY FOR WATER TREATMENT

In recent times, the general use of nanomaterials in water purification has risen as nanotech- nology continues to grow and develop. These nanomaterials are effective in the desalination of water, as well as in other forms of water purification. Other nanomaterials, in particular nanoscale metals, have the properties of reactivity, adsorption, as well as hydrophilic and hydrophobic interactions which can be used to contain and remove impurities from drinking water. An example of this is the structure of silver nanoparticles which have the properties of killing bacteria, viruses and fungi that reside in bodies of water. This makes it easier of other nanomaterials with adsorption and filtering properties to collect the dead pollu- tants and remove them from the body of water without the fear of them reproducing and multiplying. Other nanomaterials such as titanium nanoparticles have the ability to induce reduction reactions that transform the structure of harmful bacteria and viruses into inactive and non-toxic substances. Since bacteria, viruses and fungi lead to the spread of water-borne diseases such as cholera and bilharzia, rendering these species inert could save countless lives in poverty-stricken areas. In relation to water desalination, most nanomaterials have been found to have increased surface porosity. This property improves salt rejection, and some metal nanoparticles play a large part in removing inorganic materials from the surface of water bodies. Other nanomaterials that play an important role in the desalination of water include graphene and CNTs. These materials have enhanced adsorption capabilities that are useful in the desalination process. There are, however, limitations to using nanomate- rials in water desalination. These limitations nanomaterials also become unusable after the initial run, requiring the manufacture of fresh particles, which is a long and costly process. The cost of the actual nanomaterials themselves also proves to be a serious limitation in their use in water purification. Most of the nanomaterials used are heavy expensive metals such as gold, silver and titanium due to their inert properties. Processing them into nanomaterials is also an expensive process because of their high tensile strength and melting points. Developing the most cost-effective method of manufacturing these nanomaterials and using them to desalinate water in the least expensive way is the goal of many scientists involved in water purification. [2].

3. CARBON NANOTUBES IN WATER PURIFICATION

There are two types of CNT membranes for water purification Single Walled Nanotube Membranes *SWNT* and Multi Walled Nanotube Membranes *W N T*. We can classify the water pollutants in three different types: Organic pollutants such as Industrial waste, pesticides, chlorinated compounds, pharmaceuticals, Inorganic pollu- tants such as soil erosion, metals, nitrates, phosphates and Microorganisms such as animal excrement and sewage. [6]

3.1. Water transport in CNT membranes

The behavior of water flowing through different configurations of CNTs has been studied to understand how these configurations influence on the flow of water. These change on the configuration of the CNT structure produces a significant change on the diffusion coefficient at high and low temperatures when the distortion is on the Z axis, On the other hand if the distortion is at XY plane or it is caused for a local defect the diffusion coefficient changes cannot be ignored. [3]

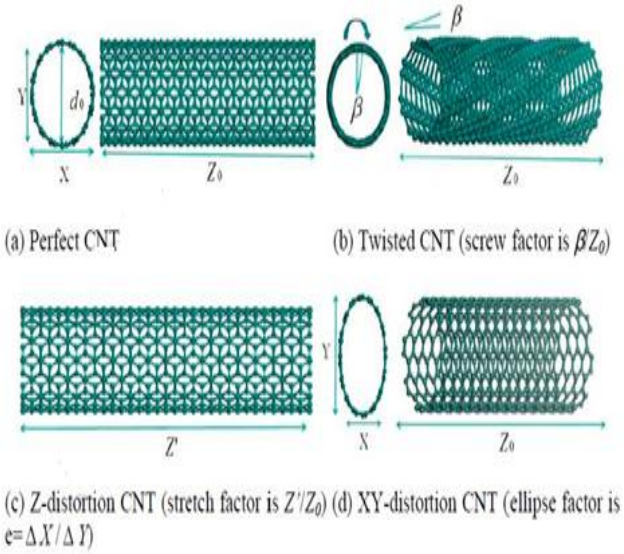

Fig. -1: Distorsion of CNT in Z an XY axis [3]

3.2. Fabrication of CNT Membranes

The preferred process is CVD because of the quality of nanotubes that can be obtained.

