

Recent advances in water and wastewater treatment using membranes with carbon nanotubes

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Abstract. Carbon nanotubes (CNTs), due to their excellent physical, chemical and mechanical properties and their ability to prepare new membranes with attractive properties, have found applications in water and wastewater technology. CNT functionalization, which involves the introduction of different types of functional groups into pure CNTs, improves the capabilities of CNT membranes for water and wastewater treatment. It turns out that CNT-based membranes have many advantages, including enhanced water permeability, high selectivity and anti-fouling properties. However, their full-scale application is still limited by their high cost. With their tremendous separation efficiency, low biofouling potential and ultra-high water flux, CNT membranes have the potential to be a leading technology in water treatment in the future, especially in desalination.

Keywords: carbon nanotube; CNT functionalization; CNT membranes; mixed matrix CNT membranes; water and wastewater treatment

1. Introduction

Access to adequate quality fresh water for drinking and other needs is a major and fundamental aspect of achieving sustainable development of societies. Water covers more than 70% of Earth, but as much as 90% of its total amount appears as a saline water, while the remaining 2% of fresh water still in 90% is in the frozen form (Sheikholeslami 2009). The water poverty is one of the main problem of XXIst century, which has to be faced by many countries over the world and it is one of the fundamental challenge for their industrial and social development (Seckler *et al.* 1999). Water is a non-renewable natural resource, thus its amount is more and more limited, what significantly influences on water access in many countries. In the previous century the water usage increase was two times greater than the population growth. According to United Nations report, in 2025, 1,800 millions of people will live in regions of complete water scarcity, while more than 60% of global population will inhabit regions of significant water stress (WHO 2012). The pressure related with 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 worldwide fresh water scarcity results in development of more efficient, economically justified and properly

oriented water treatment strategies from in-place available resources, which are environmentally neutral and safe for humans health, but also mentally accepted. It causes the dynamic growth of a number of research dedicated to energy-efficient water treatment technologies enabling the production of safe, potable water. The reuse of wastewater as well as reclamation and recycling of side water streams have been found essential for reliable water access and supply and additionally they have been shown to be safe for public health. The civilization growth and industrialization, however, have widen the qualitative and quantitative character of contaminants deposited to natural waters causing a series of health issues. It is commonly known that 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 over 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 (Nawrocki 2010, Bodzek 2019).

Membrane filtration, especially its pressure driven type, is found to be one of the most promising and widely applied method for wastewater, surface and ground water treatment (Bodzek 2019, Madhura *et al.* 2018). The selection of the membrane process is dependent of the type of raw stream to

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be treated and contaminants/admixtures to be removed (Bodzek and Konieczny 2017, 2006). 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 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 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 alternative for 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 (Lee *et al.* 2011, Kochkodan and Hilal 2015). Hence, a series of research on the novel, improved membranes of adjusted properties and efficiency are carried out (Kochkodan and Hilal 2015). The main features defined for future generation of membranes are targeted on 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 with the total rearrangement of almost one hundred years old conventional water treatment process (Goh *et al.* 2013a). In recent years 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 have been observed (Bodzek *et al.* 2020a, b, c, Qadir *et al.* 2017, Pendergast and Hoek 2011, Kim and Van Der Bruggen 2010). The design and synthesis of novel nanomaterials, which are introduced to polymeric membranes and adsorbents in the form of nanoparticles is in the research interest of material sciences and other fields. Nanomaterials characterize 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.* 2019a), carbon nanotubes (CNTs) and fullerenes, what is

related with 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 characterize 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.* 2019a), carbon nanotubes (CNTs) have gained significant attention in regard to their features found as favourable 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 elimination of 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.

