

# Carbon Nanotube Membranes in Water Treatment Applications

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Carbon nanotube (CNT)-based membranes combine the promising properties of CNTs with the advantages of membrane separation technologies, offering enhanced membrane performance in terms of permeability and selectivity. This review looks at the existing membrane architectures based on CNTs and their main advantages and disadvantages for water treatment applications. The different types of CNT-based membranes that are reported in the literature are highlighted, as well as their corresponding fabrication methods. Available methodologies for tailoring the final membrane properties and behavior are thoroughly discussed, making special emphasis in chemical modification of the CNT surface. Finally, the most common applications of CNT-based membranes in water treatment are reviewed, including seawater or brine desalination, oil–water separation, removal of heavy metals, and organic pollutants. The main limitations and perspectives of CNT-based membranes are also briefly outlined.

sectors; however, freshwater resources do not get replenished at the same rate at which these are consumed. Consequently, potable water scarcity has increased, especially in developing countries, where agricultural activities are heavily affected, and farms lack access to enough water resources to meet their needs. This situation is glaring especially in the Middle East, Africa, Asia, and Latin America, where about 2.3 billion people are living without safe drinking water at home, and nearly 4 billion people experience severe water scarcity during at least one month every year.<sup>[1]</sup>

Due to the benefits it offers, in recent years, membrane separation technologies have attracted great interest as an

alternative to conventional separation methods for purifying water with an economical, superior operating efficiency in eliminating contaminants, and reusable capability.<sup>[2]</sup> Different types of materials have been tested as adsorbents for water contamination remediation. Over the past decades polymeric membranes have achieved remarkable contributions on both scientific research and industrial applications, due to their high capacity and high rate of adsorption.<sup>[3]</sup> Nevertheless, despite the great advances, their easy degradation in harsh solvents and their limited antifouling and mechanical properties result in a lack of stability in long-term applications, shortening their working life span.<sup>[4]</sup> The driving factors for which a material is selected for the development of new adsorbents include pore size distribution, wetting susceptibility, porosity, mechanical strength, cost, fouling resistance, stability, durability, and chemical stability. Therefore, the optimization of these features is crucial to achieve an intelligent design of new adsorbents with optimized membrane performance.

In recent years, nanomaterial-based adsorbents, and concretely carbon-based nanomaterials, are catching the attention of a wide number of researchers for the development of membranes for water treatment with enhanced efficiency and adsorption capacities, and have appeared as promising materials to fulfill the membrane requirements.<sup>[5–9]</sup> Nanomaterials are the tiniest structures synthesized by humans, with a size range from  $\approx 1$  to 100 nanometers. Furthermore, due to their small particle sizes, the chemical activity and adsorption capacity of the final adsorbent material is increased.<sup>[5]</sup> Among the different types of carbon-based nanomaterials that have been employed for wastewater remediation, the introduction of carbon nanotubes (CNTs) into advanced membrane separation technologies has emerged as cutting-edge research in the fields

## 1. Introduction

Daily human activities cause the production of high volumes of wastewater across the domestic, industrial, and agricultural

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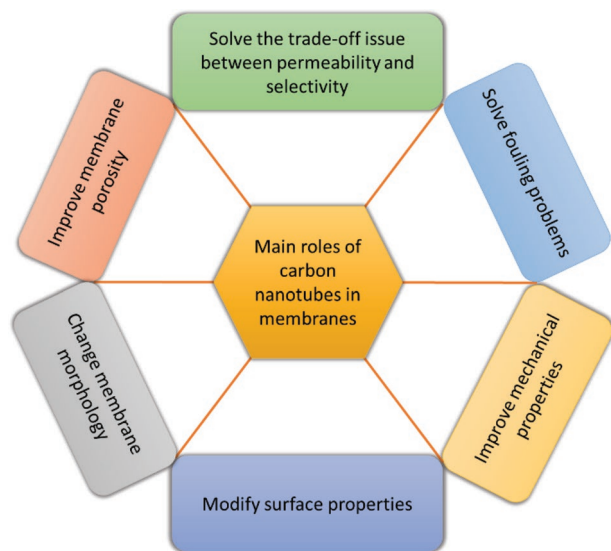
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**Figure 1.** Summary scheme on the roles of CNTs in membranes.

of nanotechnology and materials science.<sup>[10–12]</sup> CNTs consist of hollow, 1D tube-like structures with thin carbon walls, and have nanosized diameters with high aspect ratios.<sup>[13,14]</sup> Their unique structure results in excellent intrinsic properties, including large surface area, high aspect ratio, interconnected open pore and layered structure, high chemical and mechanical stabilities, and tunable chemistry, which provide potential for use as adsorbents. The main roles of CNTs in membrane separation technologies are summarized in **Figure 1**. The improvement of these properties is commonly followed by remarkable membrane performances.

CNTs can be used as additives for conventional membranes to control membrane fouling effects;<sup>[10]</sup> however, CNT potential can be further extended, to a great degree, through their assembly into macroscopic 2D-architectures, known as CNT membranes.<sup>[15,16]</sup> CNT membranes refer to thin-sheet planar materials with a highly porous network and improved tensile strength.<sup>[11,12]</sup> The concept of CNT membrane was first introduced more than 20 years ago by Li and Richard, who studied the mass transfer phenomena in single-walled carbon nanotubes (SWCNTs).<sup>[17]</sup> Thanks to their tubular structure, that is a key point to provide higher pore sizes and empty spaces enhancing the porosity of membrane structures, CNTs are believed to solve the typical trade off issues between permeability and selectivity and improve the fouling resistance ability of the resulting membranes.<sup>[18]</sup> The nature of the employed CNTs also has an influence on the final membrane performance. According to their number of concentric walls, CNTs are classified into SWCNTs and multiwalled carbon nanotubes (MWCNTs). The water flux rate will be governed by the different pore sizes and the hydrophobic effect of the CNT layers.<sup>[19,20]</sup> In general, as the number of CNT walls is augmented, the membranes exhibit improved water flux with a general improvement of the membrane performance. Thus, MWCNTs should allow the passage of a greater number of water molecules. However, there will be a cooperative effect between the growing number of walls and the hydrophobic effect of the CNT layers. Theo-

retical studies have demonstrated that in low diameter CNTs, the smallest SWCNTs reveal better water transport when compared to MWCNTs of identical inner diameter. This is due to the lower hydrophobic contribution of the SWCNT walls.<sup>[20]</sup> Furthermore, CNTs with small diameters (SWCNTs) allow the fabrication of highly permeable and very selective high-density membranes through the fabrication of vertically aligned CNT platforms, with water permeances that exceed those of conventional nano- and ultrafiltration membranes.<sup>[21]</sup> On the contrary, for large-diameter CNTs, the pore size effect is relevant in comparison to the hydrophobic character, and water transport is improved as the number of walls is increased.<sup>[20]</sup> Selectivity is also affected by the diameter of the CNTs. By the way of example, several theoretical studies have demonstrated that, in desalination processes, increasing the tube diameter decreases ion rejection, therefore, many variables contribute to the performance of the final membrane and a good compromise between water flux and ion rejection is required.<sup>[22]</sup>

Chemical modification of CNTs has been widely employed to tailor the membrane final properties. In general, CNT functionalization provides membrane hydrophilicity by introducing functional groups onto the CNT surface that results in changes in porosity, surface roughness, permeability-selectivity trade-off, and antifouling properties.<sup>[23,24]</sup> The hydrophilicity brought by functionalized CNTs enhances water entering, which enhances overall water permeability of the membrane, improving the high water permeability of hydrophobic membranes.<sup>[25]</sup> The improvement of antifouling properties is also closely related to the membrane hydrophilicity, because many foulants are naturally hydrophobic and the tendency of organic substances to get trapped on the membrane's surface is decreased. In general, hydrophilic modified membranes are negatively charged, which will play an essential role in repelling negatively charged organic substances on the membrane surface increasing antifouling performance.<sup>[26]</sup>

More recently, catalytic antifouling response has been observed in porous materials through novel chemomechanical strategies that inhibit the fouling of the membrane via self-cleaning.<sup>[27,28]</sup> For this purpose, the surface pores are armed with oxygen evolving water oxidation catalysts based on polyoxometalates,<sup>[29]</sup> that help to create nascent oxygen bubbles in the presence of hydrogen peroxide as chemical trigger, inducing the displacement of the foulants that reach out the surface of the porous architecture guaranteeing a long-term efficiency of the material. Furthermore, through the assembly of an oxygen evolving polyoxometalate cluster with tailored MWCNTs an improvement in the oxygen-evolving activity was achieved, thanks to the sequential electron transfer to the electrode that favour energy dispersion and relieve catalytic fatigue.<sup>[30]</sup>

Several reviews have addressed the potential applications of CNT-based membranes for water treatment, detailing the different types of existing membranes, fabrication methods, and the current hurdles for practical applications.<sup>[11,12,18,31,32]</sup> In this review, we first outline the different strategies for incorporating CNTs into membrane architectures and their fabrication methods. Then, the most common applications of different types of CNT-based membranes in water treatment are comprehensively reviewed, including seawater or brine desalination,

oil–water separation, removal of heavy metal ions and organic pollutants. The challenges associated with existing membranes and the future research directions toward advanced separation technologies are discussed as well.

## 2. Types of Carbon Nanotube Membranes

Based on the fabrication strategies, CNT-based membranes can be classified into three different types: vertically aligned (VA-CNT), CNT-based composite membranes (CNT-CPS), and buckypaper CNTs (BP-CNTs).<sup>[7,12]</sup> A brief comparison of their most important properties is provided in **Table 1**.

