# Composition and Arrangement of Carbon-Derived Membranes for Purifying Wastewater

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**Abstract** Wastewater can be treated in many ways, out of which membrane separation technology is considered the most effective and unique one. Especially, carbon nanotubes (CNTs)-based membranes are getting noteworthy attention owing to the combined merits of CNTs and membrane separation. This results in offering superior membrane properties. This chapter discusses the classification and characterization of CNTs based membranes. It also reviews the fabrication methods for mixed CNTs based membranes in detail. Furthermore, the future direction and challenges related to CNTs based membranes are also briefly outlined.

**Keywords** Carbon nanotubes · Classification · Preparation · Characterization · Challenges

## 1 Introduction

Freshwater is an important and vital part of human's life. It also acts as an important storage unit for various other industries. According to a report, 75 percent of the world population could be underwater shortage conditions by 2025 [32, 34, 35, 38, 83]. It is known that millions of people will suffer from water scarcity conditions by 2050 [27]. Extensive efforts are being made to protect the world from this blooming water crisis.

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M. Jawaid et al. (eds.), *Environmental Remediation Through Carbon Based Nano Composites*, Green Energy and Technology,
https://doi.org/10.1007/978-981-15-6699-8_8

The three Rs, reuse, recycle, and recovery, for water have proved to be beneficial in generating freshwater with no side effects on human health. The most prevalent technology is membrane filtration, which is used to purify all kinds of water, including waste, sea, and brackish [33, 36, 37, 83]. Membranes are categorized with the classifications based on the compositions and the cut-off molecular weight. Membrane techniques like ultrafiltration, microfiltration, reverse osmosis, nanofiltration, pervaporation, and distillation of membranes are the most extensively used techniques for water purification. Polymers, ceramic, and hybrid materials are the main elements from which membranes are composed [32, 34, 35]. Polymeric membranes find their usage in purification and desalination of water because of their greater selectivity and high mechanical strength Ceramic membranes are normally used for challenging water purification processes owing to their better thermal and chemical stability. Both these membranes have a lot of setbacks and can still be modified for better performance [32, 34, 35]. In contrast to ceramic membranes, the polymer membranes are lesser chemically stable and have low resistance toward fouling but are cheaper than ceramic ones [76]. Hence Ceramic membranes are considered only for small-scale industries. In modern times, a lot of modifications in nanomaterials like nanoparticles, metal/metal-oxide, and carbon nanoparticles, dendrimers, and zeolites have been employed for the water purification [43–45]. But because of the high surface area, better mechanical strength, and high thermal stability, CNTs have received much attention in this industry. They are used in removing a lot of impure particles present in the solution [4, 5, 32–37]. Carbon nanotubes have also contributed in the development of modified membranes for water decontamination [13, 25, 46, 50, 52, 53, 56, 84, 88, 95, 96, 100]. The significant properties that make CNTs as an excellent material in the water purification are their enhanced surface area along with high aspect ratio, rapid water transport, and ease of modification [52, 53]. For improvising its efficacy, the carbon nanotubes can also be utilized as filler/packing components. This chapter explores the classification, characterization (Table 1) as

**Table 1** Carbon nanotubes characterization

| S. No. | Characterization techniques | Major aims | References |
|---|---|---|---|
| 1 | SEM/TEM | Analysis of morphology (diameter, defects, length, and purity), state of arrangement (SWCNTs and MWCNTs), several layers, and distance between multi-walled nanotubes) | [30] |
| 2 | Energy-dispersive spectroscopy (EDS) | Elemental composition, functionalization | [7] |
| 3 | Fourier transform infrared spectroscopy (FT-IR) | Functionalization | [7] |
| 4 | TGA | Purity, functionalization | [55] |
| 5 | XPS | Elemental composition, functionalization | [91] |

well as the composition of the CNTs based membranes. The challenges related to the future of the CNTs based membranes are also discussed at the end of the chapter.