In recent years several important review articles on the use of nanomaterials in water desalination and water and wastewater treatment have been published (Pendergast and Hoek 2011, Lee *et al.* 2016, Santhosh *et al.* 2016, Stefaniuk *et al.* 2016). Nevertheless, the rapid development and implementation of nanomaterials create a need of the often revision of state of the art in the field of CNTs and CNTs containing membranes, which due to possibility of functionalization (f-CNTs) gain unique features specified for removal of contaminants from water and wastewater. 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 earlier mentioned. CNTs and f-CNTs membranes characterize also with desalination properties, they can be used to removal of 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 combination of 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 critical evaluation of the current progress, knowledge gaps and future research areas.

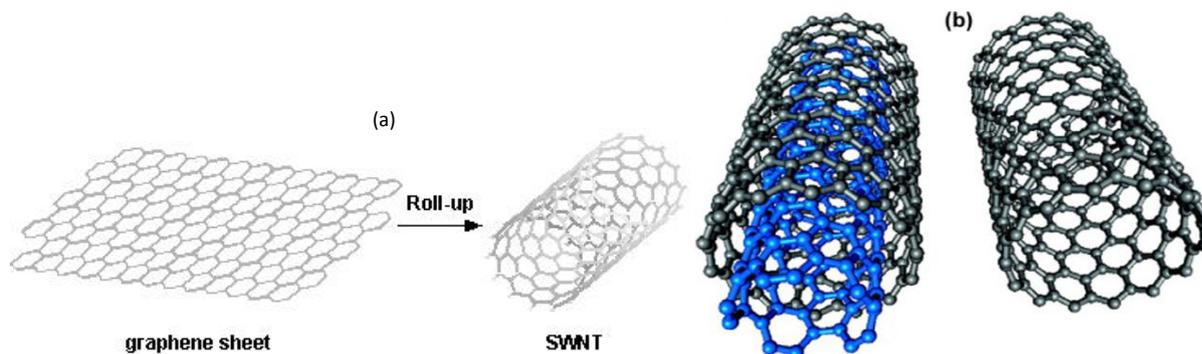


Fig. 1 (a) Rolling of a single layer of graphite sheet into SWCNT, (b) Structures of multi-walled and single-walled carbon nanotubes

2. Carbon nanotubes fundamentals

Nanotubes are supermolecular cylindrical structures, which are empty inside. Currently, carbon nanotubes, discovered at the beginning of 1990s, are the best recognized. 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.

2.1 Structure and properties

Carbon nanotubes (CNTs) are allotropic form of carbon. Their walls are built of graphene (single-atom graphite layer) rolled up in a tubular structure (Dai 2002, Ahmad *et al.* 2012) (Fig.1a). Microscopic observations confirm that in many cases nanotubes structures are not symmetrical. Native CNTs can be hence 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 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, hence their length: 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 are 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 approach, chemical bonds in CNTs comprise exclusively of sp^2 bonds of length $1.44 \cdot 10^{-10}$ m, which is slightly higher than 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 plane, 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, carbon nanotubes characterize with higher heat and electric conductivity as well as mechanical strength, while chemical and biological activity of their surface is much better (Dobrzańska-Danikiewicz *et al.* 2015).

The basic feature characterizing SWCNTs structure is its chirality, i.e., the method of rolling of single graphene sheet into a cylinder, which determines ca. optical properties of nanotubes. A chiral object characterizes with differences between its basic spatial structure and mirror reflection of this structure, what results in specific feature of such an object (Dobrzańska-Danikiewicz *et al.* 2015, Dresselhaus *et al.* 1998). There are also two types of achiral nanotubes, i.e., armchair and zigzag nanotubes (Ahmad *et al.* 2012, Balasubramanian and Burghard 2005). The names of a chiral structures reflect to the shape of the cross-section of a single ring of the hexagonal structure. The structure shape results from the way the graphene is rolled into a cylinder. As an example, one may imagine a sheet of paper rolled from its corner, which can be considered as one design, and a different design is obtained when the paper is rolled from its edge. Numerically, the chirality of nanotubes can be described using two parameters: chirality vector Ch and chirality angle θ . The graphical presentation of the dependence between the chiral vector Ch and the chiral