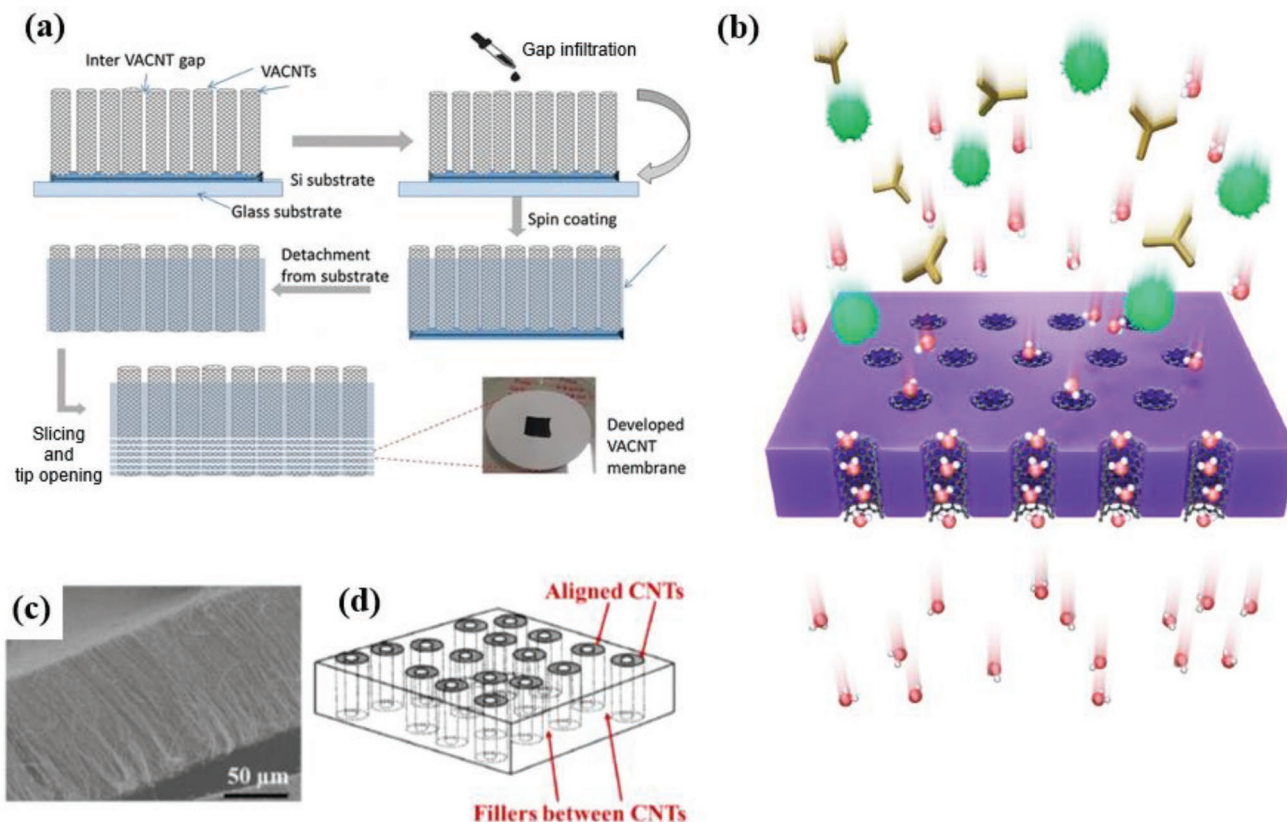
### 2.1. Vertically Aligned CNT Membranes

In VA-CNT membranes the CNTs are perpendicularly arranged yielding opened and aligned nanochannels with fast transport properties,<sup>[33]</sup> where the fluid passes through the hollow CNT interior or between the bundles of the resulting isoporous structure. Due to the vertically oriented water transportation and high packing density, VA-CNTs show the main advantage of allowing a high flux of water through the CNTs.<sup>[34,35]</sup> The first VA-CNT membranes were reported in 1998 by Martin group,

**Table 1.** Comparison of the most important properties for different types of CNT-based membranes.

VA-CNT	CNT-CPS	BP-CNT
Vertical arrangement	Random arrangement	Random arrangement
Compact network	Loosely fit	Compact network
High water flux rate	Moderate water flux rate	Moderate water flux rate
Complicated fabrication process	Simple fabrication process	Simple fabrication process
Require special operating system	Simple operating system	Simple operating system
Moderate mechanical strength	Excellent mechanical strength	Limited mechanical strength

when chemical vapor deposition (CVD) was employed for the synthesis of aligned CNTs on porous alumina membranes.<sup>[36]</sup> VA-CNT membranes can be prepared by embedding the CNTs into a polymer matrix, or by growing them onto a substrate, utilizing a CVD process. If they are directly grown onto the surface of a substrate, a filler material (normally a polymer or an inorganic filler) is required to fill in the interstitial voids between the CNTs (**Figure 2a,c,d**). Previous to the filling process, both ends of the CNT are covered with fullerene caps. Then the resulting membrane composed of aligned CNTs is removed



**Figure 2.** a) Conventional fabrication method of VA-CNT membranes. Reproduced with permission.<sup>[35]</sup> Copyright 2016, Springer. b) Schematic representation of a VA-CNT membrane used for water treatment. The image shows water molecules, unwanted molecules, and an impermeable material filling the interstitial spaces between carbon nanotubes (CNTs) and VA-CNTs. Reproduced with permission.<sup>[47]</sup> Copyright 2020, MDPI. c) Scanning electron microscope (SEM) image of a vertically aligned array of CNTs. d) Schematic diagram of VA-CNT membrane structure. Reproduced with permission.<sup>[38]</sup> Copyright 2004, AAAS.

from the underlying substrate, and the ends of the closed tubes are opened through etching or oxidation methods.<sup>[37,38]</sup> Non-filled VA-CNTs, where the interstitial space between CNTs is vacant and an additional permeation area is available, have also been reported.<sup>[37,39,40]</sup> However, in pressure-driven processes, the mechanical strength of nonfilled VA-CNT membranes is normally deficient and does not maintain the VA form, which limits their practical applications.<sup>[41]</sup>

Over the years, several theoretical and experimental studies have demonstrated that VA-CNT membranes exhibit a considerable flow enhancement with respect to other membranes with similar pore sizes,<sup>[42–45]</sup> mainly due to the high permeability provided by the atomic smoothness and hydrophobicity of the inner wall of CNTs and high rejection rates related to the nano-sized pores and uniform pore sized distribution (Figure 2b).<sup>[46]</sup> CNT density is one of the most important parameters of VA-CNT membranes, as it is directly related to the permeability of the membrane.<sup>[47]</sup> A higher number of pores per unit area results in higher permeability, therefore many studies have been focused in achieving an increment of CNT density to obtain better permeability rates. Among the different attempts to do so, densification of the VA-CNTs through capillary-forces or mechanical densification approaches, providing additional membrane pores, has been the most promising method.<sup>[40,43,48]</sup> For example, additional membrane pores were achieved by using n-hexane as a volatile liquid. In this work, solvent evaporation allowed the reduction of the gaps between CNTs from 30 to 3 nm,<sup>[40]</sup> resulting in a density of  $2.9 \times 10^{12}$  pores  $\text{cm}^{-2}$ , which was ten times higher than the density prior to densification. Highly volatile solvents, such as acetone, have demonstrated to lead to closer contact between the aligned CNTs, enabling the fabrication of reinforced networks with high plasticity and mechanical strength.<sup>[49]</sup> However, recent studies have demonstrated that pore density affects permeability but it is not a decisive factor. In fact, permeability depends on several aspects such as pore density, CNT size, and the number of CNT walls.<sup>[21,47,50]</sup>

Permeability and selectivity of the VA-CNT membranes can also be controlled via tip/sidewall functionalization with suitable chemical groups.<sup>[12,51,52]</sup> Practical applications of VA-CNTs are often limited by their surface properties; however, the surface can be chemically modified in order to meet the specificity of each particular application. In VA-CNT membranes, functionalization approaches are usually conducted after membrane fabrication.<sup>[24]</sup> For example, the VA-CNT membrane wettability can be controlled through oxidation techniques. By using oxygen pulsed direct-current plasma<sup>[53]</sup> or pure oxygen plasma etching,<sup>[54]</sup> oxygen groups are grafted onto the VA-CNT tips, leading to a more hydrophilic surface. The superhydrophobic character can be restored by  $\text{CO}_2$  laser irradiation.<sup>[53]</sup> Plasma oxidation was also employed by Majumder et al. to introduce carboxylic groups onto the CNT tips.<sup>[55]</sup> The carboxylated CNT membrane was further modified by other functional groups through different chemical approaches, such as alkanes, dye molecules, or amine derivatives, for controlling the flow and selectivity of chemical transport through the CNT membrane. Further advancements were achieved by using electrochemical diazonium grafting chemistry, which increased the number of carboxyl groups onto the CNT tips by  $\approx 5$ –6 times compared to

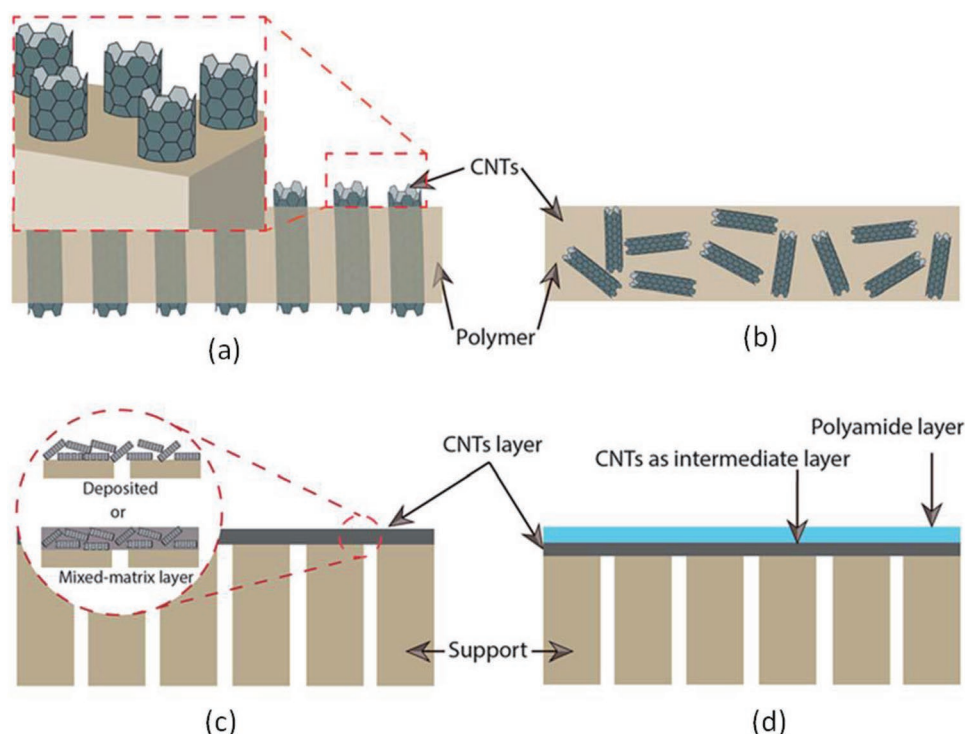
the plasma oxidation technique. This resulted in an improvement in the ionic transport of positively charged species.<sup>[56]</sup>