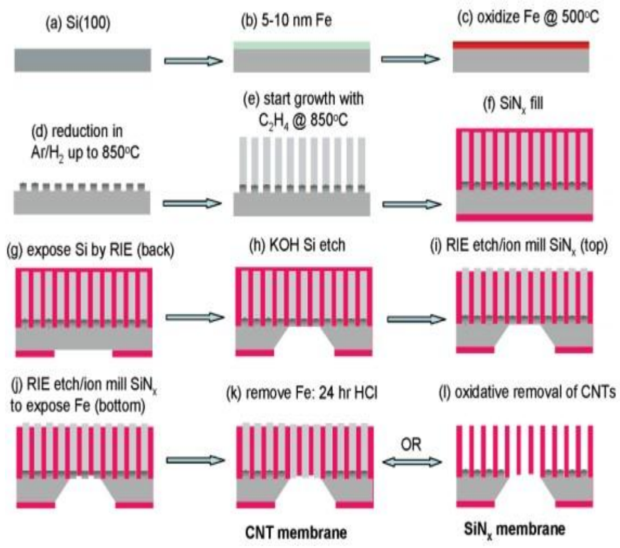

Fig. -2: CVD fabrication process [1]

4. CNT MEMBRANES TECHNOLOGY

4.1 Swnt Membranes

Vertical aligned CNT were synthesized using water assisted CVD. The microstructure of the CNT was characterized using SEM images. The inner structure, inner diameter and wall number of the CNTs were statistically measured, and the pores of the open-ended membrane were observed from transmission electron microscopy (TEM) images recorded using a JEOL JEM-3000F high-resolution transmission electron microscope at an acceleration voltage of 300 kV. The following results were obtained.[5]

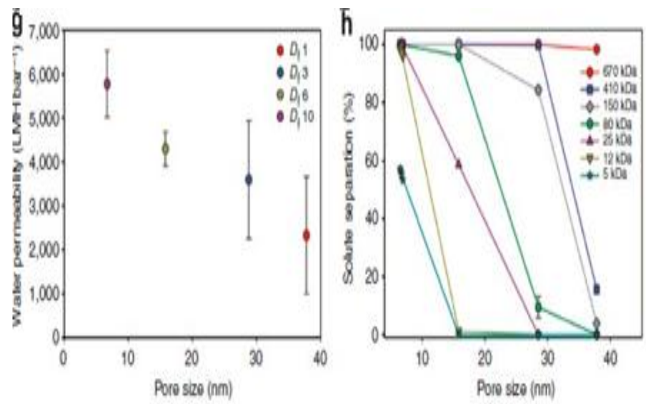

Fig. -3: Performance of the outer wall membrane. [5]

Sample	Densification factor (D_f)	Ratio of area ($A\ A_0^{-1}$)	Pore diameter (nm)*	Pore density (10^{10} cm^{-2})	Length (mm)	Tortuosity	Purified water volume rate (l h^{-1})	Water permeability (LMH bar^{-1})	Flow velocity (cm s^{-1})	Pore area (cm^2)	Cap opening method
Outer-wall CNT membrane	1	1	37.8 ± 0.7	8.14 ± 0.2	1.3	1.20	0.117	2,300 ± 1,330	0.034	0.968	—
	3	0.36	28.8 ± 0.2	26.4 ± 0.8	1.3	1.10	0.181	3,600 ± 1,340	0.056	0.896	—
	6	0.16	15.8 ± 0.1	50.8 ± 1.5	1.3	1.06	0.216	4,300 ± 390	0.075	0.799	—
	10	0.098	6.7 ± 0.1	83.3 ± 2.5	1.3	1.01	0.290	5,800 ± 760	0.120	0.670	—
	Thermal purification	0.098	6.9 ± 0.1	83.3 ± 2.5	1.3	1.01	0.662	13,200 ± 810	0.274	0.670	—
CNT wall membrane	10 (Thermal purification)	0.098	6.5 ± 0.1	166.6 ± 5	1.3	1.01	1.490	29,600 ± 460	0.440	0.938	O_2-plasma
Open-ended CNT membrane	1	1	6.4 ± 0.1	8.14 ± 0.2	0.2	1.20	0.070	1,200 ± 150	0.742	0.026	Mechanical
	O_2-plasma-treated	1		8.14 ± 0.2	0.2	1.20	0.096	2,000 ± 100	1.015	0.026	Mechanical
	O_2-plasma-open	1		7.76 ± 0.2	1.3	1.20	0.091	1,900 ± 120	1.016	0.025	O_2-plasma

CNT, carbon nanotube; LMH, litre per square metre per hour; SEM, scanning electron microscopy.

