New generation of semipermeable membranes with carbon nanotubes for water and wastewater treatment: Critical review

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Abstract: Environmental applications of carbon nanotubes (CNTs) have recently attracted worldwide attention due to their excellent adsorption capacities and promising physical, chemical and mechanical properties, as well as the preparation of novel membranes with attractive features for water purification. This paper critically reviews the recent progress on the preparation and applications of CNT based membranes in water and wastewater treatment. Various synthesis techniques for the preparation of CNT based membranes are discussed. The functionalization of CNTs, which involves chemical/physical modification of pristine CNTs with different types of functional groups, improves the capabilities of CNT for water and wastewater treatment and/or removal of waterborne contaminants. The CNT-based membrane applications are found to possess a variety of advantages, including improving water permeability, high selectivity and antifouling capability. However, their applications at full scale are still limited by their high cost. Finally, we highlight that CNT membranes with promising removal efficiencies for respective contaminants can be considered for commercialization and to achieve holistic performance for the purpose of water treatment and desalination. This paper may provide an insight for the development of CNT based membranes for water purification in the future. With their tremendous separation performance, low biofouling potential and ultra-high water flux, CNT membranes have the potential to be a leading technology in water treatment, especially desalination.

Introduction

The access to proper quality fresh water dedicated to potable purposes and other anthropogenic activities is the main and primary aspect of reaching sustainable growth of societies, which may complete their needs without affection of resources preserved for future generations. Climate changes, related to global increase of temperatures, cause disturbances in natural resources balance, including ice melting, sea level increase, evaporation intensification and global fresh water scarcity. The water poverty is one of the main problems of the 21st century, which has to be faced by many countries over the world and it is one of the fundamental challenges for their industrial and social development (Seckler et al. 1999). According to the United Nations report, in 2025, 1,800 million people will live in regions of complete water scarcity, while more than 60% of global population will inhabit regions of significant water stress (WHO/UNICEF, 2019). The pressure related to the global assurance to fresh water access is constantly growing, especially in regard to the intensive population growth, which forces the demand toward safe water supply to both, humans and agriculture (Liu et al. 2017).

The selection of the treatment technology depends on a raw stream origin and character (i.e. water, wastewater, ground water, surface water, etc.). The most simple systems are usually applied for ground water, as they commonly need to assure elimination of excessive amount of natural substances. On the other hand, surface water and wastewater require more complex systems due to the appearance of dangerous contaminants, often of anthropogenic and industrial origin. Regardless of the raw stream type, one may distinguish processes, which are usually involved in treatment systems, i.e. chemical precipitation, adsorption, ion exchange, membrane processes, coagulation and flocculation, flotation and extraction, irradiation, electrochemical treatment techniques, advanced oxidation and biological processes (Bodzek 2019).

Membrane filtration, especially its pressure driven type, is found to be one of the most promising and widely applied methods for wastewater, surface water and seawater treatment (Bodzek 2019, Madhura et al. 2018). The selection of membrane
process is dependent on the type of raw stream to be treated and contaminants/admixtures to be removed (Bodzek and Konieczny 2017). In general, reverse osmosis (RO) is used to retain monovalent ions and most of low-molecular weight compounds and it is commonly used to water desalination and demineralization and to remove organic and inorganic micropollutants. Nanofiltration (NF) is used to retain bi- and polyvalent ions as well as low molecular weight organic and inorganic compounds. The process is mostly applied to water softening as well as to the elimination of micropollutants. Low pressure driven membrane processes, i.e. ultra- (UF) and microfiltration (MF) are mostly dedicated to direct removal of colloids, suspensions and microorganisms and they are successfully utilized directly in water clarification and disinfection as well as in elements of integrated or hybrid systems for removal of organic and inorganic pollutants/micropollutants. Other membrane processes like forward osmosis (FO), membrane distillation (MD) and capacitive deionization (CDI) have recently gained attention as an alternative for the removal of some micropollutants as well as desalination (Bodzek 2019, Madhura et al. 2018).

The main limitations of membrane processes, which are usually carried out with the use of polymeric membranes, are membrane fouling as well as chemical, mechanical and/or thermal instability (Kochkodan and Hilal 2015). The new generation of membranes are targeted at facing specific water streams by individualizing membranes’ structural and physico-chemical properties, including hydrophilicity, porosity, surface charge, thermal and mechanical stability and functionalization with antibacterial, photocatalytic or adsorptive character.

The exponential progress in the field of nanotechnology and the use of nanomaterials in environmental applications is especially related to the total rearrangement of almost one hundred years old conventional water treatment process (Goh et al. 2013a). In recent years there has been observed the impressive breakthrough in the use of nanostructural materials, like carbon nanomaterials, metals and metals oxide nanoparticles, zeolites, titanium dioxide and silicon dioxide as well as nanocomposite materials in water and wastewater treatment (Bodzek et al. 2020a, b, c, Qadir et al. 2017). The design and synthesis of novel nanomaterials, which are introduced to polymeric membranes and adsorbents in the form of nanoparticles are in the research interest of material sciences and other fields. Nanomaterials are characterized with large specific surface area, high reactivity and specific affinity to many contaminants present in aquatic streams. Moreover, unique features of nanomaterials, like selectivity and significant permeability, create the opportunity to develop more efficient and improved water and wastewater treatment materials (Madhura et al. 2018).

The most promising materials in regard to water and wastewater treatment are carbon based nanomaterials (CNMs), especially graphene and graphene oxide (Bodzek et al. 2020a), carbon nanotubes (CNTs) and fullerences, what is related to their unique mechanical, chemical and thermal stability, antibacterial features and electric conductivity (Daer et al. 2015, Song et al. 2015, Tian et al. 2015). CNMs have been found as agents potentially able to change disadvantageous dependence between membranes’ permeability and selectivity, what creates the opportunity of membrane separation economy adjustment (Shen et al. 2014, Hinds et al. 2004, Goh et al. 2013a). These materials additionally are characterized with flexibility during modification/functionalization, what creates the opportunity of their use in a variety of water and wastewater treatment processes (Goh et al. 2016a, b). Except for graphene and graphene oxide (Bodzek et al. 2020a), carbon nanotubes (CNTs) have gained significant attention in regard to their features found as favorable during water and wastewater treatment, i.e. large specific surface areas, simple functionalization, high length to diameter ratio and fast water transport (Lee et al. 2016). A series of research on the use of CNTs to eliminate a number of contaminants from aquatic environment (Ihsanullah et al. 2015a, 2016a, b) has been carried out. CNTs can be used directly as water filters or they can be introduced to conventional membrane materials (polymers, ceramic) in order to improve capacity. It is estimated that the flux of membranes which contain CNTs is 3–4 orders of magnitude higher than the flux resulted from Hagen-Poiseuille equation (Li et al. 2014, Majumder et al. 2005; Holt et al. 2006, McGinnis et al. 2018). CNTs, either used directly as membranes or as a component of polymeric matrices also reveal antifouling and disinfection properties and high retention of contaminants. The available literature analysis indicates that adsorbents and CNTs membranes gain the attention of scientists involved in innovative water and wastewater management technologies, due to their unique features, which have not been mentioned earlier. CNTs and functionalized CNTs (f-CNTs) membranes are characterized also with desalination properties, they can be used to remove heavy metals, organic micropollutants and microorganisms, and they can be also applied in order to minimize conventional membranes’ fouling.

The current article aims to present several aspects related with carbon nanotubes, i.e.:

1. the state of the art in the field of preparation of CNTs and f-CNTs containing membranes,
2. potential uses of CNTs and f-CNTs based membranes in water and wastewater treatment,
3. antifouling and antibacterial features of CNTs and f-CNTs, and
4. critical evaluation of the current progress, knowledge gaps and future research areas.

**Carbon nanotubes fundamentals**

Nanotubes are supermolecular cylindrical structures, which are empty inside. Currently, carbon nanotubes, discovered at the beginning of the 1990s, are the best recognized nanotubes. They reveal extreme resistance to breakage and unique electrical properties as well as excellent heat conductivity. These features make nanotubes very promising materials for many branches of science and techniques, including science of materials for environmental engineering (Huczko et al. 2015).

Carbon nanotubes (CNTs) are allotropic form of carbon. Their walls are built of graphene (single-atom graphite layer) rolled up in a tubular structure (Ahmad et al. 2012) (Fig.1a). Microscopic observations confirm that in many cases nanotubes structures are not symmetrical. Native CNTs can be divided into two types, i.e., single walled carbon nanotubes (SWCNTs) and...
multi walled carbon nanotubes (MWCNTs) (Lam et al. 2008). A single walled carbon nanotube comprises of rolled single layer sheet of graphene, while a MWNT comprises of many coaxially oriented graphene sheets (Fig.1b). The diameter of SWCNTs ranges from fractions to several nanometers (0.3–2 nm), while in the case of MWCNTs from several to several dozens of nanometers (2–100 nm) (Zhao and Stoddart 2009). The length of nanotubes, including single- and multi-walled ones, may reach several micro- or even millimeters, whereas their diameter ratio is extremely high and varies from $10^3$–$10^5$, what allows for their classification as one-dimensional objects. SWCNTs are usually of 1 nm in diameter and comprise of two separate regions of different physical and chemical properties. The first region is a side wall of a nanotube and the second – terminating caps, or simply ends of nanotubes (Ahmad et al. 2012). SWCNTs possess important electrical features, which are not revealed by MWCNTs. Lengths and diameters of MWCNTs are of course significantly different than those of SWCNTs, the same as their other properties (Ahmad et al. 2012). The distance between neighborhooding graphene cylinders in MWCNTs is usually ~0.34 nm, what corresponds to the constant of graphite lattice toward c-axis equal 0.335 nm. Additionally, van der Waals forces interact between graphene layers, what assures the proper co-arrangement of cylinders.

In regard to quantum chemistry, chemical bonds in CNTs comprise exclusively sp$^2$ bonds of length $1.44 \cdot 10^{-10}$ m, which is slightly higher than the length of C-C bond in graphite, i.e. $1.42 \cdot 10^{-10}$ m (Dobrzańska-Danikiewicz et al. 2015). The bonds in CNTs are much stronger than sp$^3$ bonds, which appear in diamond or alkenes, what results in the unique durability of CNTs (Wang et al. 2009). The basic structure of nanotubes is hexagonal graphene lattice of honeycomb shape rolled up in a cylinder around translational T vector. The rolling of the graphene plane into a cylinder leads to distortion of sp$^2$ bond and their σ-π rehybridization. Interdimensional σ bonds are delocalized slightly outside the graphene place, while perpendicular to it π bonds are squeezed inside a cylinder and delocalized slightly outside the nanotube, what results in unique features of carbon nanotubes. In comparison to graphite, CNTs are characterized with higher heat and electric conductivity, mechanical strength, while chemical and biological activity of their surface is much better (Dobrzańska-Danikiewicz et al. 2015).