Even so VA-CNT membranes could be ideal candidates for their application in membrane processes that require hydrophobicity to operate, these membranes still show limitations mainly related to the complicated fabrication methods associated with the synthesis of highly oriented VA-CNT arrays with optimal pore microarchitecture (i.e., pore size and porosity).<sup>[12,47]</sup> The complex fabrication techniques are a big hurdle of these membranes for large-scale applications; however, important advances have been made in their application in wastewater regeneration or desalination processes that will be reviewed in the following sections.

## 2.2. CNT-Based Composite Membranes

CNT-CPS membranes emerged with the main aim of improving the performance of existing membranes (mainly polymeric), through the incorporation of CNTs into their structure.<sup>[11,12]</sup> CNT-CPS membranes consist of heterogeneous structures with randomly aligned CNTs embedded into a polymeric matrix, where the CNTs can be incorporated on the top layer of the membrane or used as intermediate layer (Figure 3).<sup>[57–59]</sup> Due to the unique properties of CNTs, such as high flexibility, effective  $\pi$ – $\pi$  interactions with aromatic compounds, very low friction coefficient on their internal walls, high aspect ratio, and the existence of a wide number of nanochannels, many studies have demonstrated the great potential of CNTs as nanomaterials for improving the polymeric membrane separation properties.<sup>[4,58–60]</sup> The major roles of CNTs in composite membranes are as follows.

- 1) Improvement of mechanical strength: The C–C bonds in the graphitic layers of the CNTs are probably the strongest chemical bonds known in nature, contributing to the high stiffness and axial strength of CNTs. Thus, through their incorporation into composite membranes these act as a robust mechanical support providing reinforced membranes.<sup>[4,61]</sup>
- 2) Tailored porosity: By choosing the inner diameter of the employed CNTs a fine control of the pore dimension at the nanometer scale can be achieved, with high retention performance for multivalent ions and organic molecules of different sizes. Matching the pore size to that of the target molecule is crucial to achieve improved selectivity and flux.<sup>[4]</sup>
- 3) Increased superhydrophobicity with superior wetting resistance is easily achieved, presumably because of the excellent slippery properties of the CNT layers.<sup>[62,63]</sup>
- 4) Better permeability: The effective dispersion of the CNTs in the polymer matrix provides high porosity with superior permeation flux. This is achieved by making CNTs hydrophilic through various kinds of functionalization. Though the introduction of chemical moieties the nonpolar-hydrophobic are converted to polar-hydrophilic CNTs, enhancing the interaction bonding between the CNTs and the polymers. This, in turn, results in increased membrane porosity and rougher or smoother membrane surface, influencing the rheological properties of the final membrane.<sup>[24]</sup>



**Figure 3.** Schematic representation that displays the differences between the structure of a) VA-CNTs membranes and b) CNT-CPS membranes. c,d) The different ways to incorporate CNTs into the CNT-CPS membranes. Reproduced with permission.<sup>[24]</sup> Copyright 2017, Royal Society of Chemistry.

5) Long-term operation stability is generally achieved thanks to the robust interfacial adhesion between the substrate, the CNT interlayer and the polymeric layer.<sup>[61]</sup>

Thus, CNTs are incorporated into the polymeric membranes to improve the membrane permeability and selectivity by fine-tuning the physical and chemical properties of the as-fabricated membranes.

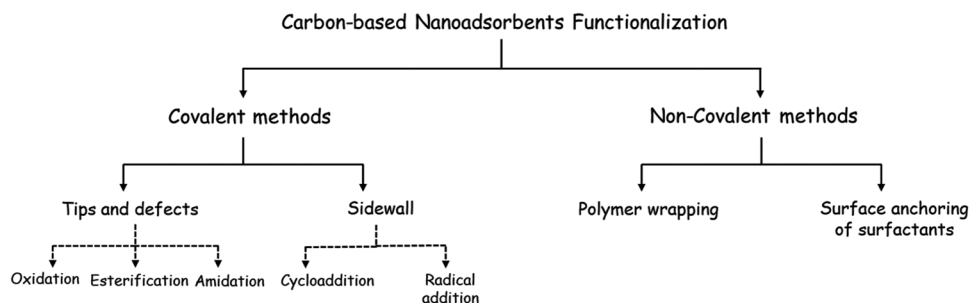
Among the most popular fabrication methods for polymeric CNTs-based composite membranes<sup>[64]</sup> the following can be highlighted.

- i) The phase inversion method has been commonly used in the fabrication of CNT-CPS membranes. In fact, this method is employed for most of the commercially available membranes due to its versatility and scalability. In this fabrication method a suitable organic solvent is employed to prepare a homogeneous solution of the polymer and the CNTs, which is cast on a substrate or allowed for wet spinning and subsequently immersed in a water bath where the exchange of solvent by coagulant and phase separation occurs resulting in a flat sheet or hollow fiber CNT-CPS membrane.<sup>[12,60,64,65]</sup>
- ii) The blending method has also been widely employed by several groups to fabricate CNT-CPS membranes with fine-tuned separation properties. Similar to the phase inversion method, a homogeneous solution of the polymer and the CNTs is prepared by sonication or mechanical stirring. However, the resulting mixture is left to dry yielding dense CNT-CPS membranes with enhanced mechanical properties.<sup>[11,12,60,66,67]</sup>
- iii) Another equally important method for membrane fabrication is interfacial polymerization. Membranes formed by the

interfacial polymerization method are referred to as thin-film composite (TFC) membranes.<sup>[12,68]</sup> This method is a type of step-growth polymerization which occurs at the interface between two immiscible phases (an organic and an aqueous phase), where two reactive monomers react to form a polymeric layer on top of a membrane support to act as an active layer for solute rejection.<sup>[69]</sup> In this type of membranes, CNTs are incorporated within the final polymeric layer through their dispersion in either the aqueous phase or the organic phase.<sup>[11,12,68]</sup> In this case, the membrane characteristics can be varied through the selection of different factors such as the type of monomers, concentration of aqueous and organic solution, type of additives, organic solvent, and choice of substrate membrane.<sup>[68]</sup> The CNT loading is one of the most important parameters, since CNTs can significantly increase the mechanical resistance of polymer materials even at low concentrations.<sup>[57]</sup>

- iv) Direct coating has been also employed to fabricate CNT-CPS membranes. In this method, CNTs are first sonicated in water with the assistance of surfactants to obtain a homogeneous dispersion that is immediately loaded on cleaned membrane substrates based on polymers, thus yielding a CNT layer on the surface.<sup>[11,64]</sup> Unfortunately, the CNT layer in these membranes shows poor stability due to the weak interaction with the membrane substrates, which results in the detachment of the CNTs during practical applications.<sup>[64]</sup>

However, CNTs are hydrophobic and preferentially aggregate and entangle together, which remains an obstacle during CNT-CPS membrane fabrication.<sup>[11,12,57]</sup> In order to achieve a homogeneous CNT dispersion in the polymer matrix, a wide number



**Figure 4.** Different types of functionalization possibilities for carbon-based nanoadsorbents.

of surface modification strategies have been reported.<sup>[24,57,70,71]</sup> Furthermore, CNT surface chemistry is also a crucial strategy to modify the adsorption capacity of CNTs.<sup>[10,24,51,60]</sup> Harsh reaction conditions may cause damage to the CNT structure, hence the chemical modification of the sidewall should be carefully carried out through suitable means in order to preserve the intrinsic properties of CNTs.<sup>[59]</sup> Chemical functionalization of CNTs can be achieved by using both the covalent attachment of functional groups to the CNT surface and the noncovalent adsorption of different types of molecules to the surface of CNTs (Figure 4).<sup>[23,51]</sup>

Air oxidation or acid oxidation has been one of the most commonly used methods for affecting the surface properties. Oxidation introduces functional groups such as  $-C=O$ ,  $-COOH$ , and  $-OH$  onto the CNT surface, which has been regarded as an effective way to increase the hydrophilicity and stability of carbon nanotube suspensions.<sup>[51]</sup> Thus, the binding efficiency between the CNTs and polar organic solvents is enhanced resulting in a greater affinity of the CNTs for polymer matrices. Through oxidation approaches, not only the CNT dispersibility is affected, but also the hydrophilic character, pore size, porosity, and roughness/smoothness of the final membrane structure are modified.<sup>[24]</sup> The presence of CNTs in the modified membrane generates more pathways for water transport, resulting in a bigger pore size and increased porosity, which enhances the overall water permeability of the membrane. However, increasing the number of oxygen groups onto the CNT surface is actually a double-edged sword, as the adsorption of nonpolar compounds is significantly reduced, due to reduced hydrophobicity, and so do planar chemicals because the contact between the CNTs and the chemicals is insufficient in this case.<sup>[72]</sup> Apart from oxidation, other covalent functionalization approaches can be employed in order to tune the CNT surface affinity toward different types of pollutants in water, such as the chemical modification of the CNT surface via aryl diazonium salts or cycloaddition reactions (Figure 4).<sup>[73–77]</sup>