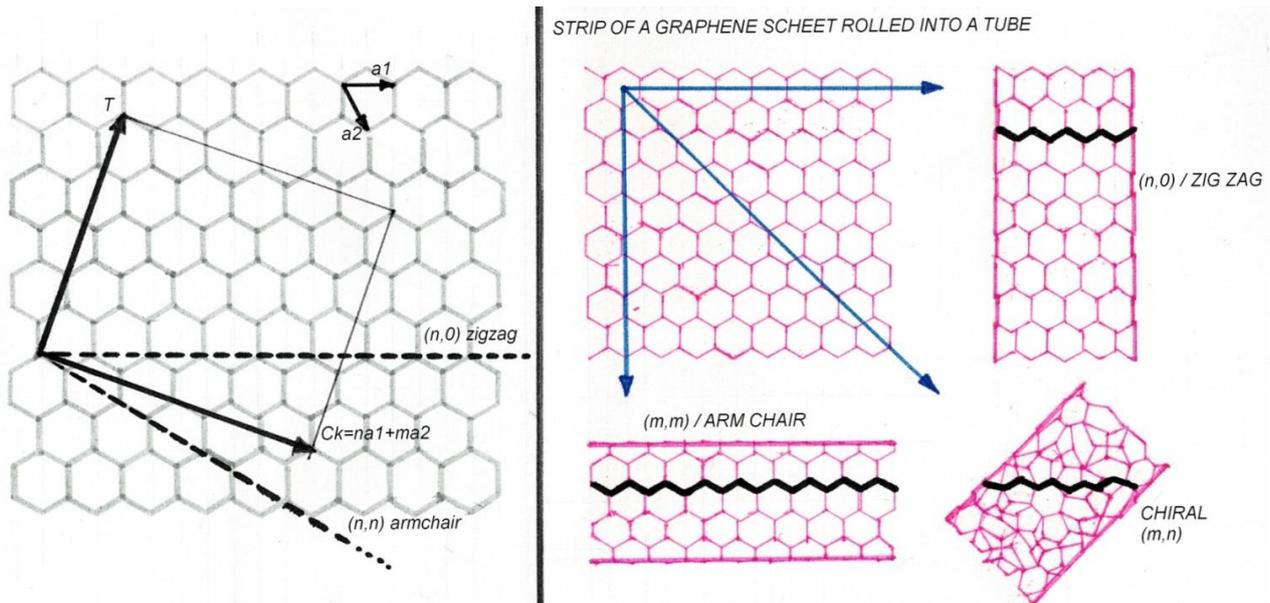


Fig. 2 (a) The scheme of 2-D hexagonal plane with chiral vector Ch , chiral angle θ and lattice vectors a_1 and a_2 , (b) three available structures of CNTs (Balasubramanian and Burghard 2005)

Table 1 The comparison of properties of SWCNTs and MWCNTs (Saifuddin *et al.* 2013, Mittal *et al.* 2015)

Property	SWCNTs	MWCNTs
Graphene layer	Single	Multiple
Synthesis	Difficult	Simple
Purity	Poor grade	High grade
Density (g/cm^3)	0.8	1.8
Heat conductivity ($\text{W}/(\text{m}\cdot\text{K})$)	6,000	2,000
Electrical conductivity (S/cm)	10^2 – 10^6	10^3 – 10^5
Thermal stability in air ($^\circ\text{C}$)	>600	>600
Electron mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	$\sim 10^5$	10^4 – 10^5
Outer diameter (nm)	<2	<2
Length (μm)	5-30	-
Specific surface area (m^2/g)	400-1,000	-

angle θ , as well as lattice vectors of a single graphene cell a_1 and a_2 are shown in Fig. 2a. In Fig. 2b different types of SWCNTs in regard to chirality and cross-section shape of a single cell of hexagonal structure are shown. The structural chiral vector of single-walled nanotube's is represented by a pair of indices (n,m) . The division of nanotubes in regard to these indices values is as follows (Ahmad *et al.* 2012, Dobrzańska-Danikiewicz *et al.* 2015): “

- $m = 0$ for all nanotubes “zigzag” structure is formed and ($\theta = 30^\circ$),
- $n = m$ for all nanotubes “armchair” is formed and ($\theta = 0^\circ$),
- when $n \neq m$ chiral nanotubes are formed and ($0^\circ < \theta < 30^\circ$).