The comparison of physical properties of SWCNTs and MWCNTs is shown in Table 1 (Huczko et al. 2015). As an addition to the discussed features, CNTs possess unique morphological and physicochemical properties, including excellent water permeability and adsorption capacity, what is especially important in the case of their usability in membrane separation.

Technologies dedicated to CNTs preparation have to characterize with high capacity as well as ability to form nanotubes of defined length, diameter, number of walls and chirality. The most commonly used CNTs synthesis methods

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**Fig. 1.** a) Rolling of a single layer of graphite sheet into SWCNT; (b) Structures of multi-walled and single-walled carbon nanotubes (https://www.cheaptubes.com/product-category/multi-walled-carbon-nanotubes/)

**Table 1.** The comparison of properties of SWCNTs and MWCNTs

<table>
<thead>
<tr>
<th>Property</th>
<th>SWCNTs</th>
<th>MWCNTs</th>
</tr>
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<tbody>
<tr>
<td>Graphene layer</td>
<td>Single</td>
<td>Multiple</td>
</tr>
<tr>
<td>Synthesis</td>
<td>Difficult</td>
<td>Simple</td>
</tr>
<tr>
<td>Purity</td>
<td>Poor grade</td>
<td>High grade</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>0.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Heat conductivity (W/(m·K))</td>
<td>6,000</td>
<td>2,000</td>
</tr>
<tr>
<td>Electrical conductivity (S/cm)</td>
<td>$10^{2}$–$10^{6}$</td>
<td>$10^{3}$–$10^{5}$</td>
</tr>
<tr>
<td>Thermal stability in air (°C)</td>
<td>$&gt;600$</td>
<td>$&gt;600$</td>
</tr>
<tr>
<td>Electron mobility (cm$^2$/V·s)</td>
<td>$&lt;10^4$</td>
<td>$10^4$–$10^5$</td>
</tr>
<tr>
<td>Outer diameter (nm)</td>
<td>$&lt;2$</td>
<td>$&lt;2$</td>
</tr>
<tr>
<td>Length (μm)</td>
<td>5–30</td>
<td>–</td>
</tr>
<tr>
<td>Specific surface area (m$^2$/g)</td>
<td>400–1,000</td>
<td>–</td>
</tr>
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As it has already been mentioned, CNTs possess unique morphological and physicochemical properties, including excellent water permeability and adsorption capacity, what is especially important in the case of their usability in membrane separation. However, the main disadvantages of native CNTs are easy agglomeration in aqueous solution and poor affinity to sorption, which limit their large scale use in the production of organic and inorganic composites, lowers the sorption capacity of native CNTs and complicates membranes formation process (Ihsanullah et al. 2016a, b, c, Lee et al. 2016). However, these limitations can be excluded by functionalization of CNTs surface, which is about to improve dispersion properties and sorption ability as well as chemical reactivity, water transport, selectivity and contaminants removal (Ihsanullah et al. 2016c, Goh et al. 2013a).

Methods of functionalization of SWCNTs and MWCNTs cover different physical and chemical processes like vaccination, oxidation (also with the use of plasma), coating or impregnation (Bahgat et al. 2011, Zhang et al. 2016, Raghavendra et al. 2017). Functional groups are attached to side walls, cores or ends of CNTs forming covalent or non-covalent bonds (Fig. 2) (Das et al. 2014a). The oxidation of native CNTs using HNO₃, H₂SO₄, HCl, H₂O₂, KMnO₄ and NaOCl are commonly used and result in the introduction of oxygenated functional groups to CNTs structure (Ren et al. 2011). Despite chemical oxidation, oxygen plasma may also be used to introduce functional groups onto CNTs surface, what eliminates the need of chemicals use and such wastes generation. The modification of CNTs with metal oxides (MnO₂, Al₂O₃ or Fe₂O₃) is another method of functionalization (Ihsanullah et al. 2016a, b, c).

The main aims of CNTs functionalization are elimination of dispersion and enhancement of the formation of membranes dedicated to effective removal of contaminants from water or wastewater (Upadhyayula et al. 2009). The increase of repulsion forces between functional groups (e.g. phenolic group) and CNTs improves dispersion in aqueous solutions and organic solvents in comparison to native CNTs, what allows for easier incorporation of CNTs to polymeric matrices (Ihsanullah et al. 2016a, b, c). The research has shown that the presence of functionalized polar groups is responsible for CNTs surface charge, what leads to electrostatic repulsions of salts ions. It is especially noticeable in separation mechanism of membranes with functionalized CNTs (Fornasiero et al. 2008).

**Challenges and opportunities**

The functionalization of CNTs, including oxidation, is commonly used to improve dispersion and adsorption features toward contaminants, which appear in water or wastewater. Chemical oxidation of CNTs is, however, performed in rough conditions (low pH, highly oxidizing environments) and results in the generation of chemical wastes. Additionally, oxidizing conditions cause defects on gaps and side walls of CNTs, what adversely affects electric and thermal conductivity as well as chemical stability. Thus, innovative functionalization techniques of CNTs functionalization completely or at least partially deprived of structural damage affinities, which are environmentally and economically acceptable, are highly desired. A series of actual challenges like synthesis, functionalization and controlled processing of high quality, CNTs based materials have to be pointed out together with determination of CNTs’ structure at molecular level, further research on electronic features and better understanding of the impact of structural defects on desired properties of functionalized CNTs.

The production of SWCNTs is still very expensive, and the research in their field should focus on the development of improved synthesis methods, which would allow for their manufacture in industrial scale (Ahmad et al. 2012). In comparison to other materials like soot, carbon fibers, clay or exfoliated graphite, CNTs’ costs significantly limit their use as adsorbents and, in the case of f-CNTs, materials appropriate for the preparation of membranes suitable for long term and efficient water and wastewater treatment in industrial scale. Every innovation in the field of CNTs production, which will be transferable to industry, will significantly improve their usage in water and wastewater treatment technology enabling sustainable CNTs utilization and reduction of costs of processes carried out with the use of novel, CNTs based materials.

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**Fig. 2.** The scheme illustrating carbon nanotubes functionalized with positive, negative and hydrophilic functional groups.
Carbon nanotubes membranes

There are two categories, which can be distinguished among novel composite membranes dedicated to water and wastewater treatment made of CNT (Bodzek et al. 2020a, c, Ihsanullah 2019, Ahn et al. 2012, Das et al. 2014b):

1. Freestanding membranes made only from CNT,
2. Composite membranes modified with CNT.

In the former group, the nano-material acts directly as a separation layer, while in the latter it is used either to modify a membrane surface or nano-particles are introduced to a polymeric membrane matrix.

Freestanding CNT membranes

Two types of freestanding CNTs membranes can be distinguished: vertically aligned (VA-CNT) and buckypaper (BP-CNT) membranes (Das et al. 2014b, Manawi et al. 2016, Sears et al. 2010). In VA-CNT membranes, particular CNTs are aligned with cylindrical poses and fluids are transported only through empty CNTs interiors and between CNTs clusters. In BP-CNT membranes are randomly distributed in non-woven structure similar to paper (Sears et al. 2010, Kar et al. 2012). The main advantages of such CNT membranes are the presence of very large porous 3D net and large specific surface.

VA-CNT membranes

The preparation of VA-CNT membranes relies on the distribution of vertically and horizontally oriented CNTs in the support layer made either from polymeric or inorganic materials using chemical vapor deposition (CVD) method (Das et al. 2014b). In order to prevent water leakage, splits between nanotubes have to be filled with polystyrene, epoxy resin, silicon nitride or a polymer of parylene type (Lee et al. 2016). Next, the digestion process is carried out to remove the excess of a filler from the surface and to open terminating caps of CNTs, what allows to obtain well-defined, nano-size pores within a membrane (Goh et al. 2016a). In Fig. 3 the SEM image of freestanding VA-CNT membrane is shown together with the scheme of such the membrane arrangement (Hinds et al. 2004; Rashid and Raloh 2017).

VA-CNT type membranes have been prepared for the first time by Hinds et al. (2004) and Majumder et al. (2005). Vertically oriented CNTs were introduced to a polymeric foil made from polystyrene (PS) creating nanoporous membrane structure (~10^9–10^10 tubes/cm², pores diameter ~7 nm) internal pores diameter of ca. 7 nm), what was confirmed by SEM images as well as gas and water permeabilities research (Hinds et al. 2004, Majumder et al. 2005). The preparation procedure was simple, but pore sizes were irregular. The authors have run a series of pressurized filtrations with the developed MWCNT/PS membrane and they have found that the water flux was 4 to 5 times higher in regard to conventional fluid fluxes estimated on the basis of Hagen-Poiseuille equation (Majumder et al. 2005) despite the fact that the pore size was one order of magnitude smaller. Holt et al. (2006), on the other hand, have developed the method of VA-CNT membranes’ manufacture, in which the internal diameter of CNTs was below 2 nm (1.6 nm in average) in order to improve nano-fluid effect. Silicon nitride was used as a filler and its aim was to assure the permeation of water only through nanopores, not through the support. The research has shown that the water flux was over three times higher than one calculated with the use of Hagen–Poiseuille equation (Holt et al. 2006). The authors have also stated that both flux and selectivity of VA-CNTs membranes could be improved by functionalization of CNTs’ ends (Manawi et al. 2016; Sears et al. 2010). Baek et al. (2014) have prepared VA-CNT membranes by introducing CNTs of pore size 4.8 nm to epoxide polymeric matrix. The permeate flux obtained for the solution of polyethylene oxide (PEO) of molecular weight 100 kDa measured for modified membranes was almost three times higher than fluxes revealed by the commercial UF membrane of similar PEO retention (78% for modified membrane and 82% for commercial membrane). A variety of fillers have been used for the preparation of VA-CNT membranes, i.e. polyether-sulphone, polystyrene, polyvinylidene-ne fluoride (PVDF), stainless steel, polyethylene imine, Fe-Al₂O₃ and others (Li et al. 2014, Majumder et al. 2005, Brady-Estevez et al. 2008, Lee and. Baik 2010, Wang et al. 2013, Park et al. 2014).

Water transport and retention of different substances revealed by VA-CNTs depend mainly on diameter and homogeneity of CNTs (Tunuguntla 2017). It has been shown that the increase of
CNTs’ diameter from 0.66 to 0.93 nm decreases ions retention from 100% to 95% (Corry 2011). Other researchers have shown that the decrease of CNTs radius from 0.39 to 0.34 nm assures permeation of water to CNTs interior and, simultaneously, results in complete retention of sodium and chloride ions (Chan and Hill 2013). Narrower nanotubes of lower radius are more difficult to be suitably produced to be further applied in, for example, RO process (Chan and Hill 2012, Ahn et al. 2012). Hence, research on manufacture of VA-CNT membranes of CNTs’ diameter range 0.6–0.8 nm and high water flux at simultaneous maximized ions retention are carried out (Ahn et al. 2012). It has been shown that CNTs’ functionalization with carboxyl or amine groups introduced to rings or gaps may be a possible solution. The introduced functional groups prevents entrance of ions (Chan and Hill 2013), but they also slightly decrease water permeability (Corry 2011).