Noncovalent functionalization with polymers or large organic molecules has also been an effective way for improving the solubility and compatibility of CNTs with the polymer matrix.<sup>[78]</sup> The main advantage of noncovalent approaches is that the structure and intrinsic properties of CNTs remain unaltered after the functionalization process. However, the noncovalent interactions between the polymers and the  $sp^2$  hybridized network of the CNTs are weak, which could result in reduced stability of the final membrane structure.<sup>[23]</sup>

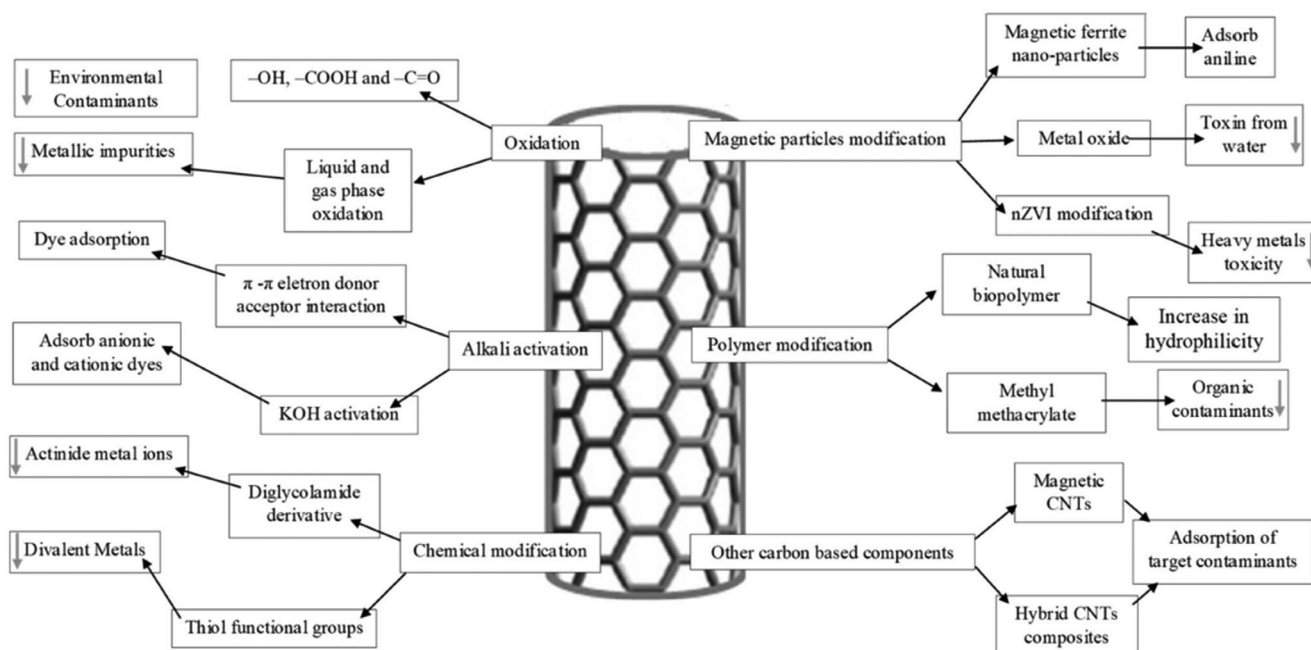
Figure 5 reports an overview of different surface modification schemes of CNTs used for targeted contaminants. While CNT-based composite membranes have been successfully fabricated through the different methods described above, there are still limitations mainly related to the controllable loading of CNTs into the polymer matrix, compatibility between the polymer and the CNTs, and the scale-up manufacturing of the membranes. Furthermore, the amount of CNTs that can be incorporated into the polymer matrix is also limited, as high concentrations of CNT may lead to agglomeration, which would affect the separation performance.<sup>[79,80]</sup>

Intensive research is being conducted on CNT-CPS membranes to solve the current shortcomings and enable their practical applications in water purification processes. Further details about the application of CNT-CPS as adsorbent materials will be outlined in the following sections.

### 2.3. CNT Buckypaper Membranes

Buckypaper (BP) membranes consist of macroscopic paper-like structures based on randomly arranged CNTs that are held together by van der Waals forces and  $\pi$ - $\pi$  interactions between the CNTs.<sup>[11,12]</sup> In BP membranes, the CNTs are self-assembled into a cohesive structure with a highly porous 3D network and high specific surface area, and retain the intrinsic physicochemical, thermal, and electrical properties. One major advantage of BP membranes compared to VA-CNT and CNT-CPS membranes is the simplicity of the fabrication method.<sup>[81]</sup> BP membranes do not require embedding or aligning the CNTs in a host matrix, which enables the simple fabrication of CNT-based membranes with enhanced properties.<sup>[16]</sup>

Vacuum filtration is the most popular method for the preparation of BP membranes based on densely packed CNT networks.<sup>[81,82]</sup> Three crucial steps are needed in order to obtain high quality BP membranes through the vacuum filtration method (Figure 6). 1) Purification and dispersion of CNTs in a suitable solvent. CNTs are highly entangled and typically contaminated with metal catalyst impurities that are frequently employed during the synthetic process, such as Fe, Co, and Ni. The purification and subsequent dispersion of the CNTs in organic or aqueous solvents is therefore a critical step during the processing of the BP membrane. Thus, a certain amount of CNTs is added into the appropriate solvent and dispersed through mechanical stirring or ultrasonic processing to obtain a homogeneous suspension. 2) The homogeneous dispersion

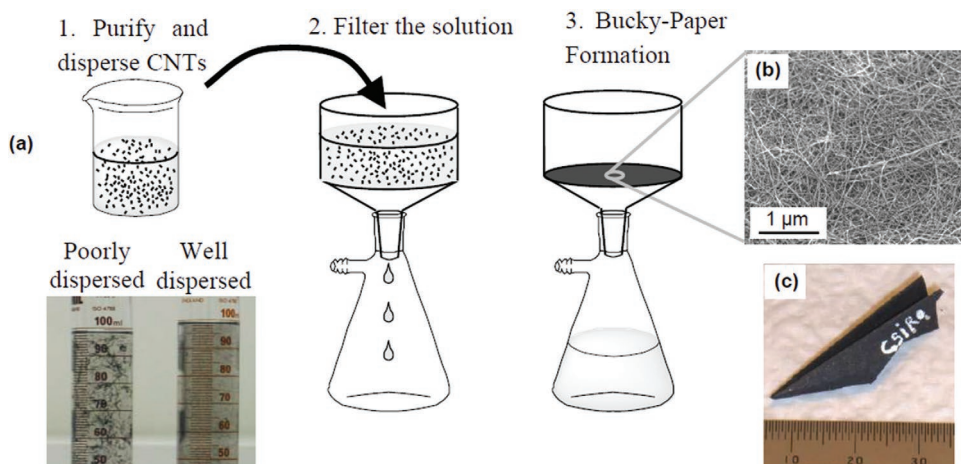


**Figure 5.** Schematic representation of surface modification schemes of CNTs used for targeted contaminants (grey arrows refer to decrease in the final effluent concentration). Reproduced with permission.<sup>[23]</sup> Copyright 2021, MDPI.

is filtered through a porous support to form the BP membrane that is allowed to dry. 3) The as-prepared BP membrane is peeled off the porous support yielding a self-standing CNT-based membrane.<sup>[12,81,83]</sup>

Chemical modification of the CNTs is also a crucial approach during BP membrane fabrication. The chemical approaches that have been described in the previous section (Figure 4) are also available methods for the chemical modification of BP-CNTs. Oxidative treatment is frequently used during the initial purification step. Acidic oxidation or heating the CNTs in an oxidative environment, such as air, is often employed to remove carbonaceous impurities, which show lower oxidation resistance than CNTs.<sup>[84,85]</sup> This treatment leads to CNTs functionalized with carboxyl and hydroxyl groups that are more

hydrophilic, improving their dispersion into polar solvents such as water, as well as the hydrophilic nature of the final BP membrane.<sup>[86]</sup> The opposite effect can also be achieved by using, for example, UV/ozone treatment followed by reaction with alkoxysilanes. Through this approach CNTs with a silicon content of up to 2.5% were achieved, which resulted in enhanced hydrophobic properties of the final material.<sup>[87]</sup> In this way, the lifespan, permeability and mechanical resistance of the hydrophobic BP membranes were increased, which had an impact on the membrane performance. The hydrophobic character of the BP membranes has also been enhanced through the attachment of hydrophobic polymers, such as polystyrene, to the CNT surface.<sup>[88]</sup> The resulting BP membranes showed high absorption capacity and good recyclability.



**Figure 6.** a) Process for manufacturing buckypapers, b) SEM image showing the buckypaper surface, and c) buckypaper origami aeroplane demonstrating their flexibility mechanical robustness. Reproduced with permission.<sup>[81]</sup> Copyright 2010, MDPI.