The values of n and m indices, defining CNTs chirality, influence on optical, mechanical and electronical properties (Dresselhaus *et al.* 1998, Dobrzańska-Danikiewicz *et al.* 2015). For example, the type of CNT structure has a direct

effect on electrical properties, i.e., when $n - m$ is a multiple of 3, the nanotube is “metallic” (highly conducting), while in the rest of cases the nanotube is a semiconductor (Huczko *et al.* 2015). The armchair design is always metallic, while other designs can be either metallic or a semiconductor. Both armchair and zigzag nanotubes are mostly symmetrical in regard to the positioning of hexagonal rings towards the perimeter. Nevertheless, the chiral structure of the nanotube is mostly met.

The comparison of physical properties of SWCNTs and MWCNTs is shown in Table 1. 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 case of their usability in membrane separation.

2.2 CNT preparation

Technologies of CNTs preparation have to characterize with high capacity and ability to form nanotubes of defined length, diameter, number of walls and chirality. The most commonly used CNTs synthesis methods include laser ablation, electric arc discharge and chemical vapor deposition (Manawi *et al.* 2018, Scoville *et al.* 2019).

Laser Ablation is the method of nanotubes formation, which relies on evaporation of carbon atoms from a carbon disc using laser impulses of high temperature (ca.1,200 $^\circ\text{C}$) in argon atmosphere and at the presence of cobalt-nickel catalyst. During the synthesis, ca. 70-90% of carbon is converted into SWCNTs. The laser ablation method enables uniform evaporation and controlled growth conditions. The flow of gas, i.e. argon, transports carbon atoms outside the heating chamber on a cooled copper collector (Dresselhaus *et al.* 1998). The final mixture needs to be treated in order to separate CNTs and metals.

Arc Discharge Method is currently applied as CNTs

formation method based on carbon arc. (Dobrzańska-Danikiewicz *et al.* 2015). During the arc discharge, the carbon is evaporated from pure graphite and next it is deposited on the cathode surface. The process is run in argon or helium atmosphere. The optimal conditions for nanotubes growth are: high internal pressure, constant distance between the anode and the cathode and constant voltage between electrodes of ca. 20V. In general, by this method defectless or almost defectless SWCNTs and MWCNTs can be formed, while their type, size and orientation depend on buffering gas type, pressure in the chamber and metallic catalyst type. Due to the use of the latter, the final product needs to be purified by means of either oxidation, centrifugation, filtration or acidic treatment.

Both arc discharge and laser ablation methods involve the condensation of carbon atoms preceded by their evaporation. The temperature, in which the nanotubes' synthesis is carried out is close to graphite's sublimation temperature, what is the significant limitation of the transfer of these methods to the industrial scale, as such the scale processes need to reveal not only high capacity, but also low energy demand

Another method used to carbon nanotubes manufacturing is chemical vapor deposition (CVD) (Dobrzańska-Danikiewicz *et al.* 2015). The formation of CNTs by means of this method requires lower temperature, what results in lower costs and enables industrial scale implementation. As a substrate, simple hydrocarbons like ethylene or acetylene are used. The substrate is directed on a heated catalyst (made from iron, nickel or cobalt), which causes the decomposition of the hydrocarbon into carbon and hydrogen atoms. Carbon atoms cause the growth of nanotubes in the temperature 500-700°C, which may condensate perpendicularly to the surface forming so called forest, or tangled batches or thin or thick film. The form of the obtained deposit depends on CVD variety, type of substrate and process conditions. In general, CVD method is used to obtain large amounts of MWCNTs. The diameters of the nanotubes depend on the type of the catalyst applied, however they possess many defects, which results most probably from too low process temperature. Methane can also be used as a substrate for nanotubes production. In such the case, the process is carried out in the temperature range 900-1,000°C, while as a catalyst, the powdered nanosize iron oxide deposited on aluminum support is used. CVD method can be most easily applied for large scale nanotubes production. The variety of hydrocarbons available as substrates as well as different types of usable catalyst enable the formation of tubes of different length and width (Dai 2000).