## 2 Classification of Carbon Nanotube Membranes

CNTs based membranes are divided based on its implementation in fabrication processes, but broadly there are two main categories:

1. Freestanding carbon nanotube membranes
2. Mixed-carbon nanotube membranes

The freestanding membrane is further classified as vertically aligned carbon nanotubes membranes and bucky paper membranes. They are used in removing salt from the water and other wastewater treatment implementations [16, 69]. Carbon nanotubes are arranged as cylindrical pores in a vertically aligned carbon nanotube to force the liquid to cross the holes [29, 61]. Bucky paper CNTs based membranes have a 3D network with large pores that have an enhanced surface area. Mixed-carbon nanotube membrane has a design like that of the reverse osmosis structured membranes. In this arrangement, the top layer is assorted with a carbon nanotube and another polymer. The vertically aligned carbon nanotubes have a profound change in the rate of flow of water because of the small length of nanochannel and dense forest of the nanotube. Therefore, these membranes are more beneficial over bucky membranes. Moreover, tedious fabrication methods are the major challenge in the preparation of these membranes for large-scale applications. Whereas, the mixed-carbon nanotube membranes possess the benefit of the simpler fabrication process, but in contrast with the vertically aligned membranes, these membranes have a lower flux rate.

## 3 Aligned Carbon Nanotubes (ACNTs) Membranes

Aligned CNT membranes are composed of a single carbon nanotube arranged in high order and a vertically aligned array. Because of this, they have a porous structure composed of tiny spaces existing internally within the single tubes. These cavities are $\approx 5$ nm in multi-walled nanotubes [31]. This diameter is similar to the size of many biomolecules and other macromolecules, which shows that the vertically aligned carbon nanotube membranes are very well be fitted for various filtration processes [22]. A vital property of ACNT membranes is that their pore dimension can be determined by managing the dimensions of the catalytic particles used during the growth of nanotube. This gives out a method by which the membrane selectivity can be customized according to the particular separation application. It is also necessary to make small adjustments in the selectivity of these substances by covalently functionalizing the edges of the carbon nanotubes with certain moieties or groups [66, 67]. It was also seen that in these membranes, it is probable to adjust the pores' diameters between 38 and 7 mm. This adjustment can be made by applying an upright outward force across the parallel dimensions of the carbon nanotubes [51]. This causes compression in nanotubes, and the permeability increases, which is higher than that in other carbon nanotube membranes. The membrane also reduces the adhesion of bacteria, demonstrating its benefit over other membranes by being less affected by the formation of biofilm and fouling. Aligned carbon nanotube membranes are made by implanting carbon nanotubes into a matrix. They can also be made by developing them on a substrate using a chemical vapor deposition (CVD) process. While growing them on the substrate, the aligned CNTs must be treated with packing material like polystyrene or $Si_3N_4$ so as to furnish the interstitial spaces among the individual carbon nanotubes [59, 68]. This opens a lot of entries of solvent, solute, and gas molecules to the openings of nanotubes. Free ACNT membranes can also be produced in the absence of any holding substance [98]. The CNTs that are manufactured by this process have large spaces across the structure that can be stretched up to tens of nanometers in diameter. These membranes can filter selective solute molecules that are available in the watery solution. In a study, macroscopic hollow cylinders were made that had multi-walled nanotubes aligned radially [93]. These were shown to retain the heavy constituents of a hydrocarbon mixture along with some microorganisms such as bacteria and viruses. Compared to UF membranes, ACNT membranes supply a better water flux, which is three times more than that of the ultrafiltration membrane [6]. The aligned carbon nanotube also shows a better and higher biofouling resistance along with low levels of bacterial adhesion [6]. In another study, a new modified ultrafiltration membrane was used with the help of multi-walled nanotube and polyethersulfone [56]. The arrangement of multi-walled is ordered within the PES matrix. It provides a path for transport of water, thus causing a change of water flux rate, which was thrice greater than that given by multi-walled/polyethersulfone membrane. The flux rate was ten times more than that of the pure PES membrane and antifouling properties [56]. The pores that are present have very small diameters in the ACNT membranes and have been receiving significant importance due to their prospective implementations in the removal of salt from water. The permeable properties of aligned carbon nanotube membranes are comparable to that of nanofiltration and ultrafiltration membranes. The drawback associated with this is that the aligned carbon nanotube's forest must be eliminated from the underlying substrate, which can comprise rigorous chemical embedding processes using harmful reagents. An additional drawback of carbon nanotube usage is that their ends must be open properly, which again needs strict conditions like plasma oxidation. Both steps are confusing and expensive. Most aligned carbon nanotube membranes produced till now posses smaller surface area, thus requiring a long step of fabrication. It has a lesser packing density, reduced mechanical stability, and has very little resistance to fouling [43, 45, 75]. Thus, numerous substitutes are being developed that are less complex and have lesser harmful steps, which can be again modified for further advancements.