Apart from chemical oxidation, other chemical approaches have also shown promise for tailoring the final properties of BP membranes. Aryl diazonium salt chemistry provides a facile and versatile route for the incorporation of different functional groups onto the CNT surface to attain desired properties and meet the application requirements. The chemical modification of CNTs films via aryl diazonium salts was first reported by Tour and co-workers in 2001.<sup>[89]</sup> The authors modified the CNT sidewalls via electrochemical reduction with a variety of aryl diazonium salts. This same approach was used in later studies for the chemical modification of BP membranes with different types of aryl derivatives.<sup>[90,91]</sup> Chemical cross-linking has also been a widely employed functionalization approach for the covalent modification of the BP membranes.<sup>[92–95]</sup> In general, BP membranes consisting of cross-linked CNTs show enhanced mechanical properties, which is crucial to provide adsorbent materials with higher resistance, stability, and long-term performance.<sup>[92,94]</sup>

Due to their highly porous 3D structure with large specific surface area and high adsorption capacity, BP membranes are potential candidates for their application in water purification processes. However, further research should be conducted to overcome some important limitations and challenges associated with BP membranes, mainly related to their mechanical stability and scalability issues.<sup>[12]</sup> The permeation quality can be influenced by several factors, such as the brittleness of BP membranes caused by the weak interactions between the CNT bundles, or the CNT delamination issues during membrane operation.<sup>[16]</sup> A method for overcoming this problem has been to reinforce the BP membranes via polymer infiltration.<sup>[96,97]</sup> However, this method comes at the expense of the thermal and electrical properties, as well as it affects the membrane permeability. Preparing a good CNT dispersion is also challenging during BP membrane fabrication. Dispersions of high quality are achieved by chemical functionalization and sonication approaches.<sup>[23,24]</sup> However, this affects the intrinsic properties of CNTs by introducing chemical and physical defects on their surface.<sup>[23]</sup> Finally, scalability of BP membranes is also an important issue due to the need of large quantities of CNTs, which implies high fabrications costs.<sup>[11,12,18]</sup> In the following sections we will highlight the potential of BP membranes for the removal of different types of water contaminants, along with the current challenges and the efforts that have been undertaken to improve their performance in water purification applications.

### 3. Water Treatment Applications of CNT-Based Membranes

#### 3.1. Water Desalination

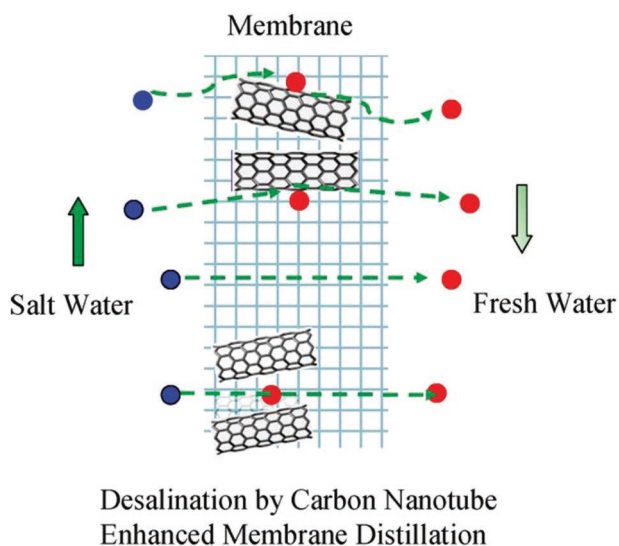
Seawater account for ≈98% of the world's water storage, and therefore, desalination processes have long been utilized to produce fresh water suitable for human consumption and irrigation in areas of water scarcity. In recent years, CNT-based membranes have shown great advancements in water desalination applications.<sup>[98–100]</sup> The salt ion rejection of CNT membranes mainly depends on the inner diameter of the

nanotubes. Previous theoretical studies have demonstrated that increasing the diameter of the CNTs results in an adverse effect on the salt rejection efficiency.<sup>[20–102]</sup> Appropriate pore diameters act as energy barriers at the channel entries, allowing water to pass through the hollow channels while salt ions are rejected.<sup>[103]</sup> Computational studies conducted by Corry et al. suggested that the ideal CNT diameter to achieve high water permeability and salt rejection should be <0.6 nm.<sup>[101]</sup> This is an important limitation during the application of VA-CNTs in water desalination that could be overcome via chemical modification of the tube ends.<sup>[104]</sup> In fact, the addition of charges at the entrance of the pores (i.e., the tips of the CNTs) has demonstrated to improve the ion rejection, which has been an alternative strategy to enhance the ion exclusion performance of large diameter CNTs.<sup>[98]</sup> Recently, further computational studies revealed that introducing chemical functionalities at the sidewalls of large-diameter CNTs, is also a promising strategy to improve the salt rejection efficiency.<sup>[105]</sup>

Despite the limitations, intensive research in the field has confirmed the promise of VA-CNT membranes in water desalination applications.<sup>[35,47,50,103,106]</sup> Early studies demonstrated that the flux of a VA-CNT membrane consisting of vertically aligned DWCNTs encapsulated with silicon nitride, whose pores had carboxylic functional groups at their tips, exceeded that of commercial nanofiltration membranes as much as four times.<sup>[107]</sup> In another study, a selective ion-separating layer based on polyamide or graphene oxide (GO) was coated onto a VA-CNT membrane to enhance the membrane desalination performance.<sup>[50]</sup> Due to the lower pore size of the coated membranes and the negative charge of the GO layer that produces electrical repulsion forces of Cl<sup>-</sup> and Na<sup>+</sup>, the desalination potential was increased. Yu et al. reported the preparation of dense VA-CNT membranes by capillary force driven shrinkage of CNT array grown by CVD. The authors demonstrated that the ion diffusion in CNT membranes exhibited a gated behavior due to the changes of water wettability on hydrophobic surface of the CNTs.<sup>[108]</sup> Later findings reported the use of hydrophilic oxidized VA-CNT membranes, synthesized by CVD process, for water desalination processes. The effect of feed concentration, temperature, pressure, and flow rate on the performance of the as-prepared membrane was studied, concluding that the maximum separation percent and improved permeate flux was obtained at the highest feed concentration, temperature and flow rate.<sup>[109]</sup>

For CNT-CPS membranes, the desalination performance also depends on the structure and function of the membrane and changes after adding the CNTs.<sup>[110]</sup> Son et al. immobilized oxidized CNTs in the porous support layer of a TFC membrane creating a novel architecture that showed improved performance for seawater reverse osmosis and brackish water reverse osmosis.<sup>[111]</sup> When compared to the bare TFC membranes, the as prepared CNT-CPS membrane showed enhanced water permeability due to the increased hydrophilicity and enhanced pore properties provided by the incorporation of CNTs. The CNT diameter also plays a crucial role in the performance of CNT-CPS membranes. Carboxylated CNTs with different diameter and concentration were incorporated into CNT-CPS membranes based on





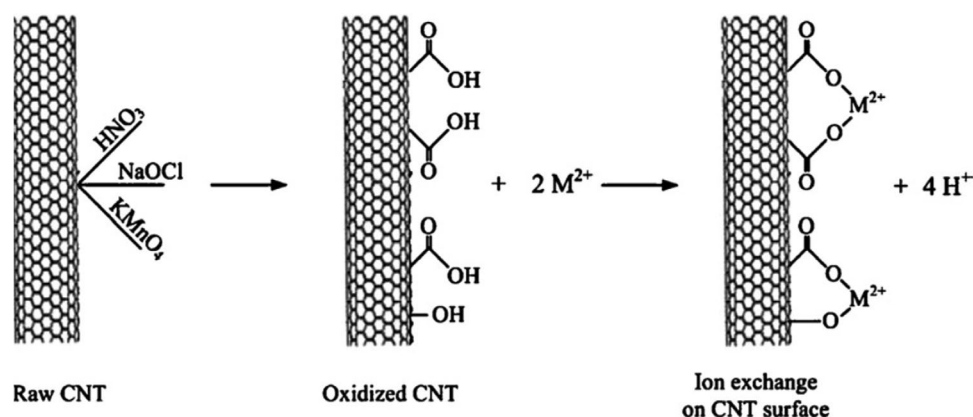
**Figure 7.** Mechanism of MD in the presence of CNTs. Reproduced with permission.<sup>[114]</sup> Copyright 2011, American Chemical Society.

polyethersulfone, which resulted in an increased flux and salt rejection.<sup>[112]</sup> The results showed that CNT-CPS membranes embedded with the thinnest CNTs obtained better filtration performances than those embedded with thicker CNTs. Furthermore, changes in the CNT concentration resulted also in variations in water flux, reaching the highest water flux for a concentration of 0.1 wt%. Membrane distillation (MD) is considered as a key technology for desalination applications.<sup>[113]</sup> In this field, Gethard et al. demonstrated that CNTs can be immobilized in MD membranes based on polyvinylidene fluoride acting as sorbents and providing additional pathways for solute transport (Figure 7).<sup>[114]</sup> Compared to traditional MD membranes, the new CNT-CPS membranes provided higher flux and salt reduction for a wide range of salt concentrations up to the equivalent of seawater. Dumée et al. conducted several studies within this line of research. In early studies, the authors prepared pure CNT membranes (buckypapers) and evaluated their potential in direct contact membrane distillation (DCMD).<sup>[115]</sup> In DCMD a hydrophobic membrane acts as a barrier between a feed of hot salty water and a permeate of cold freshwater.<sup>[116]</sup> The BP membranes were prepared by vacuum filtration of CNTs dispersed in pure propanol and then peeled off from the membrane support. Desalination was successfully demonstrated using the BP membranes in a DCMD setup. However, the formation of microcracks during operation resulted in a decrease in flux with time and delamination issues.