Fig. -4: Characteristics of the CNT membranes. [5]

4.2. Functionalized CNT Membranes

To functionalize carboxylic CNTs (COOH-CNT) with PEG, 10 g of PEG were melted in a round bottom flask on a hot plate at 90 C and 1 g of COOH-CNTs was then added. The mixture was allowed to stir about 10 min, followed by addition of few drops of sulfuric acid (H2SO4) as a catalyst. Then, the reaction proceeded for 5 h under nitrogen atmosphere followed by cooling at ambient temperature. The resulting mixture was repeatedly washed and precipitated with petroleum ether until no more PEG could be observed in the super- natant solution. After that, the precipitated PEG-CNTs were decanted with acetone as a final washing step before drying overnight under vacuum at 85 C. The obtained results reveal that the concentration of PEG-CNTs in the casting solution decreased the tensile strength and the modulus of the membranes until a specific loading (0–0.25 wt% PEG-CNTs) but after this loading the mechanical properties were increased dramatically.[4]

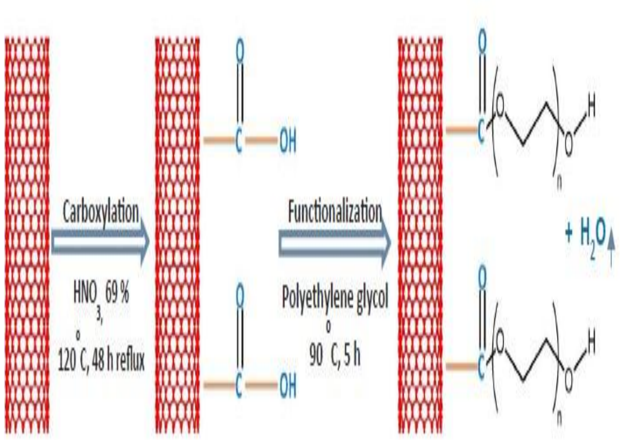

Fig. -5: Preparation of PEG funtionalized CNT.[4]

Membrane code	PEG-CNTs loading	Mean pore size, rm (nm)	Bulk porosity, ε %	Pore tortuosity, τ
M1	0%	12.53 (±0.82)	44.56 (±1.31)	5.43 (±0.25)
M2	0.1%	14.41 (±1.03)	50.43 (±0.58)	4.44 (±0.08)
M3	0.25%	21.27 (±0.36)	54.44 (±1.30)	3.89 (±0.16)
M4	0.5%	19.84 (±0.44)	48.47 (±0.56)	4.74 (±0.09)
M5	1.0%	17.68 (±0.65)	47.11 (±1.18)	4.96 (±0.20)

Fig. -6: Different types of membranes synthesized.[4]

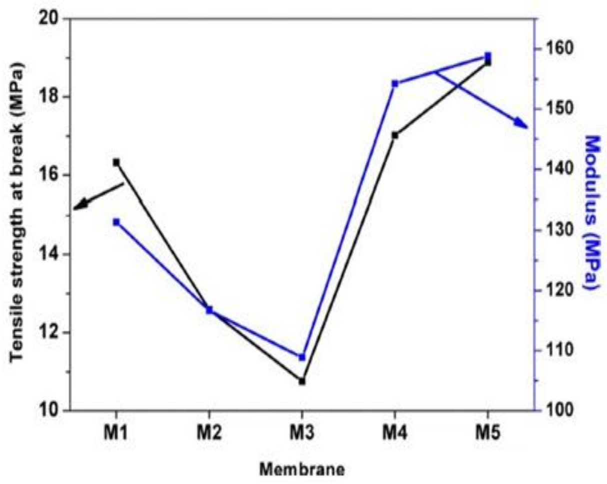

Fig. -7: Tensile Strength and Young Modulus. [4]

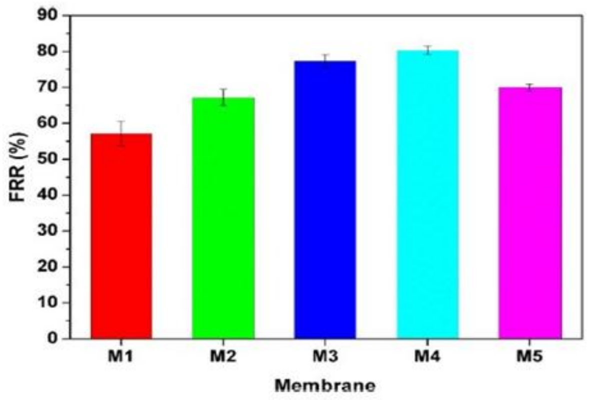

Fig. -8: Flux Recovery ratio.[4]

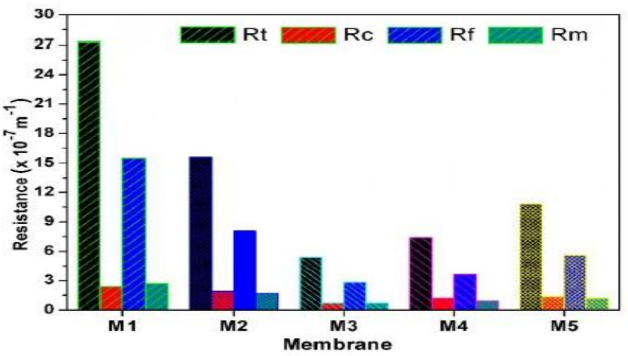

Fig. 9 Filtration Resistances. [4]