The current trend of the research in the field of nanotubes preparation is the improvement of growth and final diameter control methods. From the commercial point of view, CNTs manufacturing methods should be economically adjusted, and the final costs of nanotubes production should be as low as possible.

2.3 CNT fictionalization

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 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 production of organic and inorganic composites, lowers the sorption of native CNTs (Ihsanullah *et al.* 2016a, b, c, Lee *et al.* 2016) and complicates membranes formation (Garzia Trulli *et al.* 2017). Low dispersity of CNTs appears mainly due to the presence of π - π bonds and Van der Waals interactions, which lead to the formation of short bond between nanotubes or their agglomerates (Vasilios *et al.* 2008). The tendency to bonds' formation increases with the decrease of graphene layers' number in a CNT structure (Bounos *et al.* 2017). During synthesis and purification, CNTs ends are often limited to a hemisphere shape as curvatures of fullerene type (Li *et al.* 2003). 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, waster transport, selectivity and contaminants removal (Oyetade *et al.* 2017, Ihsanullah *et al.* 2016c, Goh *et al.* 2013a).

The functionalization of SWCNTs and MWCNTs cover physical and chemical processes like vaccination, oxidation, coating or impregnation (Bahgat *et al.* 2011, Zhang *et al.* 2016, Raghavendra *et al.* 2017). Functional groups are attached to CNTs side walls, cores or ends forming covalent or non-covalent bonds. The oxidation actions toward native CNTs using HNO₃, H₂SO₄, HCl, H₂O₂, KMnO₄ and/or NaOCl are commonly used and result in introduction of oxygenated functional groups to CNTs structure (Rao *et al.* 2007, Ren *et al.* 2011). Despite chemical oxidation, oxygen plasma may also be used to introduce functional groups onto CNTs surface, hence no chemical wastes are generated. The modification of CNTs surface with metal oxides like MnO₂, Al₂O₃ or Fe₂O₃ is another method of functionalization, what widens the possibility of environmental CNTs use (Ihsanullah *et al.* 2016a, b, c).

The main aims of CNTs functionalization are elimination of dispersion and enhancement of 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 (Vasilios *et al.* 2008, Ihsanullah *et al.* 2016a, b, c). Oyetade *et al.* (2017), while investigating selective adsorption of Pb²⁺ and Zn²⁺ using MWCNTs functionalized with nitrogen have found that the ability of adsorption on f-MWCNTs significantly increases due to the increase of adsorption surface and active sites able to complex the investigated contaminants.

The recent researches have shown, that the f-CNTs adsorption ability depends on properties of introduced functional groups as well as adsorbates parameters (van Hooijdonk *et al.* 2013, Santhosh *et al.* 2016, Li *et al.* 2017). Wang *et al.* (2007) have found that the increase of acidity of MWCNTs favors sorption of polar compounds due to assurance of hydrophilic active sites, while it adversely

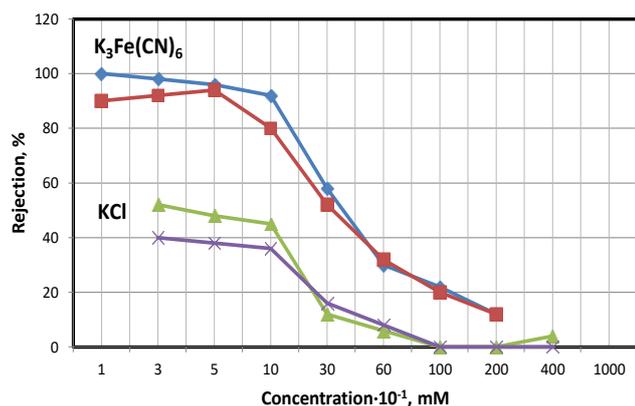


Fig. 3 The dependence of retention of $K_3Fe(CN)_6^{3-}$ and KCl on concentration using CNTs functionalized with $-COOH$ at the pores' entrance