Hummer et al. (2001) have used molecular dynamics simulation to show that a chain of water molecules can be fast and frictionless transported with ballistic motion through CNTs. It is possible due to the formation of hydrogen bonds in water molecules’ chain, which are introduced to smooth and hydrophobic coke of CNTs interior and any interaction of CNTs walls is minimal CNT (Hummer et al. 2001). Even though molecular dynamics is often used to model the flow of a variety of particles through CNTs, the availability of empirical data on water and wastewater treatment confirming transport properties of such membranes is limited.

Despite higher flux and removal efficiency of different salts, VA-CNTs membrane reveals strong antibacterial properties. Brady-Estevez et al. (2008) have proposed SWCNT filter to remove pathogens from water, and the filter revealed high antibacterial activity toward Escherichia coli K12 (E. coli). Lee et al. (2015) have prepared UF membrane of 1mm thickness and extremely high water permeability, the antibiofouling potential of which was determined using Pseudomonas aeruginosa PA01 as representative microorganism. It has been found that CNTs are resistant to biofilm formation and impede bacteria’s adhesion.

It has to be mentioned, however, that despite fast rate of fluids transport through VA-CNTs membranes, the controlled distribution and agglomeration of CNTs in matrices of relatively high surface area is still a significant challenge. Hence, further research is required in regard to verify the manufacturability and practical aspects of VA-CNT membranes use in industrial scale. However, the future development of high flux, selective and antifouling membranes is expected in the field of water and wastewater technology (Mauter and Elimelech 2008).

**Buckypaper CNT membranes**

Within a membrane structure, CNTs may also be oriented horizontally and as such they form a layer for membrane filtration. Such the structural design for a membrane is called “buckypaper” (BP) and comprises of CNTs randomly situated on a porous support. In BP-CNT membranes, CNTs are hold by means of Van der Waals forces, which are responsible for strong aggregation of CNTs, thus they form coherent structure of high specific surface arranged in a large 3D lattice. BP-CNT membranes are prepared using such methods like vacuum filtration (Peng et al. 2007), layer by layer (LBL) (Zhang and Chen 2011) or electrospinning (Kar et al. 2012). However, one of the most important stages of their preparation is CNTs purification. For this purpose, oxidation methods are most often applied and they efficiently remove contaminants from CNTs surface. On the other hand, the oxidation may cause damage and decrease nanotubes’ length. Nevertheless, it enables functionalization of CNTs with carboxylic and hydroxyl groups, which prevent CNTs aggregation in polar solvents and increase their hydrophilicity (Sears et al. 2010).

In Fig. 4 a typical process of BP-CNT membranes manufacture together with SEM image of the surface of such a membrane are shown (Sears et al.2010). The main manufacturing stages are CNTs purification and dispersion in properly selected solvent followed by filtration of homogeneous solution through a porous support, which catches nanotubes forming optically transparent BP-CNT films. These ultrathin films after immersion in ethanol are removed from the support. Peng et al. (2007) have formed freestanding BP-CNT membranes using vacuum filtration of suspension of oxidized SWCNTs through polycarbonate membrane. The obtained CNT membranes have had a thickness from several dozens to several hundred nanometers. The authors suggest that freestanding BP-CNT films with well-defined nanostructure may potentially be widely used in membrane separation, sensors and catalysis.

Despite many advantageous features, BP-CNT membranes after long terms exploitation reveal significant decrease of water flux as well as delamination due to micro-cracks initiated by the removal of water by capillary forces. This issue may be minimized by the development of methods of CNTs chemical modification, which includes: UV/ozone treatment used to form active hydroxyl an carboxyl sites and coating with thin PTFE layer (Dumée et al. 2011). Such actions lead to the improvement in membranes’ flux, due to higher hydrophilicity of the materials, and elongate their lifespan.

Both types of membranes possess advantageous and disadvantageous features. For example, freestanding CNT
membranes characterize with high water flux, however their manufacture is very complex and limits the common, industrial application of such modules. On the other hand, composite membranes containing CNTs are relatively simple manufactures, however their capacity (i.e. water flux) is much lower in regard to freestanding membranes.

**Modification of polymeric (mixed nanocomposite) membranes using CNT**

The second type of membranes, which include CNTs in their structure, covers polymeric composite CNT membranes (Ahn et al. 2012). The main target of the formation of composite (nanocomposite) CNT membranes is the improvement of conventional membranes capacity (mainly polymeric ones) and the development of an alternative for freestanding CNT membranes, which have a tendency to agglomerate, what limits their wide application (Kang et al. 2007). Additionally, CNTs and f-CNTs possess a number of attractive features, including surface’s hydrophilicity, thermal and mechanical stability, antifouling and antibacterial properties and improved salts retention, which all allow for the modification of conventional, semipermeable membranes (Ihsanullah 2019, Ali et al. 2019, Goh et al. 2016a, b, Raghavendra et al. 2017, Choi et al. 2006).

A modification of polymeric membranes may be made by the introduction of a nano-material either to a membrane’s surface or to casting solution followed by membrane formation from the mixture of a polymer and a nano-material (Bodzek et al. 2020a, c).

**Modification by introduction of nano-material on polymeric membranes’ surface**

Due to difficulties related to the preparation of membranes containing vertically oriented CNTs, many researchers have focused on the preparation of thin film nanocomposite (TFN) membranes based on CNT, in which CNTs are introduced to the separation layer (e.g. during interfacial polymerization of polyamide thin film composite (TFC) membranes) (Xue et al. 2016; Chan et al. 2013). As CNTs are hydrophobic and non-reactive, what often causes incompatibility with polymeric matrices, a number of methods of chemical or physical modification have been developed to improve CNTs dispersion in membrane separation layer (Park et al. 2010a). The most efficient method is the acidic treatment, which allows to form –OH and -COOH groups at CNT ends making them more hydrophilic and more reactive (Balasubramanian and Burghard 2005). Functionalized CNTs may be subsequently introduced to thin skin (separation) layer made from polyamide (Xue et al. 2016), what significantly influences physico-chemical properties of membranes, i.e. as hydrophilicity, porosity, charge density, additional water channels (Yin and Deng 2015), and improves antifouling properties (Manawi et al. 2016).

The modification of a membrane surface may be performed by direct imposition of the nano-material by means of a layer by layer method (Park et al. 2010b, Liu et al. 2013), vacuum filtration (Wang et al. 2016a,b; Stankovich et al. 2006), coating with solution (Ahmed et al. 2013) or interfacial polymerization with TFC membrane surface resulting in the formation of TFN membrane (Kim et al. 2014, Shen et al. 2013, Park et al. 2010c, Wu et al. 2010a, Zhao et al. 2014, Zarrabi et al. 2016, Zhang and Chen 2011, Zheng et al. 2017). The preparation of membranes by introducing nano-material on a membrane surface by means of covalent, electrostatic or coordination bonding in order to increase separation efficiency may also be applied (Bodzek et al. 2020b). The modification of membrane surface requires relatively low amount of nano-material, what is economically beneficial and limits the impact of nano-material production on the environment.

One of the most often used methods of polymeric membranes surface modification is **interfacial polymerization (IC)** (Wang et al. 2015a, b, Wang et al. 2016b, Li et al. 2017, Vatanpour and Zoqi 2017, Zheng et al. 2017). The process takes place at the interface between two immiscible phases (generally two liquids), what results in a polymer constrained to the interface. There are several IC alternatives, which result in several types of polymer topologies, but in regard to a membrane preparation ultra-thin film formation is the most important (Adamczak et al. 2019). In Fig. 5, the scheme of RO membrane produced with the use of conventional interfacial polymerization on microporous support made from polysulphone is shown. CNTs of open ends of diameter ca. 0.8 nm are placed on the separation layer, whereas the thickness of the layer is much lower than the length of CNTs, what enables the nanotubes to be easily oriented in the matrix, whereas channels spreading through the matrix allow for selective water permeation with the rate almost 2 times higher than in case of conventional membranes, whereas the increase in salts retention is negligible (Ratto et al. 2010).

Polyamide reverse osmosis (RO) membranes with carbon nanotubes (CNTs) are frequently prepared using interfacial polymerization with n-hexane solution of trimesoyl chloride (TMC) and aqueous solutions of m-phenylenediamine (MPD) containing functionalized CNTs (Kim et al. 2014; Zhao et al. 2014). The functionalized CNTs are prepared by the reactions of pristine CNTs with acidic mixture (sulfuric acid and nitric acid.

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**Fig. 5. The cross section of TFN membrane containing CNTs in the active layer**

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of 3:1 volume ratio). It has been shown that with the increase in the CNTs load, the membrane’s morphology distinctly changes, what leads to significantly improved flux without affection of the solute rejection, and the surface of the nanocomposite membrane becomes more negatively charged than the surface of pristine polyamide membrane. Furthermore, the durability and chemical resistance against NaCl solutions of the membranes containing CNTs are found to be better in comparison with membranes without CNTs. The nanocomposite membranes reveal better antifouling and antioxidative properties than CNT-free polyamide membranes, what suggests that the incorporation of modified CNTs in polymeric membranes is an effective method for their performance improvement.

Shen et al. (2013) have prepared thin film nanocomposite (TFN) membranes containing functionalized multi-walled carbon nanotubes – (MWCNTs)/poly(methyl methacrylate) (PMMA) – using interfacial polymerization in microemulsion. Similarly, Xue et al. (2016) have used three different functional groups to functionalize MWCNTs, i.e. carboxylic (MWCNT-COOH), hydroxyl (MWCNT-OH) and amine (MWCNT-NH2) ones, and next functionalized CNTs have been introduced to piperazone (PIP) aqueous solution in order to obtain TFN membranes via interfacial polymerization. The optimum concentration of MWCNTs has been established at 0.01% (m/v), and at this concentration all casted membranes have revealed high permeability toward pure water and high retention of salts. Among all prepared MWCNTs based membranes, TFN MWCNT-OH membrane has revealed the highest water flux and salt retention. The authors have explained this high capacity by the synergy of -OH groups present in MWCNTs with -NH2 groups in PIP. Additionally, MWCNTs-NH2 membranes have been characterized by better salt retention and stability in comparison to MWCNT-COOH membranes due to adhesion between -NH2 and -COOH in PA matrix.

Chan et al. (2013) have used vacuum filtration to introduce positively and negatively charged CNTs to high quality RO membranes. In the first stage, polyethersulfone (PES) was immersed in surfactant solution in order to increase pore size and hydrophilicity, while next CNTs functionalized with positive and negative functional groups were filtered under vacuum through PES membranes. Finally, interfacial polymerization between solution of methylene diamine (MPD) mixed with trimesoyl chloride (TMC) was carried out on the surface of PS/CNTs membrane support. The obtained CNTs base membranes characterized with four time higher water permeability than non-modified membranes, while the retention of both membranes has been comparable. The authors explained this higher permeability toward water with ultrafast transport through CNTs, which were uniformly distributed in ultrafiltrin membrane skin layer.