## 4 Bucky Paper Membranes Buckypapers (BPs)

Bucky paper membranes have a simpler structure and comprise an array of individual carbon nanotubes supporting themselves [24, 47]. Bucky paper membranes are flexible and have considerable chemical and physical stability [92]. Because of their inherent thermal, mechanical and electrical properties, bucky paper is suggested for various implementations like in microscopic servomechanism, nanosensors, electronic filters, for mimicking natural muscles, and cathodes field-emission electron gun [17, 48, 80, 99]. They are made from carbon nanotube dispersions, which are developed by involving extremely high energy samples comprising nanotubes along with the prospective dispersant. When the dispersions are filtered on a holding membrane in the vacuum, then the bucky paper membranes are fabricated [26, 94].

Due to the simple and cheaper manufacturing mechanisms of bucky paper, it is possible to make bucky paper for large-scale industries in contrast to aligned membranes. A close observation of the buck paper surfaces with the help of scanning electron microscopy tells about a highly disarranged structure including carbon nanotubes held together by weak forces along with pi–pi interactions [101]. The interior assembly of bucky paper membranes consists of pores varying from small to large is in correlation with the spaces in between and the bundles of carbon nanotubes, respectively. The pores in bucky paper accord to 60–70% of their total volume, thus befitting as a medium for filtration. Apart from this, the filtration characteristics of bucky paper have also been observed but only in small numbers because of their weak mechanical properties owing to their brittle nature. A method to overcoming this is to strengthen bucky paper membranes with the help of polymer intercalation [15]. The infiltration of various polymers, for instance, polystyrene, polyvinyl acetate into bucky paper membranes gives rise in the tensile strength, Young's modulus, tough character, and straining to crack values [15]. The addition of biopolymers like proteins and polysaccharides into bucky papers comprised of single-walled nanotubes can improvise their mechanical abilities [8]. A detailed analysis has shown that some biopolymers were left in the bucky paper membranes after vacuum filtration because of their ability to non-covalently interact with the nanotube. Improvising the mechanical properties of bucky paper membranes is again crucial as it reduces the risk which occurs because of the excretions of single carbon nanotubes into the environment.

There have been observations into the biological consequences of exposure to CNTs due to the similarity of these materials to asbestos elements. These studies have also shown that carbon nanotubes provide a specific effect like oxidative stress, disruption of membrane and interference with cell signaling pathways [19, 23, 63, 70, 74, 81, 85]. Consequentially, it is crucial to consider those very small quantities of carbon nanotubes should not break from bucky paper membranes or any other carbon nanotube membrane. It can be achieved by joining the nanotubes to each other using a covalent bond in bucky paper or aligned membrane. Because of their cheap manufacturing methods, it is possible to prepare bucky papers on a larger scale than aligned.

## 5 Preparation of CNTs

The main techniques that are implemented to prepare considerable amounts of carbon nanotubes are laser ablation, arc discharge, gas-phase catalytic growth from carbon monoxide, and chemical vapor deposition from hydrocarbons [79]. Arc discharge and laser ablation approaches are only good to prepare small numbers of carbon nanotubes. The products prepared often have some quantity of impurity in the form of particles of catalyst and amorphous carbon [79]. Purification techniques are needed to separate the nanotubes from unwanted by-products before investigating their characteristics and prospective functions. The results observed provided prospective encouragement to explore the CNT membrane material for filtration purposes. This has been strengthened after observing the cytotoxic properties of carbon nanotube membranes. This shows that these materials are least influenced by biofouling in comparison to that of traditional polymeric membranes and also displayed enhanced membrane lifetime duration via eliminating microbes [9].

## 6 Production of CNTs

Purification procedures require the separation of nanotubes from unwanted byproducts before being implemented for further instigation. The gas-phase techniques that produce nanotubes at low temperatures are changeable to the non-interrupted manufacture of a vast number of CNTs as continue flowing of gas would significantly moderate the source of the preparatory material.