In an attempt to optimize the properties of these BP membranes, the same authors prepared several types of CNT-CPS membranes. To this purpose, the reported BP structures were sandwiched with polymer supports or polymer-infiltrated, yielding CNT-CPS membranes with comparable flux, permeability, and desalination performance, but improved mechanical properties.<sup>[117]</sup> In a later study, the authors addressed the mechanical issues via chemical modification of high purity CNTs in two different steps: i) UV/ozone treatment to create active hydroxyl groups onto the outer walls of the CNTs, and

ii) substitution of the hydroxyl groups with alkoxy silane moieties. The alkoxy silane modified CNT membranes presented increased hydrophobicity compared to their untreated counterparts, which resulted in increased lifespan and permeability.<sup>[87]</sup> Fluorosilanized CNTs afforded a homogeneous dispersion of the nanotubes in organic solvents and produced strong interfacial bonds with polymers, allowing the preparation of superhydrophobic CNT-CPS membranes.<sup>[118]</sup> The resulting membranes were tested in DCMD for desalination purposes using different CNT concentrations (0.5 to 3 wt%). The membranes with the highest concentration of CNTs presented a large pore size and high hydrophobicity, which resulted in enhanced permeability of the membrane without severe wetting. In a similar study, Tijng et al. prepared CNT-CPS membranes with 5 wt% of CNTs incorporated into the top layer of the membrane.<sup>[63]</sup> The resulting membrane showed a highly porous structure and superhydrophobic properties due to the increased roughness of the upper layer. The authors concluded that CNT protrusions were formed on the top layer, which increased the surface roughness leading to superior hydrophobic properties and high potential for DCMD desalination applications. Similarly, membranes consisting of CNT-polyamide composites showed significant changes in surface roughness by increasing the amount of CNTs.<sup>[119]</sup> Membranes containing a CNT concentration of about 12.5 wt% clearly improved degradation resistance against chlorine exposure and water flux, while the salt rejection performance was maintained. A CNT-CPS membrane based on plasma treated ultralong CNTs deposited onto a mixed cellulose ester porous support was reported for the removal of salt by adsorption rather than rejection.<sup>[120]</sup> The ultrahigh adsorption capacity was attributed to the defective sites and amorphous network generated via plasma-mediated conversion of the outer layers of the CNTs, that greatly enhanced the hydrophilicity and ion-binding properties of the membrane. In a recent study, a CNT-CPS membrane made from CNTs and chitosan was fabricated through the evaporative casting method. The resulting membrane showed enhanced mechanical properties due to the presence of CNTs and provided a simultaneous increase in flux and salt rejection capacity, which was attributed to the packing of hydrophilic chains in the matrix and the presence of internal nanochannels formed by the CNTs.<sup>[121]</sup> Another desalination alternative was developed by Noy and co-workers, who inserted short segments of CNTs into lipid bilayers to form TFC membranes that simulated biological water channels.<sup>[122]</sup> The desalination efficiency was tested by measuring water and chloride ion transport by fluorescence-based assays. The authors demonstrated that the as-synthesized membranes showed strong rejection of chloride anions and water-salt permeability comparable to that of commercial membranes.

In summary, tailoring the CNT-based membrane properties is a key approach to achieve a membrane with potential application in desalination processes. According to the findings in the literature, we can conclude that porosity is the most important factor affecting membrane performance. Thus, the mean pore size, pore volume, and pore size distribution are key determinants for controlling the membrane separation efficiency.



**Figure 8.** Schematic diagram of the major mechanism for sorption of divalent metal ions onto CNT surface. Reproduced with permission.<sup>[127]</sup> Copyright 2007, Elsevier.

### 3.2. Removal of Heavy Metal Ions

Contamination of water by heavy metals is a major problem nowadays and represents a threat for human health. CNTs can also be exploited for the removal of heavy metals from contaminated water.<sup>[123–126]</sup> The presence of polar functional groups on the CNT surface demonstrated to have a positive effect onto the adsorption of heavy metals, since the sorption mechanism of metal ions appeared mainly attributable to chemical interaction with the surface functional groups.<sup>[127]</sup> Surface modification improves the adsorption capacity of CNTs toward metal ions, probably due to the increased number of active binding sites that are generated, better ion-exchange properties, and adherence of new functional groups on the external surface of the CNTs.<sup>[128]</sup> However, the metal ion sorption capacity did not have direct correlation with the specific surface area, pore volume or pore diameter.<sup>[127]</sup> Therefore, the efficient removal of metal ions requires the surface modification of CNTs as pristine CNTs may be ineffective.<sup>[123]</sup>

Theoretical studies conducted by Anitha et al. demonstrated that carboxylated SWCNTs had  $\approx 150\text{--}230\%$  higher adsorption capacity of heavy metal ions than bare SWCNTs and SWCNTs functionalized with  $-\text{OH}$  or  $-\text{NH}$ .<sup>[129]</sup> Chemical adsorption was the dominant mechanism to explain this finding. The carboxylic groups attached to the CNT surface have protons that get exchanged with heavy metals, which get sorbed onto the surface releasing  $\text{H}^+$  ions and thereby reducing the pH of the solution (Figure 8).<sup>[130]</sup> Thus, chemical modification of CNTs with oxidizing agents, such as nitric acid, sulfuric acid, gaseous oxygen, ozone, or plasma, has been a widely employed approach to increase the affinity of CNTs toward metal ions.

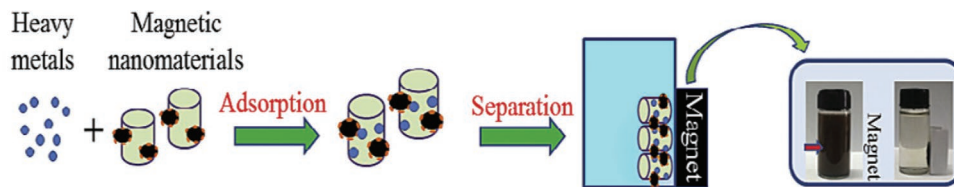
In an experimental study, MWCNTs were oxidized by nitric acid and their efficiency to adsorb  $\text{Ni}^{2+}$  was tested.<sup>[131]</sup> The authors concluded that the pH had an effective role in the removal efficiency and observed that metal ion adsorption was highest at high pH. This was attributed to the surface charge variation with pH. At low pH, the surface of the CNTs became positively charged and  $\text{Ni}^{2+}$  ions could be hardly adsorbed on the surface of oxidized MWCNTs, since the  $\text{Ni}^{2+}$  ions are hydrated cations. Chemically oxidized CNTs have been also utilized to go for additional chemical reactions and further functionalize the CNTs, improving the adsorption efficiency.

Alimohammady et al. prepared carboxylated MWCNTs chemically modified with 3-aminopyrazole through amidation reaction.<sup>[132]</sup> The functionalized CNTs revealed great potential as adsorbents for adsorbing  $\text{Cd}^{2+}$  from aqueous solutions. When oxidized CNTs were modified with poly-amidoamine dendrimers, superhigh removal capacities of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  were achieved.<sup>[133]</sup> The studies revealed that the adsorption behavior was pH-dependent showing the maximum adsorption at  $\text{pH} = 7$ . The decreasing adsorption capacity with decreasing pH was attributed to the competition of the heavy metal ions with protons. In a different approach, carboxylated CNTs could be converted into acyl chlorides, a process that opens the way to further functionalization. Through this strategy, acyl-chloride-modified CNTs were functionalized with melamine to yield cross-linked polyamide/CNT composites.<sup>[134]</sup> The synthesized polyamide/CNT composites revealed high efficacy for the removal of lead ions, which was attributed to the presence of polyamide that provides sites for metal ions adsorption.

Apart from oxidation, other functionalization approaches have also demonstrated to be helpful in the removal of heavy metal ions from water. For example, click chemistry was employed for the direct building of triazole dendrimers onto the CNT surface. Their chelating abilities toward toxic metal ions were evaluated, confirming their promise to selectively remove toxic metals from aqueous media. Magnetic functionalized CNTs have also been employed to remove heavy metals from water, mainly due to the easy magnetic retrieval by an external magnetic field for recycling.<sup>[135,136]</sup> In this case, magnetic CNTs are prepared and then retrieved by magnetic separation after the adsorption process (Figure 9), which is an effective way to recycle the CNTs.

As in the former examples, several studies have reported the introduction of these functionalized CNTs into CNT-based membranes for the removal of heavy metal ions.

In early studies, CNTs were grown on  $\text{Al}_2\text{O}_3$  surfaces by CVD and the adsorption capacity of the resulting membrane was compared with active carbon powders. The as-prepared membranes revealed an extraordinary adsorption capacity without further treatment or oxidation.<sup>[137]</sup> Soyekwo et al. prepared a CNT-CPS membrane based on cross-linked polyethyleneimine (PEI) CNTs.<sup>[138]</sup> The resulting membrane was modified with  $\text{Zn}^{2+}$  via coordination bond with the amine groups of the



**Figure 9.** Retrieval of magnetic nanomaterials after the adsorption process. Reproduced with permission.<sup>[135]</sup> Copyright 2018, Elsevier.

cross-linked PEI chains, thus, rejection rather than adsorption was the governing mechanism of the as-synthesized membranes. The positively charged and hydrophilic functionalized nanocomposite membrane displayed outstanding water permeance and good rejection of divalent heavy metal cations such as  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  or  $\text{Cu}^{2+}$ . The rejection effect of the as-prepared membranes was attributed to the Donnan exclusion effect that is based on the electrostatic repulsion of co-ions. Ali et al. prepared CNT-CPS membranes based on oxidized MWCNTs embedded with poly-vinyl-chloride.<sup>[139]</sup> The resulting membranes revealed high removal efficiencies of  $\text{Zn}^{+2}$  from synthetic water and wastewater effluents, respectively. In a recent study, aluminum oxide-impregnated CNT membranes were developed via a sintering process.<sup>[140]</sup> Due to the electrostatic interactions between the negatively charged CNT membrane surface and  $\text{Cd}^{2+}$  the maximum removal was observed at  $\text{pH} = 7$ , the resulting membrane was able to remove low concentrations of  $\text{Cd}^{2+}$  from aqueous solutions.

To summarize, removal of heavy metals from water by CNT-based membranes is mainly affected by  $\text{pH}$  and surface charge, and therefore chemical modification of the CNTs plays an important role in the adsorption efficiency. High  $\text{pH}$  values are in general more suitable to improve the adsorption capacity, as low  $\text{pH}$  values result in positively charged CNT surfaces and hydrated metal ions with reduced adsorption capacities.

### 3.3. Oil–Water Separation

Water pollution due to oil spills and industrial accidents has turned into a global problem in the past years. Oil/water separation, and especially emulsified oil/water separation, is a difficult and challenging task because of the environmental and economic demand.<sup>[141]</sup> In recent years, numerous types of adsorbents have been extensively developed for the separation of oil from water;<sup>[142–144]</sup> however, most of these materials have some major drawbacks such as low adsorption capacity, poor recyclability and selectivity as they absorb both water and oil.