Liu et al. (2013) have prepared PES/f-MWCNTs using a spray-assisted layer-by-layer process. The negatively charged f-MWCNTs were blended with poly(sodium 4-styrenesulfonate) (PSS), and next deposited on 20 kDa PES substrate. Finally, positively charged poly(diallyldimethylammonium chloride) (PDDA) was also sprayed onto the first layer (Liu et al. 2013). The process was repeated several times, hence several bi-layers of thin PSS/MWCNTs-PDDA film were placed on PES support membrane. The first PSS/MWCNTs-PDDA layer was bonded to the support by hydrogen and hydrophobic bonds, while the second by the interaction between positively charged PDDA layer and negatively charged PSS/MWCNTs support, hence by electrostatic attraction and Van der Waals forces. The obtained membrane characterized with more favorable transport and antifouling properties than commercially available PES membrane.

Ahmed et al. (2013) have obtained nanocomposite nitrocellulose membranes using dip coating in 97% wt. solution of polyvinyl-N-carbazole (PVK) and 3% wt. of SWCNTs. The prepared membranes revealed excellent antimicrobial activity toward Gram-positive and Gram-negative bacteria (~80–90%); and they exhibited ~2.5 logs virus removal efficiency.

Tirerferri et al. (2011) have demonstrated novel methods for functionalized with carboxylic group CNTs’ immobilization on polyamide membrane skin layer, which involve strong covalent bonding (Fig. 6). Before modification, CNTs were functionalized with carboxylic groups and next carboxylic groups of polyamide thin layer were transformed to semi-stable amino-reactive using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC/NHS) solution in order to enable reaction with ethylene diamine (ED). The characterization of the SWCNTs-functionalized surfaces has demonstrated the formation of membranes with unique properties that exhibited high performance in water separation processes. The presence of surface-bound antimicrobial SWCNTs has been confirmed by experiments with E. coli cells that showed an enhanced bacterial cytotoxicity for the SWCNTs-coated membranes. The SWCNTs membranes have allowed to achieve up to 60% inactivation of bacteria attached to the membrane within 1 h of contact time. The results have suggested the potential of covalently bonded SWNTs to minimize the onset of membrane biofouling during operation.

**Modification by introduction of nano-material into polymeric membrane matrices**

The introduction of carbon nano-materials into polymeric membrane matrix influences its structure and antibacterial properties as well as affects hydrophilicity, retention and mechanical strength (Zhang et al. 2013; Chung et al. 2017; Zhao et al. 2013a, b).

The method which is the most often used to introduce CNTs to polymeric membrane matrix is a phase inversion process (Choi et al. 2006; Celik et al. 2011; Wu et al. 2010b; Brunet et al. 2008; Shah and Murthy 2013; Khalid et al. 2015). It is the process in which polymer transformation from a liquid phase to solid phase runs in a controlled way. There are four basic techniques used to create phase inversion membranes: precipitation from vapor phase, precipitation by controlled evaporation, thermally induced phase separation, and immersion precipitation (Fig. 7). Among them, immersion precipitation is the most widely-used for polymeric membranes preparation. In reference to conventional membranes (without nano-material), the surfaces of modified membranes characterize with denser pore structure, which results from precipitation of nano-material during phase inversion process. The increased water permeation of modified membranes is the result of increased hydrophilicity. Hence, the introduction of carbon nano-materials allows for membranes exploitation in dry state without permeability affection, what is especially important considering membrane resistance to microorganisms and enhances transport.
**Wet phase inversion method** is primarily used for the preparation of ultrafiltration or microfiltration membranes.

Zhang et al. (2013) have combined graphene oxide (GO) with oxidized carbon nanotubes (CNT) to modify ultrafiltration of PVDF membrane. They have applied wet phase inversion method using PVDF and PVP as the solute materials, DMAc as the solvent, low-dimensional carbon materials as the additive, and distilled water at room temperature as the nonsolvent coagulation bath. Different ratios of GO and MWCNTs mixtures in total amount of 1% wt. (mass of low-dimensional carbon materials/mass of polymer) were first introduced into DMAc solvent, then the solution was sonicated and next PVP (1 g) and PVDF (15 g) powders were added. The presence of long and curled CNTs has allowed to prevent GO aggregation, due to their tendency to bind with neighborhood GO nano-sheets. The modified GO-CNTs membrane has shown much higher hydrophilicity and antifouling properties than membranes modified only with GO or only with CNTs. Additionally, the water flux of GO-CNTs modified membranes in weight ratio equal 1:1 increased by 252% in comparison to PVDF reference membrane.

Wu et al. (2010b) have prepared a composite UF membrane by introducing MWCNTs to brominated poly(phenyl oxide) (BPPO) using wet phase inversion method with N-methyl-2-pyrolydone (NMP) as a solvent and water as a membrane coagulant. MWCNTs were added to BPPO solution and the mixture was sonicated. The obtained solution was spread on a clean glass plate. Coagulation/precipitation of membrane ran in deionized water (DI) at 30°C for at least 24 hours in order to completely remove solvent and merge the formed structure.

Choi et al. (2006) have prepared ultrafiltration membranes of MWCNTs/polysulphone (PSf) type using wet phase inversion with water as a coagulant. The uniform solution of MWCNTs was prepared in N-methyl-2-pyrolydone (NMP) and mixed with PSf. The surface of the MWNTs/PSf blend membranes was found to be more hydrophilic than in the case of pristine PSf membrane, because of the hydrophilic character of MWNTs. The morphology and permeation properties of the blend membranes depended on the amount of MWNTs used. The pore size of the blend membranes increased with the contents of MWNTs up to 1.5%, in their content range 1.5–4% it decreased, and at 4.0% of MWNTs, it was smaller than pore size of pristine PSf membrane, but measured flux and rejection were higher than ones measured for PSf membrane without MWNTs. Also, Brunet et al. (2008) have examined PSf ultrafiltration membranes prepared using carbon nanotube/polymer nanocomposites, according to the wet phase inversion method. The addition of MWCNTs (4wt.%) did not cause any disturbances in asymmetric membrane structure as well as in permeability and hydrophobicity, while the roughness of the membrane increased. The antibacterial effect was also tested with two different methods, and neither of them revealed the minimization of bacteria growth due to the presence of nanotubes.

Celik et al. (2011) have introduced MWCNTs (0.5–4wt.%) to polyethersulphone (PES) ultrafiltration membrane and synthetized the novel C/P membranes using phase inversion method. The C/P membranes have been found to be more hydrophilic due to higher pure water flux measured in reference to PES membranes. The amount of MWNTs in the blend membranes has also been shown to be an important factor affecting membranes’ morphology and permeation properties. After 24 h of surface filtration of TOC solution of concentration 7 mgC/L, C/P blend membranes showed higher flux and lower affinity to fouling than PES membranes. The filtration experiments were followed by foulants desorption. It has been found that the amount of foulant desorbed from PES membrane was 63% higher than for C/P membrane of 2wt.% MWCNTs content. Hence, the presence of nanotubes has been proved to prevent membrane fouling caused by organic matter present in natural water.

In opposite to MF and UF membranes, reverse osmosis (RO) and nanofiltration (NF) membranes are primarily
prepared using **dry phase inversion** method. The number of investigations on the preparation of polymer-nanotube composites have been made by mixing both, the nanotubes and a polymer in a suitably selected solvent, which was next evaporated to obtain a composite film (Dalmas et al. 2005; Dufresne et al. 2002; McCarthy et al. 2002). The main benefit of dry phase inversion method is the de-aggregation and dispersion of nanotubes added to a solvent in the form of a powder facilitated by agitation. In general, there exist several variations of a basic solution-processing method, which comprises the following stages: i) dispersion of nanotubes in either a solvent or in a polymer solution by energetic agitation; ii) mixing of nanotubes and polymer in solution; iii) casting of the solution onto a clean surface; iv) evaporation of the solvent at controlled condition; (v) formation of a composite film. The most popular methods of agitation include magnetic stirring, shear mixing, reflux, or, most commonly, ultrasonication.

Mehwish et al. (2015) have applied dry phase inversion method to synthesize nanocomposite nanofiltration membranes of composition PVDF/poly(styrene-butadiene-styrene) (SBS)/thiocyanate and silver modified MWCNTs. PVDF and SBS mixture was prepared by dissolution and mixing of both polymers (1:1) in tetrahydrofuran at room temperature. Modified MWCNTs (0.01–0.1wt.%) were added to the homogenous polymeric mixture, which was next casted on a glass plate and left for evaporation at room temperature for membrane formation. Pure water flux, salt rejection and capacity recovery have been found optimal for 0.05wt.% of silver in modified MWCNTs based system. The novel nanofiltration membranes have revealed characteristics suitable for their possible utilization in advanced water treatment industrial scale plants.

Shawky et al. (2011) have prepared nanocomposite membranes comprised of MWCNTs/aromatic PA to reverse osmosis using dry phase inversion with N,N-dimethylacetamide (DMAc) as a solvent. MWCNTs were dispersed in DMAc with ultrasounds, and next benzoyl peroxide was added to the solution in order to improve dispersion and to assure better homogeneity of MWCNT’s-PA solution. The obtained solution was casted on a dried, clean glass plate, which was next placed in a dryer at 90°C for 30 min for solvent evaporation. The formed, uniform, thin membrane of 200 µm was immediately cooled and immersed in DI bath for at least 15 h at room temperature. It has been found that the addition of MWCNTs improved the rejection of salt and organic matter in comparison to 10% PA membrane base. The nanocomposite membrane synthesized with 15 mg MWCNTs/g in a 10% PA casting solution rejected NaCl and humic acid by 3.17 and 1.67 times better, respectively, in comparison to the PA membrane without MWCNTs, while membrane permeability decreased by 6.5%.

**Challenges and opportunities**

Membranes containing CNTs and f-CNTs dedicated to water and wastewater treatment and water desalination have been successfully developed and tailored using different preparation techniques, including interfacial polymerization, phase inversion or coating. However, both science and engineering focused on CNTs and f-CNTs membranes need to be continuously developed and face a series of issues, among them:

- effective functionalization and CNTs dispersion,
- controlled introduction of CNTs to polymeric/ceramic membranes,
- active integration of separation layers with supports,
- the increase of pores density at unit area,
- scaling up and membranes synthesis costs,
- the achievement of proper alignment in the case of vertically aligned (VA)-CNT membranes.

The capacity of CNTs/f-CNTs membranes depends on proper and stable distribution of CNTs in a membrane matrix and on interfacial interactions between a polymer and CNTs. Hence, in order to prepare nanocomposite CNTs membranes the uniform dispersion and attachment of CNTs to polymeric matrix have to be unquestionably assured. However, the impact of factors like specific pore size, membrane’s porosity, surface hydrophilicity and charge density influencing efficiency and capacity of membranes is not enough recognized and requires further, holistic research.