An additional advantage related to the fabrication of the carbon tube with the chemical vapor deposition is the enhanced purity of the getting material (Fig. 1), which reduces the requirement for accomplishing all the stages [73]. With the help

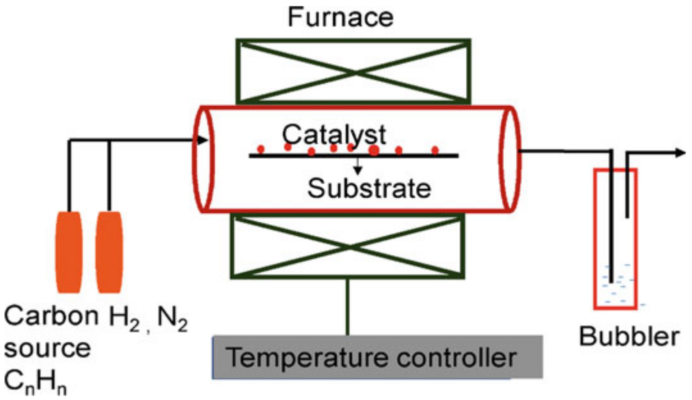


**Fig. 1** Diagrammatic representation of the CVD equipment

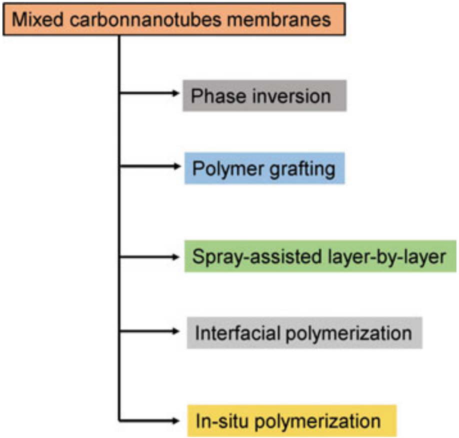
**Table 2** Methods used for preparing CNT-based composite membranes

| Type of membrane | Synthesis method | References |
|---|---|---|
| CNT/PA | Interfacial polymerization | [43, 45] |
| MWCNT/PSf (C/P) | Phase inversion | [12] |
| MWCNT/PA | Polymer grafting | [89] |
| (VACNTs)/polyaniline (PANi) | In situ polymerization | [18] |
| MWCNTs/PAN | Phase inversion | [65] |
| DDA-MWNTs/PSf | Phase inversion | [40] |
| (TNRs)/MWCNTs/PES | Phase inversion | [90] |
| TFC/polysulfone (PS-20)/MWCNT | Interfacial polymerization | [2] |
| PSF/CNTs | Phase inversion | [41] |
| A-MWCNTs | Phase inversion | [102] |
| Zwitterionic membrane | Phase inversion | [28] |
| Polymer membranes | In situ polymerization | [1] |
| Graphene oxide-incorporated thin-film nanocomposite membrane | In situ polymerization | [49] |
| Thin-film nanocomposite membrane | In situ polymerization | [97] |
| Polyester thin-film composite membrane | In situ polymerization | [64] |
| Carbon nanotube/PSf | Immersion precipitation | [39] |
| MWCNT/PVDF/PDMS | Deposition/coating | [62] |
| MWCNT/PVDF | Phase inversion | [60] |
| Acid-modified MWCNTs/nanosilver/PSf | Interfacial polymerization and phase inversion | [42] |
| F-MWCNTs/PES | Phase inversion | [104] |
| (NCNT)/PES | Modified phase inversion | [77] |
| PVDF/$Fe_2O_3$/MWCNTs | In situ polymerization | [3] |
| Surface-modified polyethersulfone (PES) composite membranes | Spray-assisted layer-by-layer | [58] |
| VA CNTs | In situ polymerization | [47] |
| MWCNT/nylon6 | In situ polymerization | [86] |

of the chemical vapor deposition method, single-walled nanotubes with the excellent purity have been fabricated in the gaseous phase by using $Fe(CO)_5$ and carbon monoxide in the increased pressure CO disproportion method [10].