affects the sorption of non-polar organic matter. Chen *et al.* (2009) have shown, that native CNTs possess higher affinity to adsorb non-polar functional groups than oxidized f-CNTs. The results of their research indicate that adsorption of polar compounds on f-CNTs is probably based on chemisorption, while adsorption of non-polar substances involves physicochemical interactions. Additionally, pH of a solution significantly influences of adsorption capacity of oxidized CNTs in regard to organic and inorganic contaminants as well as microorganisms. CNTs efficiently adsorb a variety of contaminants (zinc, cobalt, cadmium, microorganisms, etc.) at pH range 7-10, while the adsorption efficiency decreases with the pH decrease (Santhosh *et al.* 2016). The research performed by Fornasiero *et al.* (2008) have 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 for solutions with ions of higher valence, e.g. $Fe(CN)_6^{3-}$. For such highly charged ions retention can reach up to 100%, i.e., much more than in case of monovalent ions (e.g. KCl) (Fig. 3).

2.4 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 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/capacities of functionalized CNTs.

The production of SWCNTs is still very expensive, and the research in their field should focus on development of improved synthesis methods, which would allow for their manufacture in industrial scale (Ahmad *et al.* 2012). In comparison with other materials like soot, carbon fibers, clay or exfoliated graphite, CNTs' costs significantly limit their use as adsorbents and, in case of f-CNTs, materials suitable for 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

3. Carbon nanotube 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, Ihsanullah 2019, Ahn *et al.* 2012, Yan *et al.* 2018, 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.

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 characterize are relatively simple manufactures, however their capacity (i.e., water flux) is much lower in regard to freestanding membranes.

Nevertheless, CNTs based membranes are regarded as new generation of membranes of improved properties in regard to water and wastewater treatment, including membrane distillation (MD), pervaporation (PV) and gas separation (GS) processes. Hydrophobic and empty inside CNTs allow for fast transport of polar water molecules, thus CNTs based membrane characterize with much lower energy demand in regard to conventional membranes used in pressure and diffusive membrane processes.

3.1 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 membranes CNTs are randomly distributed in non-woven structure similar to paper (Sears *et al.* 2010, Kar *et*