One has to also notice, that similar to coating with organic agents, coating or deposition of CNTs on membranes’ surface also need to face nanomaterial loses and leakage to the environment. Hence, further research related to the improvement of CNTs bonding to membrane surface in order to maintain long-term antifouling properties has to be run. Additionally, careful control and monitoring of nanoparticles released from modified membranes is a serious issue in regard to toxic effect of such membranes (Tiede et al. 2009). The combination of CNTs based membranes with other separation and treatment techniques (catalysis, adsorption) accompanied with detail understanding of integrated CNT’s based membrane processes is an interesting option for further research. Such research should be based on scientific and technical approach to hybrid processes in regard to water chemistry, membrane separation parameters and freestanding and composite CNTs membranes’ properties. Further research should also be focused on standardization of CNTs membranes preparation methods, what will simplify commercialization of membranes dedicated to water and wastewater treatment at industrial scale.

The application of CNTs containing membranes in water and wastewater technology

**Desalination**

Water desalination is crucial technical solution dedicated to replenishment of fresh water in desert and coastal areas and in all regions with poor fresh water resources (Goh et al. 2016b,c). Conventional membrane desalination methods, mainly RO and NF, are characterized by high energy demand and costs (Yang et al. 2013a). In recent years, a number of research on the development of desalination techniques based on membranes containing nanoparticles, including carbon nanotubes, have been carried out. Among potential processes not only high pressure driven methods (RO and NF), but also forward osmosis, membrane distillation and electrochemical desalination processes (electrodialysis (ED) and capacitive deionization – CDI) are mentioned (Daer et al. 2015). Among requirements, which are listed for CNTs based membranes
dedicated to water desalination, the most important are fast water transport, maximum salt retention and minimal fouling (Ahn et al. 2012).

Transport simulation models on water and salts transport in CNTs channels have shown that water molecules chain permeates fast and frictionless through hydrophobic core of CNTs (Ansari and Kazemi 2012, Hummer et al. 2001) due to the formation of hydrogen bonds in the chain. A single CNTs (Ansari and Kazemi 2012, Hummer et al. 2001) due permeates fast and frictionless through hydrophobic core of CNTs channels have shown that water molecules chain of diameter as small as 0.83 nm, if only proper pressure conditions are assured. Another important structural feature, which is exhibited by CNTs as favorable water desalination material is the ability to retain dissolved salts. The research shows that CNTs diameter plays an important role in selective exclusion of substances (e.g. ions) during their entrance to CNTs channels (Corry 2011, Chan and Hill 2013). Corry (2008, 2011) in his research with the use of molecular dynamics simulations and on the basis of nanoparticles size has estimated VA-CNTs membranes’ permeate flux and retention of salts for nanotubes diameter range from 0.32 to 0.75 nm. The efficiency of salts retention has changed with the pore size increase as follows: 100%, 100%, 95% and 58% (Table 2) (Hoon et al. 2012). Molecular dynamics simulation carried out for VA-CNT membranes which possess the desalination capability comparable to RO membranes shows that internal diameter of CNTs should be ca 0.6 nm (Hoon et al. 2012). However, currently available technologies do not allow for the formation of tubes of such a small diameter and practically tubes of 1–2 nm of internal diameter size are produced. On the other hand, it is stated that there exists a critical pore size equal 0.7 nm, below which the transport of water molecules and hydrated ions is slowed down due to the closing of channels of nanotubes (Corry 2008, Selvan et al. 2010).

The capacity of CNTs membranes depends not only on nanotubes density in a membrane, but it has been found to decrease with the increase of ions concentration in aquatic solution. Formisiero et al. (2008) have shown that the efficiency of ions exclusion exhibited by CNT membrane depends on an ion valence and electrostatic interactions rather than on spherical effect. By the increase of surface charge of a CNT membrane one may exclude even sodium ions, even though their diameter is smaller than pores’ diameter. Hence, it may be concluded that pore size does not have to be the most important condition in regard to CNT membranes performance improvement.

The efficiency of salts retention and water flux of VA-CNTs membranes may also be modified by CNTs surface functionalization. Structural changes and f-CNTs optimization result in significant improvement of both, water flux and contaminants retention for anions and cations (Vatanpour et al. 2017). It has been found that CNTs functionalized with both, positive and negative functional groups, as for example -COO- and -NH3+ ones exhibit significant desalination efficiency improvement. The negative charge prevents the transport of chlorides, while positive functional groups repulse sodium ions, what results in practically complete retention of both ions before their enter pores of the membrane (Fig.8) (Raghavendra et al. 2017, Goh et al. 2013a, Corry 2008, Chan and Hill 2012). The small pore size may create energy barriers, which favor retention of ions. However, the water flux decrease is also observed in the case of CNTs due to the decrease of neutral and smooth internal structures of modified nanotubes in comparison to non-modified ones. Still, f-CNTs characterize with significantly higher water fluxes than commercially available polymeric desalination membranes.

In Table 3 the summary of efficiency for different RO CNTs membranes is given (Ahn et al. 2012). According to molecular dynamics simulations, VA-CNT membrane water flux equals to ca. 70–270 L/m²·h (10–15 L/m²·h·bar), i.e. 5 times higher than the flux for brackish water (BW) RO desalination membranes (Corry 2008). Similarly, the flux of composite membranes, e.g. double walled DWCNTs/PA one, may reach above >4 L/m²·h·bar, what is 1.5 times higher than the flux of BWRO membranes (Ratto et al. 2010).

The main advantage of CNTs membranes is low affinity to fouling in comparison to commercial RO and NF membranes. CNTs nanoparticles cause inactivation of bacteria cells by attacking their cellular walls (Kang et al. 2007). In reference to MWCNTs, SWCNTs (or DWMCNTs) reveal a better antifouling and antibiofouling efficiency and decrease the surface available for bacteria growth (Jia et al. 2005; Rodrigues and Elimelech 2010), when compared to commercial NF and RO membranes. The next unique feature of CNTs based membranes is low energy demand for water transport through nanotubes. The flow of particles through smooth and hydrophobic CNTs interiors does not require high pressure pump, which usually consumes a lot of energy (Ihsanullah 2019; Ahn et al. 2012).

In addition, research on the introduction of CNTs to membranes used in forward osmosis FO, membrane distillation MD and capacitive deionization CDI processes is carried out and it is focused on the increase of capacity, desalination efficiency and decrease of concentration polarization (Dumée et al. 2011, Goh et al. 2013b, Hou et al. 2014).

In tables 4 and 5 the summary of the results of research on water desalination and water pretreatment before desalination with the use of SWCNTs and MWCNTs membranes is presented.

Table 2. The efficiency of salt retention and flux of VA-CNT membrane (CNTs density CNT = 2.5×10⁷/cm²) based on molecular dynamic simulations (process parameters: TMP = 5.5 MPa; osmotic pressure = 2.4 MPa)

<table>
<thead>
<tr>
<th>Internal diameter (nm)</th>
<th>Salt retention (%)</th>
<th>Permeate flux (L/m²·h)</th>
<th>Improvement coefficientα</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>100</td>
<td>66.7</td>
<td>2.42</td>
</tr>
<tr>
<td>0.49</td>
<td>100</td>
<td>112.5</td>
<td>4.21</td>
</tr>
<tr>
<td>0.59</td>
<td>95</td>
<td>175.0</td>
<td>6.39</td>
</tr>
<tr>
<td>0.75</td>
<td>58</td>
<td>270.8</td>
<td>9.76</td>
</tr>
</tbody>
</table>

α Improvement coefficient calculated in regard to commercial RO FILMTECH SW30H4-380 membranes
Removal of heavy metals

A number of research (Pillay et al. 2009, Bahgat et al. 2011, Usman et al. 2017) on the use of f-CNTs or f-CNTs containing membranes in the removal of inorganic contaminants, especially heavy metals and arsenic from water have been carried out (Table 6). The large adsorption capacity in regard to inorganic substances revealed by f-CNTs is related to large specific surface and highly porous and empty structure of nanotubes as well as functional groups presence on CNTs surface and favorable interaction between water contaminants and f-CNTs (Bahgat et al. 2011, Ihsanullah et al. 2016a, b, c). Due to these properties, integration of f-CNTs with polymeric membranes significantly improves the removal of heavy metal ions and arsenic by means of adsorption on CNTs containing membranes. The adsorption appears mainly on external surface, in interstitial channels and grooves, while the internal structures of nanotubes are not as much involved and not as much efficient (Ihsanullah et al. 2016a, b, c).

The results of the research have shown that the ability of heavy metals adsorption on f-CNTs is usually higher than in the case of non-functionalized CNTs. Usman et al. (2017) have stated that high adsorption of metal ions exhibited by CNT membranes functionalized with, e.g., plasma, results from the presence of a large number of functional groups containing oxygen which are able to bond ions. Such the high adsorption is caused by electrostatic interaction between negatively charged CNTs surface and bi- or polyvalent metal ions (Usman et al. 2017).

In regard to protonation/deprotonation of f-CNTs, pH is also important considering efficiency of metal ions adsorption by f-CNTs membranes (Fig. 9) (Lu and Chiu 2006, Kabbashi et al. 2009, Chen et al. 2012, Al-Khaldi et al. 2013, Ihsanullah et al. 2016a, b, c). In general, cations adsorption is better at alkaline pH due to increased negative charge density of f-CNTs surface whereas at acidic pH the removal of contaminants is not satisfactory (Ihsanullah et al. 2016a, b, c). Vuković et al. (2010), while investigating the removal of Cd from aqueous solution with the use of MWCNTs functionalized by oxidation of ethylene diamines addition have found that the removal of Cd with the former f-CNTs types strongly depends on pH, whereas MWCNTs functionalized with ethylene diamine reveal high adsorption capacity towards Cd at pH range 8–9.

Except for pH, the competition between cations and anions on CNTs surface also influences the removal of metals’ ions. For example, Pb²⁺ adsorption on f-CNTs is efficient at the presence of sodium dodecyl benzene sulphonate (SDBS) due to the formation of complexes between Pb²⁺ and DBS⁻, while it is worse at the presence of benzalkonium chloride due to adsorption competitiveness (Li et al., 2011). Except for solution chemical properties and composition, the impact of f-CNTs geometry on the removal of heavy metals is also important. Even though the f-CNTs surface available for contaminants adsorption increases with CNTs diameter decrease, the investigations have not proved the significant impact of CNTs diameter on heavy metals adsorption capacity.