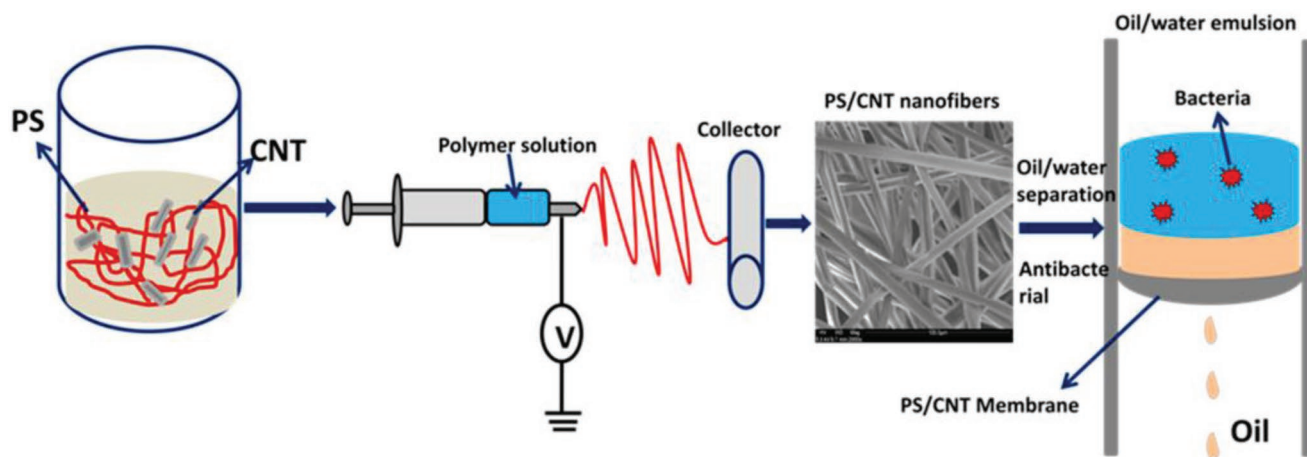
CNTs are suitable candidates for the development of superhydrophobic and superoleophilic membranes, offering a large number of advantages.<sup>[145,146]</sup> The chemical functionalization of the CNT surface also plays a crucial role, since the hydrophobic/oleophilic properties can be tailored through the addition of the appropriate functional groups.<sup>[94,147,148]</sup> However, the intrinsic hydrophobicity of the CNT-based membranes can also be adjusted by surface roughness.<sup>[145]</sup>

Lee and Baik reported for the first time a VA-CNT membrane with both superhydrophobicity and superoleophobicity, which revealed efficient macroscale separation of water/oil mixtures, even for surfactant-stabilized emulsions.<sup>[149]</sup> The super-

hydrophobic properties were attributed to the increased surface roughness resulting from the microscale porosity of the structure and the nanoscale intertubular space, while the superwetting capillary action of the interstitial space between the aligned tubes was responsible of the oleophilic properties.

CNT-CPS membranes have been extensively exploited in this field. A TFC membrane containing a thin hydrophilic nanocomposite layer was used as a filtration medium to separate oil/water emulsions.<sup>[150]</sup> The hydrophilic layer consisted of cross-linked poly(vinyl alcohol) (PVA) incorporating surface oxidized MWCNTs. The presence of CNTs into the PVA layer enhanced the permeate flux and the water adsorption ability and showed high rejection ratio in oil/water emulsion separation. In another study, electrically conducting CNT–PVA composite membranes were fabricated by vacuum filtration method and covalent cross-linking approaches.<sup>[151]</sup> The resulting membrane showed randomly entangled CNTs and served as both selective layer and working electrode during filtration. On the basis of previous studies that confirmed that oil droplets are negatively charged due to the adsorption of hydroxyl ions,<sup>[152]</sup> the authors inferred that there would be an increased electrostatic repulsion between the charged oil droplets and the membrane, that would benefit both oil removal rate and membrane fouling resistance. The membrane revealed improved oil removal efficiency and fouling resistance which was attributed to the electrostatic repulsions. Superhydrophobicity was achieved through the covalent attachment of a hydrophobic polymer, such as polystyrene, onto CNT-based membranes.<sup>[145]</sup> The resulting membrane revealed good separation properties for oils and surfactant-stabilized water in oil emulsions. When the CNT–polystyrene membranes were irradiated with gamma radiations, chain rupture and cross-linking occurred, modifying the surface properties and achieving superhydrophobic/superoleophilic behavior with improved water rejection (**Figure 10**).<sup>[153]</sup>

In a similar study, a CNT-CPS membrane was fabricated by growing two different polymers: a hydrophobic polymer such as polystyrene, and a hydrophilic polymer such as poly(*N,N*-dimethylaminoethyl methacrylate) were grown from different sides of the CNT membrane via self-initiated photografting and photopolymerization.<sup>[154]</sup> Due to the anisotropic wettability of the resulting membranes, these were useful to selectively separate both, surfactant stabilized water-in-oil emulsions and oil-in-water emulsions, with high separation efficiency and promising flux. Freestanding membranes consisting of PEI coated CNTs with hierarchical nanostructures were fabricated via vacuum-assisted self-assembly method.<sup>[155]</sup> After membrane fabrication, trimesoyl chloride was used to postmodify the membranes, followed by hydrolysis of the acyl chloride groups, which resulted in enhanced mechanical strength and hydrophilicity. The synergy of the hierarchical nanostructure and the



**Figure 10.** Schematic representation of the fabrication of polystyrene/CNT-CPS membranes and its application in oil/water separation. Reproduced with permission.<sup>[153]</sup> Copyright 2019, MDPI.

outstanding hydration capacity endowed the membrane with underwater superoleophobicity and long-term antifouling properties, with an efficient separation of oil-in-water emulsions. In another study, MWCNT/polysulfone composite membranes with 5 wt% CNT loading were fabricated through the phase inversion method.<sup>[156]</sup> The authors studied the effect of dispersion efficiency on the final performance of the membranes. For this purpose, different dispersion methods were employed for the incorporation of the CNTs into the membranes, confirming further that the CNT dispersion method affects the performance of the resulting membranes during the separation of oil–water mixtures. With poorly dispersed CNTs, low oil rejection was observed, which was attributed to the formation of interfacial defects between the CNTs and the polymer matrix.

As alternative to polymer-based membranes, freestanding CNT network films (BP membranes) have also been reported to realize oil/water separation with good performance.<sup>[147]</sup> Ultrathin SWCNT films with tunable thickness separated both micrometer and nanometer-sized surfactant-free and surfactant-stabilized water-in-oil emulsions with good performance.<sup>[157]</sup> The water flux of these membranes was 2–3 orders of magnitude higher than commercial ones which was attributed to the nanometer scale thickness of the membrane and the superoleophilic properties of the as-prepared films. As mentioned above, surface functionalization or control of the CNT film surface roughness can help manipulate the wettability of the resulting membrane and lead to hydrophobicity. Huang et al. prepared MWCNT films with superhydrophobic and superoleophilic properties through the noncovalent attachment of alkyl pyrenes to the CNT sidewall, employing the vacuum filtration method.<sup>[158]</sup> The resulting film was easily recycled yielding brand-new water–oil separation filters, and due to the simple fabrication method it was easily scaled up. Covalent methods have also been recently employed for the development of chemically modified BP-CNT membranes with optimal properties for oil/water separation processes. Superhydrophobic BP membranes were prepared through the covalent attachment of fluorine-bearing organosilane derivatives onto OH-modified CNTs.<sup>[148]</sup> The flux and surface wettability of the final membrane were tailored by adjusting the feed volume ratio of the

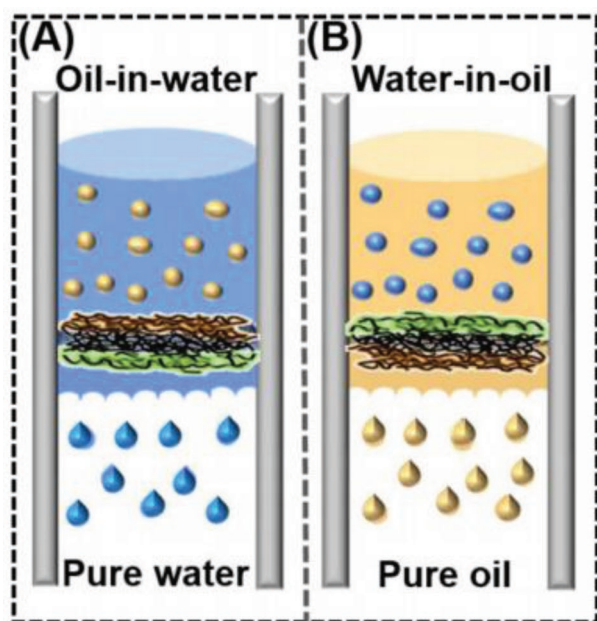
organosilane employed to modify the CNTs. The as-prepared membranes effectively separated various water-in-oil emulsions with high efficiencies. In a recent study by our research group, freestanding BP membranes were fabricated from chemically cross-linked SWCNTs.<sup>[94]</sup> By controlling the degree of cross-linking, we were able to modify the nanostructure, porous features, and specific surface area of the resulting materials, in turn, allowing the control of the adsorption capacity for the removal of organics and oils from contaminated water.

BP membranes that allow Oil/water separation by rejection of oil rather than adsorption have also been reported.<sup>[159]</sup> For this purpose, electrooxidation was employed to convert natively hydrophobic CNT mats into hydrophilic, while the morphology, conductivity, and mechanical strength of the pristine material were retained. The resulting membranes showed high water-permeation and oil-rejection behavior.

In summary, tailoring the wetting behavior of the membranes by modifying surface properties and roughness through the addition of functional groups is the most important factor to achieve good separation of water/oil mixtures. Chemical modification of CNTs yielding CNT-based membranes with superhydrophobic/superoleophilic properties is highly desired because the resulting membrane will show high adsorption of oils and water repellence, being promising for the separation of water-in-oil emulsions (Figure 11). However, for separating oil-in-water emulsions, membranes with superhydrophilic/superoleophobic properties are necessary (Figure 11).