5. COMPARISON OF CNT MEMBRANES WITH OTHER MEM- BRANES

Membrane technologies achieved using CNTs has been found to perform more efficiently in the process of water desalination as compared to other conventional membranes such as re- verse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). This is because of a number of reasons that have been well-researched by scientists specializing in the manufacture of membranes for water purification. The first reason is that CNTs are hollow and hydrophobic, allowing polar water molecules to flow easier within them. The other membranes do not have the hydrophobic interior, while others are hydrophobic to a lesser extent as compared to CNTs. Secondly, CNTs have better water permeability than the other membranes, namely the RO membranes which have the highest level of permeability among the other membranes. The water permeability among armchair CNTs was found to be four times higher than in RO membranes. CNTs also have a higher level of salt rejection among the membranes. However, the NF membrane performs similarly to the CNTs in this section. A CNT membrane with an increased pore diameter could theoretically retain more solute particles that make up a salt, and it is possible to manufacture. Such an alteration in the pore diameter of a CNT membrane results in a % removal of salts dissolved, a rate that is much higher than that of RO membranes. While CNTs and RO membrane currently yield the same rates of salt rejection, the CNT membranes can be modified to yield a higher rate at a reasonable cost of production. Aside from the differences in the efficiency of the membranes in the process of water desalination, there are also numerous physical differences between CNT based membranes and the other conventional membranes. In terms of materials used to produce the membranes, CNTs are made out of carbon arranged in tubular form, while RO and NF membranes are manufactured from organic polymers such as polyamide, UF membranes are made from polysulfone and acrylic, and MF membranes are manufactured using polypropene and polyurethane. In terms of thickness, CNTs are usually 2 6 um thick, which is within the nanoscale. The thickest membranes are the UF membranes which range from 150 300 um, while the thinnest membranes are the RO membranes with a thickness of 0.1 0.2 um. In terms of self-cleaning capability, the CNTs have full capability while the other membranes require functionalization. [2]

6. CONCLUSIONS

1. For SWNT Membranes higher water permeability, purified water volume and flow velocity were obtained with smaller pore sizes.

2. For a PEG-CNT loading from 0.25% properties such as tensile strength, flux recovery ratio and filtration resistances start growing.

3. This enhanced in flow properties are a big step towards the improvement of membranes efficiency, however the theoretical values are still far from being reached. More research in this field and new fabrication techniques and improvements on the current techniques will be a key factor on the development of this technology.

REFERENCES

[1] Olgica Bakajin, Aleksandr Noy, Francesco Fornasiero, Costas P. Grigoropoulos, Jason K. Holt, Jung Bin In, Sangil Kim, and Hyung Gyu Park. Chapter 11-nanofluidic carbon nanotube membranes: Applications for water purification and desalination. In Anita Street, Richard Sustich, Jeremiah Duncan, and Nora Savage, editors, *Nanotechnology Applications for Clean Water (Second Edition)*, Micro and Nano Technologies, pages 173 – 188. William Andrew Publishing, Oxford, second edition edition, 2014.

[2] Rasel Das, Md. Eaqub Ali, Sharifah Bee Abd Hamid, Seeram Ramakrishna, and Zaira Za- man Chowdhury. Carbon nanotube membranes for water purification: A bright future in water desalination. *Desalination*, 336(Supplement C):97 – 109,2014.

[3] Jiamei Feng, Peirong Chen, Dongqin Zheng, and Weirong Zhong. Transport diffusion in deformed carbon nanotubes. *Physica A: Statistical Mechanics and its Applications*, 493:155 – 161, 2018.

[4] Arsalan Khalid, Ahmed Abdel-Karim, Muataz Ali Atieh, Saqib Javed, and Gordon McKay. PEG-CNTs nanocomposite PSU membranes for wastewater treatment by mem- brane bioreactor. *Separation and Purification Technology*, 190:165–176, jan 2018.

[5] Byeongho Lee, Youngbin Baek, Minwoo Lee, Dae Hong Jeong, Hong H. Lee, Jeyong Yoon, and Yong Hyup Kim. A carbon nanotube wall membrane for water treatment.

[6] Neeta Pandey, S. K. Shukla, and N. B. Singh. Water purification by polymer nanocom- posites: an overview. *Nanocomposites*, 3(2):47–66, apr 2017.