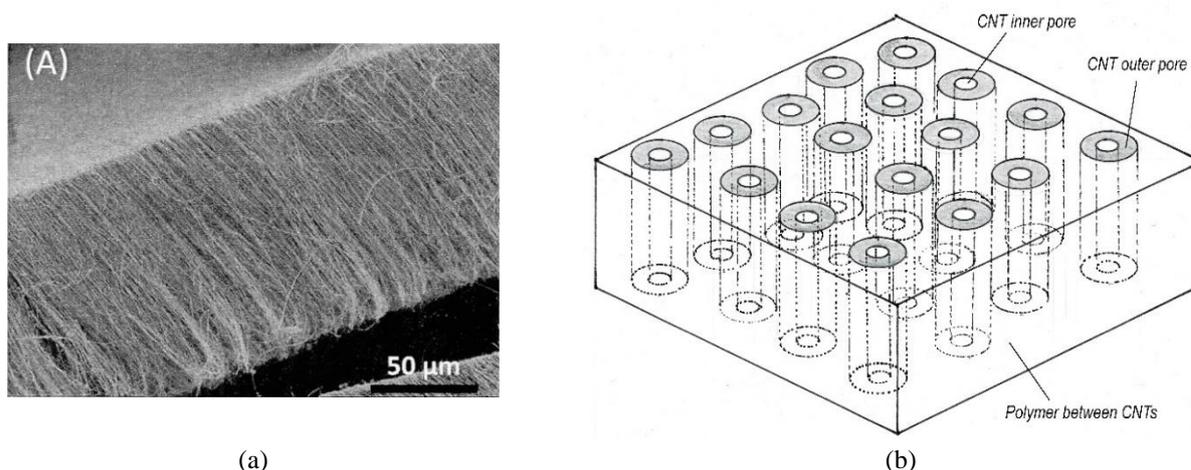


Fig. 4 (a) Scanning electron microscope (SEM) image of a vertically aligned array of CNTs obtained by means of Fe-catalysed chemical vapor deposition (CVD) process, (b) schematic illustration of the structure of an aligned CNT membrane (Hinds *et al.* 2004, Rashid and Raloh 2017).

al. 2012, Qu *et al.* 2013). The main advantages of such CNT membranes are the presence of very large porous 3D net and large specific surface.

3.1.1 VA-CNT membranes

The preparation of VA-CNT membranes relies on 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.4 the SEM image of freestanding VA-CNT membrane is shown together with the scheme of such the membrane arrangement (Rashid and Ralph 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 (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 introduction of 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). The modified membrane also characterized with higher biological resistance than the commercial UF membrane.

In Table 2 the properties of VA-CNT membranes prepared with the use of a variety of fillers are presented.

Water transport and retention of different substances revealed by VA-CNTs depend mainly on diameter and homogeneity of CNTs (Thomas and Mcgaughey 2009, 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 the 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

Table 2 The properties of VA-CNT membranes prepared with the use of different fillers

Substrate/ filler	Main properties	References
CNTs/ polyether-sulphone	<ul style="list-style-type: none"> 3 times higher water flux for VA-CNT membrane (~100 l/m²·h at 60 psi pressure) in comparison with the flux measure for a membrane prepared by simple mixing of PES and CNTs with random orientation and over 10 times higher than the flux measured for PES membrane 	Li <i>et al.</i> 2014
CNTs/ /polystyrene	<ul style="list-style-type: none"> High chemical separation potential Negligible interaction of ions with CNTs terminating caps Possible permeation of two different substances (ruthenium bipyridine [Ru-(bipy)₃²⁺] and methyl viologene [MV²⁺]) The fluxes of Ru-(bipy)₃²⁺ and MV²⁺ particles through CNT containing membranes were 9.57 and 21.05 (±2.32) nmol/h, respectively 	Hinds <i>et al.</i> 2004 Majumder <i>et al.</i> 2005
CNTs/styrene monomer/ polystyrene– polybutadiene (PS–PB) copolymer	<ul style="list-style-type: none"> Higher water flux revealed by CNTs/polymer membranes in refer to other composite VA-CNT membranes Calculated Young modulus for CNT/PS/PS–b–PB membranes in the range from 470 to 980 MPa 	Kim <i>et al.</i> 2014
CNTs/Si ₃ N ₄	<ul style="list-style-type: none"> Water flow of CNT based membrane >3 orders of magnitude higher than one calculated from Hagen–Poiseuille equation Pores (<2 nm) in CNT based membrane enhanced ion selectivity and water permeability. 	Holt <i>et al.</i> 2006
CNTs/epoxy resin	<ul style="list-style-type: none"> High water permeability 	Du <i>et al.</i> 2011
CNTs/PS/epoxy resin	<ul style="list-style-type: none"> Water flux ca. 3 times higher (1,100 L/m²·h·bar) than water flux measured for commercial UF membrane (477 L/m²·h·bar) Higher resistance to biofouling at ca. 15% flux reduction and ca 2 log lower bacteria adhesion than in case of conventional UF membrane 	Baek <i>et al.</i> 2014
CNTs/polyvinylidene fluoride (PVDF)	<ul style="list-style-type: none"> Water permeability measured for UF, CNTs containing membrane of thickness 1 mm - 30,000 L/m²·h·bar, while the flux measured for conventional UF membrane - 2,400 L/m²·h·bar. CNTs wall were found resistant toward biofilm creation, thus bacteria adhesion was impeded. CNTs based filter able to separate diesel oil and water. 	Brady-Estevez <i>et al.</i> 2008
CNTs/stainless steel mesh	<ul style="list-style-type: none"> Diesel oil flux - 4,692 kg/m²·h·Pa at 400 Pa and 8,415 kg/m²·h·Pa at 800 Pa, while water flux equal 0. At much higher pressure (1,820 Pa) water flux - 85.6 kg/m²·h·Pa. 	Lee and Baik 2010
CNTs/polyethylene imine	<ul style="list-style-type: none"> After functionalization degrades contaminating chemicals. 	Wang <i>et al.</i> 2013a
CNTs/Fe–Al ₂ O ₃	<ul style="list-style-type: none"> Pure water flux of VA-CNT and conventional UF membranes - 1,000 L/m²·h·bar and 400 L/m²·h·bar, respectively BSA retention increase from 71% to 90% (pH 7.4) due to modification using graft-polymerization method with methacrylic acid. 	Park <i>et al.</i> 2014