Removal of organics

Natural organic matter (NOM) and micropollutants are the main groups of organic impurities which appear in waters and wastewaters. Among the latter group one may distinguish:

![Fig. 8. Pictures illustrating functionalized CNTs pores entrances according to molecular dynamics simulations: A) COO⁻, B) NH₃⁺, C) combination of COO⁻ and NH₃⁺, and D) OH⁻.](image)

<table>
<thead>
<tr>
<th>CNT membrane</th>
<th>VA-CNT membrane</th>
<th>Composite CNT membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water flux, L/m²·h·bar</td>
<td>10–15</td>
<td>4–6</td>
</tr>
<tr>
<td>Salt retention</td>
<td>BWRO</td>
<td>BWRO³</td>
</tr>
<tr>
<td>Anti-fouling properties</td>
<td>not available</td>
<td>30%</td>
</tr>
<tr>
<td>Type of membrane module</td>
<td>Frame plate (ab. 1m²)</td>
<td>Spiral(8 in.)</td>
</tr>
</tbody>
</table>

* Assumptions: for both RO CNT membranes inner diameter of CNT were 1 nm and pore density – 2.5×10¹¹ CNT/cm²,
* Balt retention 93% at pressure 0.5–3.0 MPa; * Biofouling reduction brings high energy efficiency
disinfection by-products (DBPs), endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs). Organic micropollutants reveal strong carcinogenic and mutagenic properties and for the removal of NOM, ECDs and PPCPs from water, direct RO and NF or integrated systems combining UF or MF with coagulation, adsorption and oxidation are frequently used. However, the main issue related to the pressure driven membrane processes (NF/RO and UF/MF) is low permeability and significant adverse dependence between process capacity and contaminants retention, what significantly limits efficiency and full-scale operation (Kang and Cao 2012, Vatanpour et al. 2014). Hence, the development of novel membranes containing CNTs of high permeability tailored for the removal of organic and inorganic contaminants from water and wastewater is required.

A number of already performed research have confirmed high affinity of CNTs to a wide variety of organic contaminants (Ali et al. 2019). The mechanisms of their removal with the use of CNTs containing membranes is mainly based on π-π interaction, hydrogen bonds, chemical adsorption and van der Waals interactions between f-CNTs and organic compounds present in water, what allows for their efficient elimination (Wang et al. 2018). The initial concentration of the contaminants in water does not influence the removal efficiency. The selected research on the removal of organic compounds from water with the use of CNTs containing membranes are presented in Table 7.

The removal of NOM using UF f-CNTs containing membranes has been discussed by Ajmani et al. (2012). The adsorption of NOM decreases with the increase of oxygen-containing functional groups on CNTs surface due to stronger electrostatic repulsions between CNTs and NOM and weaker π-π interactions between aromatic rings of CNTs and NOM (Engel and Chefetz 2016, Yang et al. 2013b). Similar phenomena may occur while pH increases due to the enhancement of electrostatic repulsion (Engel and Chefetz 2016). CNT layered membranes have shown high resistance to fouling caused by NOM, thus they are potential materials for sustainable water treatment (Bai et al. 2015). Another research has shown that BP membranes are useful for the elimination of humic acid from water, while the recovery efficiency may reach above 93% (Rashid and Ralph 2017). It has also been demonstrated that carboxylic and hydroxyl functional groups present on CNTs water, while the recovery efficiency may reach above 93% (Rashid and Ralph 2017). It has also been demonstrated that carboxylic and hydroxyl functional groups present on CNTs increase hydrophilicity what significantly contributes to the effectiveness of nanotubes as filtration media.

A promising hybrid nanofiltration membrane prepared using reduced graphene oxide (rGO) intercalated with MWNTs has been developed. The resulting rGO/MWCNTs has been next loaded onto an anodic aluminium oxide microfiltration membrane using vacuum filtration (Chen et al. 2016).

The resulted hybrid rGO/MWCNT membrane has been used to purify drinking water and enable the retaining of a wide range of organic compounds, including humic and fulvic,

<table>
<thead>
<tr>
<th>Materials</th>
<th>Feed/Operational conditions</th>
<th>Efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs-Cu nanolayer</td>
<td>Brackish water</td>
<td>The efficiency improvement with the increase of CNTs amount in the composite.</td>
<td>Park et al. 2014</td>
</tr>
<tr>
<td>Carboxylated CNTs</td>
<td>NaCl solution of concentration 3.4%</td>
<td>Stable membrane operation during long term operation. Water flux: 19.2 kg/m² h</td>
<td>Bhadra et al. 2013</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>KCl solution</td>
<td>Retention mechanism: electrostatic interactions between membrane charge and ions.</td>
<td>Fornasiero et al. 2008</td>
</tr>
<tr>
<td>CNTs</td>
<td>Saline water</td>
<td>CNTs increase membrane’s surface porosity and hydrophilicity of surface and its permeability</td>
<td>de Lannoy et al. 2013</td>
</tr>
<tr>
<td>CNTs of zwitterionic structure</td>
<td>Saline water</td>
<td>High water flux and salt retention. Significant resistance to biofouling.</td>
<td>Chan et al. 2013</td>
</tr>
<tr>
<td>MWCNTs oxidized with HNO₃ and H₂SO₄</td>
<td>Saline water</td>
<td>Max. % separation was achieved at highest salt concentration in feed water</td>
<td>Tofghi et al. 2011</td>
</tr>
<tr>
<td>0.1% MWCNT/ polyamide (PA)</td>
<td>NaCl solution (2,000 ppm, pH 7, 25 °C, TMP 16 bar)</td>
<td>Water flux: 28.05 L/m² h, NaCl retention &gt;90% .</td>
<td>Zhao et al. 2014</td>
</tr>
<tr>
<td>MWCNT/PA aromatic (15 mg MWNT/1gPA)</td>
<td>NaCl solution (4,000 ppm and 20 °C, TMP 39 bar)</td>
<td>Water flux: 0.71 L/m² h bar, NaCl retention: 76%.</td>
<td>Shawky et al. 2011</td>
</tr>
<tr>
<td>0.1% MWCNT/ polyamide (PA)</td>
<td>NaCl solution (2,000 ppm, 25°C, TMP 16 bar)</td>
<td>Water flux: 71 L/m² h, Retention: 98% .</td>
<td>Zhang et al. 2011</td>
</tr>
<tr>
<td>PES/0.45% MWCNT</td>
<td>Na₂SO₄, MgSO₄ and NaCl solutions (200 ppm, TMP 4 bar, pH = 7.0, 25°C)</td>
<td>Pure water flux: 23.7 L/m² h, Salts retention: Na₂SO₄ – 65%, MgSO₄ – 45% and NaCl-20%</td>
<td>Vatanpour et al. 2014</td>
</tr>
</tbody>
</table>
and also organic acids dyes, proteins, organophosphates, and sugars. The nano-membrane has also been found highly effective at removing bovine serum albumin (BSA), and the organophosphate insecticide phoxim. The retention rate above 90% has been obtained, while the permeability of water has been determined to be between 22 and 30 L/m²·h·bar, i.e. markedly larger than one reported for graphene nanofiltration membranes discussed in the literature (Han et al. 2013).

Wang et al. (2015a,b) have described the removal of pharmaceuticals and personal care products (PPCPs) using UF nanocomposite membranes containing SWCNTs and MWCNTs. The membranes have been tested toward rejection of triclosan (TCS), acetaminophen (AAP), and ibuprofen (IBU) to establish the capabilities and mechanisms of selected PPCPs removal. The elimination of contaminants ranged within 10–95% and it increased with the increase of a number of aromatic rings (AAP<IBU<TCS), with the decrease of surface oxygen content (oxidized MWCNT<MWCNT), with the increase of specific surface area (MWCNT<SWCNT), and with the elimination of natural organic matter. The change of solution pH from 4 to 10 has also influenced PPCP removal by up to 70%. The greater efficiency was obtained for neutral molecules due to weaker electrostatic repulsion (TCS and IBU) or formation of hydrogen bond (AAP). The research results suggest that the performance of CNTs membranes to remove PPCPs from water is satisfactory due to the existence of strong adsorption caused by favorable PPCPs-CNTs interactions.

Kaminska et al.(2016) performed studies on the effect of the amount of SWCNTs incorporated into polyacrylonitrile (PAN) matrix membranes on their ability to remove bisphenol A (BPA) and 4-nonylphenol (4-NP), as well as on permeate flux. The permeate flux established for PAN-CNTs membranes was about 80% higher than that for an unmodified PAN membrane. The increase of the amount of SWCNTs in the membranes from 0 to 0.5%, resulted in a significantly enhanced removal of both micropollutants. However, further increase of the amount of SWCNTs up to 1.0% surprisingly adversely affected the recovery levels, while the permeate flux kept the increasing tendency.

Recently, a new methodology for the rapid and straightforward preparation of an enzymatically active MWCNT BP for organophosphate bioremediation has been developed (Mechrez et al. 2014). This novel BP-CNTs membranes have been prepared using carboxylated MWCNTs (MWCNT-COOH), and dispersed solution of MWCNTs was filtered under vacuum onto a cellulose support membrane to produce a composite MWCNT BP membrane. To produce an enzymatically active OPH/MWNT BP membrane, organophosphate hydrolase (OPH) was subsequently covalently immobilized onto the nanotube surface. To demonstrate its bioremediation features, an aqueous solution of methyl paraoxon, a model organophosphate contaminant, was filtered using the OPH/MWNT BP. A significant decrease in the concentration of methyl paraoxon was achieved due to its in situ hydrolysis by the immobilized enzyme during the filtration process.

**Removal of microorganisms**
Pathogenic microorganisms, which most often appear in water and wastewater include bacteria, viruses and protozoa (Bodzek et al. 2019). A number of research have shown that CNTs inactivate or remove a variety of microorganisms, including bacteria (e.g. *Micrococcus lysodeikticus*, Escherichia coli, *Salmonella* and *Streptococcus mutans*), protozoa (e.g. *Tetrahymena pyriformis*) and viruses (e.g. bacteriophages MS2) (Table 8).

Brady-Estévez et al. (2008; 2010) were among the first, who demonstrated the antimicrobial properties of BP-CNTs membranes, and their ability to efficiently remove bacteria and viruses from contaminated water. During the experiments, they examined BP-CNTs membranes prepared from dimethylsulfoxide (DMSO) solutions containing SWCNTs (Brady-Estévez et al. 2008) further used to filtration experiments. They have showed that the majority of the bacterial cells has been retained, while measurements of their metabolic activity have indicated that only 6% of the E. coli cells remained metabolically active after the process. Very high viral removal capabilities have also been exhibited by the hybrid SWCNT/PVDF membranes (Brady-Estévez et al. 2008). It is postulated that the excellent antibacterial properties shown by SWCNTs themselves are a result of their ability to cause significant damage to cells’ membranes (Kang et al. 2007).

Kang et al. (2008) have shown that SWCNTs cause more severe damage of *E. coli* bacteria cellular membrane than MWCNTs. Additionally, it is supposed that SWCNTs inactivate *E. Coli* bacteria more efficiently due to permeation to their cellular walls caused by direct contact with nanotubes, what is accompanied with changes in metabolic activity, genes expression level and metabolic cell’s morphology. Moreover, Kang et al. (2007) have shown that chemically modified CNTs have higher affinity to cellular walls destruction than native CNTs and polymeric membranes. During the experiments with *Salmonella typhimurium* and nanotubes aqueous suspension it has been demonstrated that SWCNTs length influences their antibacterial action (Brady-Estévez et al. 2010).