# 7 Techniques for the Fabrication of Mixed CNTs Membranes

The following are the methods (Table 2) used for preparing the mixed-carbon nanotube membranes:



## 7.1 *Phase Inversion*

Multi-walled carbon nanotubes blend membranes prepared through the phase inversion process with a coagulant in the form of water [14]. A homogeneous multi-walled carbon nanotubes solution was made in N-methyl-2pyrrolidone (NMP) and blended with PSf solution. Dodecylamine functionalized multi-walled CNTs (DDA-MWNTs) were fabricated by Khalied and co-workers. The nanocomposite polysulfone/DDA-MWNts was casted by the phase inversion method. The fabricated nanocomposite membrane displayed excellent fouling resistance and flux recovery [40]. Phase inversion process with dimethylacetamide as a solvent and polyvinylpyrrolidone as a porogen was used to prepare flat sheet nanocomposite PSf/DDA-MWNTs membranes. A novel polyethersulfone (PES) membranes were prepared with the help of phase inversion method with the increased loading of the functionalized oxidized MWCNTs (OMWCNTS) together with the Arabic gum. The prepared OMWCNTs were characterized by various techniques like scanning electron microscopy and transmission electron microscopy, energy-dispersive X-ray spectroscopy [71].

## 7.2 Interfacial Polymerization

By employing interfacial polymerization, polyamide reverse osmosis membranes (RO) with the carbon nanotubes were fabricated. In this process, the functionalized CNTs were fabricated by the reaction of CNTs with the acidic mixture of sulfuric acid and nitric acid (in ratio 3:1), at different amounts of reaction conditions. The synthesized carbon nanotubes were observed to be well settled in the PA layer; this has been confirmed via various analytical techniques. The polyamide RO membranes containing well-dispersed CNTs possess an enhanced flux rate than the polyamide amide membranes devoid of CNTs [43, 45]. Polyamide thin-film membranes were prepared on polysulfone (PS-20) base by using interfacial polymerization of aqueous m-phenylenediamine (MPD) solution and 1,3,5-benzenetricarbonyl trichloride (TMC) in n-hexane organic solution. MWCNT were carboxylated by the heating of MWCNT powder in the sulfuric acid and nitric acid under continuous sonication at various intervals. Polyamide nanocomposites were then synthesized by the incorporation of MWCNT and the carboxylated MWCNT at various concentrations. The salt rejection and water flux performances of the prepared membrane revealed superior performance with that of other membranes [2]. CNT-enhanced thin-film composite membranes were fabricated by the incorporation of CNTs into the active layers of membranes for increasing its efficacy for the water treatment. MWCNT grafted via poly(methyl methacrylate) PMMA was prepared by microemulsion polymerization of methyl methacrylate(MMA) in the presence of c-MWNTS (acid-modified MWCNTS). The prepared membranes have proven significantly improved selectivity and permeability [72].

## 7.3 Spray-Assisted Layer-by-Layer

Using the spray-aided layer-by-layer method, a functionalized multi-walled CNT was fabricated by [57]. For improving the commercial polyethersulfone (PES) ultrafiltration (UF) membranes, antifouling properties negatively charged functionalized MWCNTs, mixed poly(sodium 4-styrenesulfonate) (PSS), and a positively charged poly(diallyldimethylammonium chloride) (PDDA) were deposited PES substrate through spray-assisted layer-by-layer L) method. The synthesized membrane displayed better anti-protein fouling and flux recovery [57]. Surface-modified polyethersulfone (PES) composite ultra-filtration membrane by using a spray-assisted layer-by-layer Liu and co-workers proved method. The prepared nanocomposite membrane displayed enhancement in the antifouling properties [58].

### 7.4 Polymer Grafting

A multi-walled carbon nanotube aromatic polyamide nanocomposite membrane fabrication was shown by Shawky and co-workers. Various instrumental techniques characterized the morphology of the surface, toughness, and roughness of the prepared nanocomposite membrane. The SEM and AFM images displayed that the MWCNTs were well dispersed in the PA (aromatic polyamide) matrix. Measurements of mechanical properties of this composite showed increasing membrane strength with increasing MWCNT content with monotonic increases in Young's modulus, toughness, and tensile strength. The prepared nanocomposite membrane displayed better salt rejection and organic matter rejection than the normal polyamide matrix membrane.