### 3.4. Removal of Organic Pollutants

Organic pollutants (OPs), such as dyes, polyaromatic hydrocarbons, antibiotics, phenols, and aromatic compounds, have become one of the most serious environmental problems, and their removal from aqueous solutions is of special concern. Most of these OPs are persistent and therefore show potential adverse health impacts. The conventional means to remove organic pollutants from contaminated water are either inefficient or expensive. Also in this case, CNTs have attracted a great deal of attention for the removal of OPs from wastewater.<sup>[160,161]</sup>



**Figure 11.** Schematic illustration of CNT-based membranes used for separating oil-in-water emulsions (A) or water-in-oil emulsions (B). Reproduced with permission.<sup>[154]</sup> Copyright 2014, American Chemical Society.

The presence of micro and mesopores, the extended conjugated  $\pi$ -network, and the attachment of specific functional groups, are the main factors responsible for higher adsorption of OPs onto CNTs.<sup>[162,163]</sup> Therefore, as with previous contaminants, the incorporation of functional groups onto the CNT surface is, in several studies, the approach of choice to improve the dispersibility of CNTs in aqueous or organic solvents as well as the adsorption capacity.<sup>[162,164]</sup> Due to their extended aromatic surface, CNTs have shown strong affinity toward nonpolar organic chemicals such as naphthalene, phenanthrene and pyrene.<sup>[165,166]</sup> MWCNTs have been widely exploited for the adsorption of several organic dyes from contaminated water.<sup>[163,167]</sup> The adsorption capacity of MWCNTs toward organic dyes demonstrated to be better than conventional adsorbents, such as activated carbon, which was attributed to the higher pore diameter of MWCNTs.<sup>[168,169]</sup> Furthermore, several studies revealed that oxidation of the CNTs or grafting with polymers or magnetic particles has a remarkable removal of dyes from wastewater, offering easy recovery and regeneration of the material.<sup>[164,170–173]</sup>

In recent years, several studies have demonstrated the efficiency of CNT-based membranes for removal of organic pollutants from water. Most of the CNT-based membranes that have been reported are based on CNT-CPS membranes.<sup>[170,174]</sup> CNT-CPS polyimide membranes containing functionalized MWCNTs (oxidized or aminated) revealed an improved membrane performance for the rejection of dyes from contaminated water, with respect to reference polymeric membranes without MWCNTs.<sup>[175]</sup> The improvement was attributed to the formation of low-resistance pathways for solvent transport at the interface between the MWCNTs and the polymeric chains. Mallakpour and Rashidimoghdam reported glutaraldehyde-cross-linked PVA/Vitamin C–MWCNT composite membranes and studied their adsorption capacity for removal of methylene

blue.<sup>[172]</sup> The resulting membranes demonstrated high capability to eliminate great amounts of methylene blue from wastewater in short times. Furthermore, the composite was used successfully for five times after regeneration by ethanol without any loss of effectiveness. Very recently, a highly adsorptive CNT-CPS membrane with excellent self-cleaning properties has been reported.<sup>[176]</sup> The membrane was fabricated by depositing CNTs onto a polypropylene support. The resulting structure was then used to anchor photocatalytic FeOOH catalysts on the outer walls of CNTs, endowing the CNT-based membrane with excellent self-cleaning properties via photocatalytic treatment. Finally, physical welding points were constructed via the silver–ammonia reaction. The as-prepared membrane exhibited superior adsorption performance for different types of dyes (Rhodamine B, methylene blue, eosin Y, and acid orange 7) and organic contaminants (bisphenol A, amoxicillin, and p-nitrophenol), when compared to other CNT based adsorbents reported in literature.

VA-CNT membranes have also been reported for the removal of dyes from wastewater. In a recent study, a VA-CNT membrane with small pore sizes and highly compact pores was developed.<sup>[177]</sup> The authors found that the aligned CNT membranes exhibited rejection to dyes two times higher than that of membranes prepared by disordered CNTs, under the same experimental conditions. The improved performance was attributed to the achievement of smaller pores through the vertical assembly. Other types of organic pollutants have also been efficiently removed from water by using VA-CNT membranes. Jafari et al. prepared VA-CNT membranes grown on anodized aluminum oxide substrates, whose fluid flow was up to four orders of magnitude faster than conventional membranes.<sup>[178]</sup> The as-prepared membrane rapidly absorbed humic acid (HA) and consequently rapid flux decline occurred because of internal pore constriction as dominant fouling mechanism. The main limitation of existing approaches is the retrieval or regeneration of the CNTs after the adsorption process. Moon et al. developed a VA-CNT membrane by packing the aligned CNTs into a polytetrafluoroethylene heat-shrink tubing.<sup>[179]</sup> The new system helped enhance their adsorption capacity for phenolic compounds, which was attributed to efficient interactions with the CNTs due to the presence of narrow interstitial channels. The as-prepared VA-CNT membrane was recoverable by heat treatment or rinse with solvents and showed long-term stability. A scale-up study was conducted by Jue et al., who fabricated large-scale area (60 cm<sup>2</sup>) VA-CNT membranes with high density of open, small diameter SWCNT pores.<sup>[21]</sup> The resulting membranes showed excellent water permeances that exceeded those of state-of-the-art commercial nano- and ultrafiltration membranes with similar pore diameters, and permitted fractionation of dyes from concentrated salt solutions.

Although BP-CNT membranes have been scarcely used for the removal of organic contaminants from water, some studies have been reported in literature. Cross-linked BP-CNT membranes allowed the effective removal of different types of organic pollutants, such as methylene blue, diquat dibromide, and 1-pyrenebutyric acid.<sup>[94]</sup> Different adsorption behavior were observed by varying the functionalization degree of the CNTs

and the thickness of the BP membranes. BP membranes have also been used to remove natural organic matter from water. Micrometre-thick surfactant-free oxidized MWCNT buckypapers were prepared through the very well-known vacuum filtration method.<sup>[86]</sup> The BP-CNT membrane demonstrated an excellent removal of HA and a long lifetime, which was attributed to the incorporation of hydrophilic functional groups that improved the BP hydrophilicity enabling faster and better contact of HA with the buckypaper surface. In a similar study, oxidized BP-CNT membranes with improved removal for HA and excellent antifouling performance were reported.<sup>[147]</sup> The authors employed CNTs with higher aspect-ratio for the preparation of the BP-CNT membrane that yielded smaller buckypaper pore sizes. In the final step, the tubes were etched via acid modification of the tips, which resulted in a dense structure with narrower pore diameters and enhanced adsorption capacity.

In brief, the porosity and surface affinity of the CNT-based membranes are determinant factors for achieving good removal efficiencies of organic pollutants. CNT diameters, arrangement, and distribution within the membrane can be modified to vary the pore size, pore volume, and pore distribution. Finally, chemical modification with different types of functional groups can be used to modify the affinity of the CNT-based membrane surface for different types of organic contaminants.

#### 4. Limitations of CNT-Based Membranes

Despite the promising findings associated with the use of CNTs for the removal of different types of water contaminants, there are still a few drawbacks mainly related to the long-term operation, synthesis, and processing of CNTs, and scale-up approaches. These issues should be overcome before wastewater treatment technologies with CNT-based membranes can be commercialized. The main limitations associated with the practical applications are given below.

- i) Most studies have focused on tailoring the wetting behavior of the membranes by modifying surface roughness through the addition of functional groups. However, such approaches easily damage the CNT structure, which could result in a decrease in flux rate and separation efficiency.
- ii) Desalination, oil–water separation, and removal of heavy metals and organic pollutants with CNT-based membranes have been demonstrated based on laboratory batch studies where only small volumes of water can be purified. Substantial efforts on the fabrication approach and scaling-up are needed to upgrade the CNT-based membrane process. Furthermore, experiments with actual wastewater, rather than simulated water in lab-scale batch experiments need to be performed with the CNT adsorbent materials.
- iii) Most of the CNT-based membranes that have been reported are assembled onto polymers yielding CNT-CPS membranes, which inevitably affect the CNT intrinsic properties. Emphasis on the development of the pure and freestanding CNT membranes is essential to comprehensively utilize the CNTs' properties.

- iv) Membrane filtration technologies based on CNTs can be effective to remove the reported pollutants with high efficiency, but several issues such as high cost, process complexity, membrane fouling, and low permeate flux should be further studied.
- v) Separation and recycling of the CNTs also need to be further explored. The separation of CNTs after use is still challenging and there is always the possibility of leaching to the environment, which may create a new problem. Hybridization could solve the leaching issues, but it happens at the cost of reduced performance due to the loss of active sites on the CNTs. Furthermore, the recycling efficiency of the CNTs must be considered when estimating the costs of the process.

#### 5. Conclusions and Perspectives

This review highlights the applications of CNT-based membranes for water purification. We have attempted to provide an insight into the CNTs potential to overcome the limitations of conventional membrane technologies in water purification systems. Different types of CNT-based membranes have been reported in the literature, including vertically aligned CNT membranes, CNT-based composite membranes, and buckypaper membranes. The main fabrication methods have been thoroughly reviewed, and challenges and solutions have been considered. Among them, physical or chemical modification of the CNTs is extensively reported to provide membranes with improved adsorption capacity or rejection rate, increased flux, and membrane selectivity. Thus, CNT-based membranes with tailored structures, morphologies, and functional groups have been reported as promising adsorbents for the removal of dyes, heavy metals, oils, phenolic and volatile organic compounds, or desalination purposes.

Due to the progress that has been achieved, there is no doubt that CNT-based membranes have a great potential for water desalination and removal of water contaminants. It can be foreseen that, in the near future, membranes based on CNTs may compete successfully with existing water purification technologies. However, to achieve successful industrial application more studies involving real water samples and longer operation periods using CNT-based membranes seems to be the next logical progression.

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#### Conflict of Interest

The authors declare no conflict of interest.

## Keywords

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