It is explained by higher affinity of longer SWCNTs to aggregate bacteria cell what creates the opportunity to more intense cells’ damages. In opposite, shorter SWCNTs reveal the tendency to agglomerate with themselves rather than with bacteria cells, thus their antibacterial potential is much lower. On the other hand, the results of research presented in Table 8 indicate that CNTs diameter may also play an important role in inactivation of microorganisms present in wastewater.

Sweetman et al. (2012, 2013) have recently investigated the permeability of water and the effectiveness for bacteria elimination of self-supporting BP-SWCNT membranes prepared from dispersions containing macrocyclic ligands and antibiotics. Each of investigated BPs has revealed >99% effectiveness toward *E. coli* from aqueous suspensions (Sweetman et al. 2013). Hence, the study has demonstrated that free-standing BP-CNT membranes can be comparably effective in the removal of microbial contaminants from water supplies as the composite CNT materials (Brady-Estévez et al. 2008, 2010).

Silver nanoparticles (Ag NPs) are well recognized as the most efficient and commonly used antibacterial agents. It is related to their capacity to damage protein and DNA molecules, interrupt electron transport chains, and disturb other cellular
functions (Xiu et al. 2012; Kim et al. 2012). Functionalization of CNT membranes with silver nanoparticles may enhance the ability of the membrane to inactivate microorganisms. For example, Ihsanullah et al. (2015c) have obtained CNTs membranes of different nanosilver content (1, 10 and 20 wt.%) using wet chemistry technique. The affinity of the developed membranes to biofouling has been examined using E. coli. It has been shown that the tested membranes enable complete elimination/death of E. coli, and the CNT membrane with 10% silver content has exhibited superior performance in regard to the others. In Fig.10, the variation of the amount of bacteria remaining in permeate as a function of time after filtration through Ag/MWCNT composite membranes with different silver shares is shown (Roy et al. 2012). The ability of removal of microorganisms from water during its treatment is assigned to toxic effect of Ag-CNTs nanoparticles.

Challenges and opportunities

The potential of CNTs and CNTs containing composites used as semipermeable membranes and adsorbents to remove contaminants from water has been widely investigated. CNTs functionalized with chemical groups possess enhanced capability of the removal of a variety of organic and inorganic contaminants as well as microorganisms. Inactivation of bacteria and viruses on f-CNT membranes may be achieved by CNTs due to their ability to destroy microorganisms’ cellular walls, what may be supported by CNTs membranes combination with other biocides (e.g. silver nanoparticles). On the other hand, due to the complex character of natural water and wastewater accompanied with appearance of competing substances, the selective adsorption of trace organic contaminants on f-CNTs membranes is quite limited. Hence, the need for the development of proper functionalization of CNTs membranes (e.g. functionalization of CNTs ends) enabling the improvement of adsorptive filtration is still valid.

Freestanding and composite CNTs membranes exhibit significant potential for water desalination. High water permeability shown by VA-CNT membranes is assigned to smooth and non-polar internal channels of nanotubes. Currently manufactured CNTs characterize with relatively high diameters, what decreases retention of salts during the treatment of brackish or seawater. Thus, for efficient water desalination further research on the manufacture of CNTs of lower diameters is required.

The industrial scale application of f-CNTs membranes to water and wastewater treatment as well as in water desalination is still in its early stage. There exist a number of solutions on the potential use of f-CNTs membranes in this field, but these are tested only in the laboratory scale, while research on larger scale, practical use of f-CNTs and f-CNTs containing membranes are very limited. The main focus of further actions should be dedicated to economic and technological feasibility of CNTs membranes manufacture in industrial scale, elaboration of additional procedures of CNTs introduction to existing or novel membranes, monitoring and determination of long-term stability of membranes operated in real conditions of water and wastewater treatment processes. In regard to practical use of CNTs and f-CNTs systematic evaluation of technical challenges, such as scaling up, CNTs leakages, health effect, environmental impact and eventual toxicity needs to be carried out. Moreover, one has to remember that separation capacity and stability of CNTs membranes determined during laboratory experiments may be significantly different from those obtained during industrial application, not only due to chemical properties of treated water, but also in regard to chemical and mechanical stability of membranes operated in demanding, environmental conditions. Still, further research on the capability of f-CNT to treat real water and wastewater during long term operation is required, while such is difficult to be performed in laboratory scale.

Currently high costs of CNTs practically do not allow for their commercial use, but the market is known to be very dynamic. Due to more intense industrial production, unit prices of CNTs based materials decreased from 1500 USD/g in 2000 to 50 USD/g in 2010 and 1.48 USD/g in 2017 (https://en.wikipedia.org/wiki/Carbon_nanotube; Wang et al., 2018). Such lower materials costs, in combination with breakthrough research results indicate a possible, industrial use of f-CNTs membranes in the nearest future. The commercialization of the use of CNTs membranes in water and wastewater treatment technology requires further research for the improvement of manufacture costs and widening of manufacture techniques to the level required in large scale applications.

In summary, the industrial, common use of CNTs membranes in water and wastewater treatment can be obtained only through the continuing of research, which should be especially focused on:

1) Optimization and introduction of efficient procedures of functionalization and modification of CNTs materials during their manufacture in large scale.
2) Development and testing of novel trends, such as the use of renewable resources in economically profitable production of CNTs based materials.
3) The run of more intense and frequent pilot and industrial scale research enabling the determination of capacity and selectivity of CNTs membranes at real and demanding process conditions.
4) Integration of conventional technologies with CNTs based processes allowing for the development of advanced water and wastewater treatment systems.

Fig. 10. The effect of time on the amount of bacteria remaining in the filtrate (expressed as colony forming units (CFU)) after passage across Ag/MWCNT membranes with different shares of silver.

![Graph of bacterial counts CFU/min](image-url)
Table 5. The review of research on water desalination with the use of f-CNT membranes

<table>
<thead>
<tr>
<th>Salt type</th>
<th>CNT membranes</th>
<th>CNTs share g/cm² or %wt/cm²</th>
<th>Removal mechanism</th>
<th>Additional remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>E-CNTs 99%</td>
<td>2g/9.3 cm²</td>
<td>Chemical interactions</td>
<td>Very high water permeability.</td>
<td>Lee et al. 2017</td>
</tr>
<tr>
<td></td>
<td>Amine-functionalized MWCNTs 20%</td>
<td>0.045 wt.%/19.6 cm²</td>
<td>Electrostatic interaction</td>
<td>Strong BSA antifouling properties, high flux and NaCl retention.</td>
<td>Vatanpour et al. 2014</td>
</tr>
<tr>
<td></td>
<td>COOH-MWCNTs &gt; 90%</td>
<td>2% w/v/18.1 cm²</td>
<td>Electrostatic interaction</td>
<td>Strong antifouling and antioxidative properties.</td>
<td>Zhao et al. 2014</td>
</tr>
<tr>
<td></td>
<td>COOH-MWCNTs 98.5%</td>
<td>0.0255/36 cm²</td>
<td>Surface complexation</td>
<td>Very high water permeability and BSA antifouling properties.</td>
<td>Vatanpour and Zoqi 2017</td>
</tr>
<tr>
<td></td>
<td>Oxidized CNTs &gt; 98%</td>
<td>0.4g/3.3×68 cm²</td>
<td>Surface complexation, electrostatic interaction</td>
<td>Excellent DOM antifouling properties.</td>
<td>Kim et al. 2014</td>
</tr>
<tr>
<td></td>
<td>Acid modified MWCNTs-nAg 88.1%</td>
<td>5.0wt%/0.01764 cm²</td>
<td>Chemical interactions</td>
<td>High permeability and retention and antifouling properties.</td>
<td>Kim et al. 2012</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>Sulphonated MWCNT-OH 96.8%</td>
<td>1g/12.56 cm²</td>
<td>Electrostatic interaction/ Donnan effect</td>
<td>Strong NOM antifouling properties.</td>
<td>Zheng et al. 2017</td>
</tr>
<tr>
<td></td>
<td>PMMA–MWCNTs &gt;99%</td>
<td>0.67g/19.62 cm²</td>
<td>N/A</td>
<td>Significantly increase in selectivity and permeability.</td>
<td>Shen et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Amine-functionalized MWCNTs 65%</td>
<td>0.045 wt.%/19.6 cm²</td>
<td>Electrostatic interaction/ Donnan effect</td>
<td>High water flux and Na₂SO₄ retention, strong BSA antifouling efficiency.</td>
<td>Vatanpour et al. 2014</td>
</tr>
<tr>
<td></td>
<td>f-MWCNTs-nAg/ TFN 95.6%</td>
<td>5.0 wt.%/0.01764 cm²</td>
<td>Chemical interactions</td>
<td>Antibiofouling properties. High salt retention and water flux.</td>
<td>Kim et al. 2012</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>amine-functionalized MWCNTs 45%</td>
<td>0.045wt%/19.6 cm²</td>
<td>Electrostatic interaction/ Donnan effect</td>
<td>High water permeability and strong BSA antifouling properties.</td>
<td>Vatanpour et al. 2014</td>
</tr>
</tbody>
</table>

*a* R – efficiency of salt rejection,%.  
*c* IC – initial concentration, mg/L.  
N/A represent not available.
### Table 6. The summary of selected research on removal of heavy metals and arsenic with the use of f-CNTs and f-CNTs containing membranes