### 7.5 In Situ Polymerization

For the removal of natural organic matter in the water, MWCNT polyaniline (PANI)/polyethersulfone (PES) membranes were synthesized by incorporation of in situ polymerized MWCNTs/PANI complex. The prepared membrane showed enhanced permeability than that of the PES membranes. Higher rates for the rejection of the natural organic matter were also observed. This greater presentation is accredited to the synergetic effect of amplified porosity, narrow pore size distribution and hydrophilicity, and positively charged of the membranes by the inclusion of MWCNTs/PANI complex. The prepared membrane also demonstrated a cent percent water flux [52, 53]. A VACNTs/polyaniline (PANi) composite membrane was also fabricated via microwave supported in situ polymerization [18]. It was proved that with the help of a microwave, a better nanocomposite membrane could be fabricated.

## 8 CNTs Characterizations

Various techniques are available to analyze the characterization of carbon nanotubes. transmission electron microscopy (TEM) along with the scanning electron microscopy (SEM) are the methods that are known to observe the top of the peak along with the sidewall and with the morphology of CNTs [7, 30, 78]. The most significant tool for the characterization of the carbon nanotubes is the Raman spectroscopy technique [20, 21, 87]. It is regularly seen to check the quality as well as the pureness of the made carbon nanotubes. A Raman spectrum of carbon nanotubes shows two chiefs first-order bands, which include D band and G band. The former band is concerned with the imperfections of the carbon nanotubes and can be seen around 1350 $cm^{-1}$. The latter band is concerned with the amount of graphitization of carbon nanotubes that are at 1600 $cm^{-1}$. Therefore, the ratio of the area of both the band is found to determine the defect level in a specific carbon nanotube sample. Hence, by modifying reactants and chemical vapor deposition preparation dimensions like a catalyst, substrate, temperature, carbon precursor, pressure, time, and rate of gas flow assisted with several customizations for functional groups and characterization techniques here optimized carbon nanotubes could be gotten for various practical applications (Table 1).

## 9 Challenges Related to CNTs

Carbon nanotube membranes have a great prospective future in the wastewater treatment industry. However, it faces a lot of challenges to produce membranes as they are in the very first stage, and various vital issues are still to be tested. Viable readiness, reducing the cost of CNT, scaling in the industries, and assessing probable lethal effects of carbon nanotubes are some encounters that are about to be finished. Manufacturing carbon nanotubes on a large scale with a considerable pore size and the way to distribute is yet a vital challenge in implementing carbon nanotube on a great economic scale. Researchers must study more changed methods to get a more economical method to create a carbon nanotube. Another obstruction that prevents the implementation of carbon nanotubes in large-scale operation is the cost, specifically that of a single-walled carbon nanotube. Because of the high rise in the industrial manufacture of carbon nanotubes, the cost related to them will be cut down in the future. The prospective hazardous issues by carbon nanotubes on the health of humans and on the atmosphere made significant questions supposed to be answered detrimentally. It is assumed that raw carbon nanotubes are more hazardous in contrast to chemically modified carbon nanotubes. This is also because of the availability of a metal catalyst in raw carbon nanotubes. Another obstacle is the difficult growth of carbon nanotubes with good alignment in vertically aligned carbon nanotube membranes. The disarranged alignment can affect membrane properties like salt rejection and flux. The mechanisms that separated the pollutants from freshwater must be examined carefully.

## 10 Conclusion

Researchers were focusing on CNTs because of them showing excellent permeability. Their level of performance is the best among other membranes derived by carbon nanotubes. The latter offers good benefits like cheap cost and higher ease at production, along with the capability to be generated at a larger scale. Investigations into the applications like desalination, ultrafiltration, nanofiltration have shown that carbon nanotube membrane often showed increased resistance to biofouling in contrast to the tradition polymer. There is also a need to investigate the differences between the characteristics of filtration of bucky papers and that of composite membranes using various carbon nanotubes and agents of dispersion.

**Acknowledgements** The authors are thankful to the Banasthali Vidyapith and the Central University of Gujarat. One of the authors, Dr. Pallavi Jain, is grateful to the SRM Institute of Science and Technology, Delhi-NCR Campus.

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