<table>
<thead>
<tr>
<th>Metal type</th>
<th>Membrane/adsorbent containing CNTs</th>
<th>Nanomaterial type</th>
<th>Initial concentration</th>
<th>CNTs amount</th>
<th>Removal mechanism</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>MWCNT-ZrO$_2$</td>
<td>2 mg/g</td>
<td>0.1 mg L$^{-1}$</td>
<td>100 mg/10 mL</td>
<td>Chemisorption/ Physical sorption</td>
<td>As (III) adsorption capacity is not related with pH.</td>
<td>Ntim and Mitra 2012</td>
</tr>
<tr>
<td>As(III)</td>
<td>MWCNT-Fe$_2$O$_3$</td>
<td>1.73 mg/g</td>
<td>0.1 mg L$^{-1}$</td>
<td>10 mg/10 mL</td>
<td>Electrostatic interaction</td>
<td>Adsorbents for water treatment.</td>
<td>Ntim and Mitra 2011</td>
</tr>
<tr>
<td>As(V)</td>
<td>MWCNT-ZrO$_2$</td>
<td>5 mg/g</td>
<td>0.1 mg L$^{-1}$</td>
<td>100 mg/10 mL</td>
<td>Chemisorption/ Physical sorption</td>
<td>As(V) adsorption capacity is not related with pH.</td>
<td>Ntim and Mitra 2012</td>
</tr>
<tr>
<td>As(V)</td>
<td>MWCNT-Fe$_2$O$_3$</td>
<td>0.18 mg/g</td>
<td>0.1 mg L$^{-1}$</td>
<td>10 mg/10 mL</td>
<td>Electrostatic interaction</td>
<td>MWCNTs modification can be used to preparation membranes/ adsorbents for water treatment.</td>
<td>Ntim and Mitra 2011</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>CNTs modified with acid</td>
<td>0.5 mg/g</td>
<td>1 mg L$^{-1}$</td>
<td>120,000 mg/500 mL</td>
<td>Electrostatic interaction</td>
<td>Cr removal efficiency increase with CNTs amount increase.</td>
<td>Atieh et al. 2010</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Functionalized MWCNTs</td>
<td>95%</td>
<td>0.1 mg L$^{-1}$</td>
<td>100 mg/10 mL</td>
<td>Ion exchange, Diffusion</td>
<td>Cr(VI) regeneration can be achieved in alkaline environ.</td>
<td>Pillay et al. 2009</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Oxidized MWCNTs</td>
<td>95%</td>
<td>10 mg L$^{-1}$</td>
<td>3,000 mg/100 mL</td>
<td>Chemical, electrostatic, hydrophobic and π-π interactions</td>
<td>High efficiency of heavy metals ions removal from wastewater.</td>
<td>Li et al. 2011</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>Functionalized MWCNTs</td>
<td>&gt; 85%</td>
<td>100 mg L$^{-1}$</td>
<td>1,000 mg/4 mL</td>
<td>N/A</td>
<td>Excellent capacity of heavy metals removal.</td>
<td>Wang et al. 2012</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Functionalized MWCNTs</td>
<td>99%</td>
<td>1.1 mg L$^{-1}$</td>
<td>90 mg/100 mL</td>
<td>Electrostatic interaction</td>
<td>The possibility of the use in heavy metals removal.</td>
<td>Mubarak et al. 2013</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Functionalized MWCNTs</td>
<td>97%</td>
<td>100 mg L$^{-1}$</td>
<td>1,000 mg/4 mL</td>
<td>N/A</td>
<td>Excellent capacity of metals removal.</td>
<td>Wang et al. 2012</td>
</tr>
<tr>
<td>Co(II)</td>
<td>Oxidized MWCNTs</td>
<td>70 mg/g</td>
<td>1,200 mg L$^{-1}$</td>
<td>50 mg/25 mL</td>
<td>Chemical interactions</td>
<td>Promising material for removal of heavy metals.</td>
<td>Tofighy and Mohammadi 2011</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>Oxidized MWCNTs</td>
<td>49.26 mg/g</td>
<td>10–200 mg L$^{-1}$</td>
<td>20 mg/50 mL</td>
<td>Electrostatic interaction</td>
<td>Greater adsorption ability than raw MWCNTs in water.</td>
<td>Kandah and Meunier 2007</td>
</tr>
</tbody>
</table>

AC – adsorption capacity of a contaminant % and mg/g, R – percentage removal efficiency, $C_0$ – initial concentration
<table>
<thead>
<tr>
<th>Contaminant type</th>
<th>Membrane/adsorbent containing CNTs</th>
<th>Nanomaterial type</th>
<th>R; AC</th>
<th>Initial concentration</th>
<th>CNTs amount</th>
<th>Removal mechanisms</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhACs and PCPs</td>
<td>CNT based nanocomposite</td>
<td>45%</td>
<td>0.1 mg L⁻¹</td>
<td>22 g/m²</td>
<td>Chemical adsorption</td>
<td>High removal rate of PhACs and PCPs from water solutions.</td>
<td>Wang et al. 2016a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNT based nanocomposite</td>
<td>95%</td>
<td>1 mg L⁻¹</td>
<td>22 g/m²</td>
<td>Electrostatic interaction, hydrogen bonding, π–π interaction</td>
<td>The increase of removal rate with increasing aromatic rings number.</td>
<td>Wang et al. 2015b</td>
<td></td>
</tr>
<tr>
<td>Humic acid</td>
<td>MWCNTs coated with calcium</td>
<td>90.2%</td>
<td>20 mg L⁻¹</td>
<td>0.5 g/L</td>
<td>Chemical adsorption</td>
<td>Excellent removal efficiency and regeneration (after 5 process cycles R&gt;99.2%)</td>
<td>Li et al. 2017</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Functionalized BP-CNT</td>
<td>&gt;93%</td>
<td>5 mg L⁻¹</td>
<td>0.05 g/20 mm</td>
<td>Physical interaction/ surface complexation</td>
<td>Excellent NOM adsorption and significant water flux increase.</td>
<td>Yang et al. 2013b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Magnetic MWCNTs</td>
<td>98.8%</td>
<td>1–37 mg L⁻¹</td>
<td>0.5 g/L</td>
<td>Electrostatic attraction and Van der Waals forces</td>
<td>Excellent dyes removal in comparison with other methods.</td>
<td>Gong et al. 2009</td>
<td></td>
</tr>
<tr>
<td>Methylene blue</td>
<td>Magnetic MWCNTs</td>
<td>99.16%</td>
<td>1–37 mg L⁻¹</td>
<td>0.5 g/L</td>
<td>Electrostatic attraction and Van der Waals forces</td>
<td>Excellent dyes removal in comparison with other methods.</td>
<td>Gong et al. 2009</td>
<td></td>
</tr>
<tr>
<td>BSA</td>
<td>Dodecylamine-Functionalized MWCNTs</td>
<td>N/A</td>
<td>200 mg L⁻¹</td>
<td>0.5 wt.%/42 cm²</td>
<td>N/A</td>
<td>Resistant to proteins fouling. Higher permeate flux.</td>
<td>Khalid et al. 2015</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNTs of polyelectrolyte type</td>
<td>99.9%</td>
<td>1 mg L⁻¹</td>
<td>N/A</td>
<td>Electrostatic interaction</td>
<td>Better antifouling features of the membrane.</td>
<td>Liu et al. 2013</td>
<td></td>
</tr>
<tr>
<td>Phenols</td>
<td>CNTs impregnated with Al₂O₃</td>
<td>99.4%</td>
<td>2 mg L⁻¹</td>
<td>0.25g</td>
<td>Ionic exchange</td>
<td>High affinity to phenols removal according to Langmuir adsorption model.</td>
<td>Ihsanullah et al. 2015b</td>
<td></td>
</tr>
<tr>
<td>Polychlorinated biphenyls</td>
<td>MWCNTs grafted by beta-cyclodextrin</td>
<td>&gt; 96%</td>
<td>4.14 mg L⁻¹</td>
<td>N/A</td>
<td>π–π interactions, steric hindrance effect</td>
<td>Higher adsorption capability than in case of pristine MWCNTs.</td>
<td>Shao et al. 2010</td>
<td></td>
</tr>
<tr>
<td>Atrazine</td>
<td>MWCNTs</td>
<td>&gt; 35 mg/g</td>
<td>0.87–26.04 mg L⁻¹</td>
<td>0.002 g/20 ml</td>
<td>N/A</td>
<td>High atrazine adsorption</td>
<td>Yan et al., 2008</td>
<td></td>
</tr>
</tbody>
</table>

AC – adsorption capacity of contaminants % and mg/g, R – %
<table>
<thead>
<tr>
<th>Micro-organism kind</th>
<th>Membrane/adsorbent with CNTs</th>
<th>Retention</th>
<th>Initial counts of microorganism in the suspension</th>
<th>Load of CNTs</th>
<th>Retention mechanism</th>
<th>Comments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Escherichia coli</em> (E. coli)</td>
<td>Silver doped-CNT membrane</td>
<td>100%</td>
<td>$1 \times 10^6$ CFU/mL</td>
<td>19.8 g/600 mL</td>
<td>Physical interaction</td>
<td>High anti-biofouling. Can be used for water purification.</td>
<td>(Ihsanullah et al., 2015c)</td>
</tr>
<tr>
<td></td>
<td>Nano-hybrid CNT-Ag</td>
<td>89.3%</td>
<td>$10^6$ CFU/mL</td>
<td>0.004 g/mL</td>
<td>N/A</td>
<td>High potential to inactivate a large number of pathogenic microbes from wastewaters</td>
<td>(Nie et al., 2017)</td>
</tr>
<tr>
<td></td>
<td>Nanocomposite Chitosan/CNT</td>
<td>3.62 log</td>
<td>$1.5 \times 10^6$ to 5.0 $10^6$ CFU/mL</td>
<td>5 wt%</td>
<td>Physical interaction and complexing</td>
<td>Very high efficiency of deactivation of microorganisms after a short time of contact.</td>
<td>(Morsi et al., 2017)</td>
</tr>
<tr>
<td></td>
<td>f-MWCNTs</td>
<td>N/A</td>
<td>$10^6$ to $10^9$ CFU/mL</td>
<td>0.02 g/100 mL</td>
<td>Electrostatic repulsion/sieve mechanism</td>
<td>CNTs dispersion is responsible for antibacterial effects.</td>
<td>(Chi et al., 2016)</td>
</tr>
<tr>
<td></td>
<td>MWCNTs-(C$_{18}$) interaction with Microwaves</td>
<td>100%</td>
<td>3.5 $\times 10^7$ CFU/mL</td>
<td>1 g/250 mL</td>
<td>Polarization</td>
<td>Microwave interaction with f-CNTs is an innovative approach that can be used to water disinfection.</td>
<td>(Al-Hakami et al., 2013)</td>
</tr>
<tr>
<td><em>Staphylococcus aureus</em></td>
<td>Nano-hybrid CNT-Ag</td>
<td>95%</td>
<td>$10^6$ CFU/mL</td>
<td>0.004 g/mL</td>
<td>N/A</td>
<td>Demonstrating high potential to inactivate large number of pathogenic microbes in waste water.</td>
<td>(Nie et al., 2017)</td>
</tr>
<tr>
<td></td>
<td>Chitosan/CNTs nanocomposite</td>
<td>5.2 log reduction</td>
<td>$1.5 \times 10^6$ to 5.0 $10^6$ CFU/mL</td>
<td>5 wt%</td>
<td>Physical interaction and complexation</td>
<td>Superior antimicrobial capacity in short contact time.</td>
<td>(Morsi et al., 2017)</td>
</tr>
<tr>
<td><em>Aspergillus flavus</em></td>
<td>Chitosan/CNTs nanocomposite</td>
<td>4.3 log reduction</td>
<td>$1.5 \times 10^6$ to 5.0 $10^6$ CFU/mL</td>
<td>5 wt%</td>
<td>Physical interaction and complexation</td>
<td>Superior antimicrobial capacity in short contact time.</td>
<td>(Morsi et al., 2017)</td>
</tr>
</tbody>
</table>
References


New generation of semipermeable membranes with carbon nanotubes for water and wastewater treatment: Critical review

25


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