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, Kofinger *et al.* 2008, Hilder *et al.* 2009, Matsumoto *et al.* 2017). Even though molecular dynamics is often use to model of 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. Majumder *et al.* (2005) have experimentally confirmed, that water flux through VA-CNT (~10⁹–10¹⁰ tubes/cm², pores diameter ~7 nm) in no-permeable polysulphone matrix is 4 to 5 times higher than the value estimated using Hagen-Poiseuille equation.

Despite higher flux and efficiency of removal of different salts, VA-CNTs membrane reveal 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 micro-organism. 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 are 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).

3.1.2 Buckypaper CNT membranes

Within a membrane structure, CNTs may also be oriented horizontally and as such they form a layer for membrane

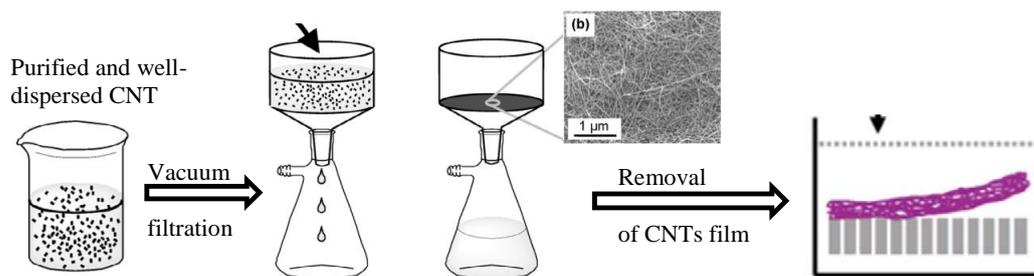


Fig. 5 The scheme of preparation of freestanding bucky-paper CNT membrane

filtration. Such the structural design for a membrane is called “bucky-paper” (BP) and comprises of CNTs randomly situated on a porous support. In BP membranes, CNTs are held 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 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). One of the most important stages of their preparation, however, 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 of 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. 5 the typical process of BP-CNT membranes manufacture together with SEM image of a surface of such the 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 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.

Mamedov *et al.* (2002) have prepared freestanding BP-SWCNT membranes using LBL techniques. The obtained membranes have characterized with high tensile strength (220 ± 40 MPa), which is several orders of magnitude higher than tensile strength of typical polymers.

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 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 and 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.

3.2 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 capacity of conventional membranes (mainly polymeric ones) and the development of alternative for freestanding CNT membranes, which have a tendency to agglomerate, what limits their wide application (Kang *et al.* 2007, Ajayan 1999). 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 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 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 (Yang *et al.* 2018, Bodzek *et al.* 2020a, c).

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

Due to difficulties related with preparation of membranes containing vertically oriented CNTs, many researchers have focused on 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.* 2016, Chan *et al.* 2012, Wu *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 next introduced to thin skin (separation) layer made from polyamide (Xue *et al.* 2016), what significantly influences on physico-chemical properties of membranes (such as hydrophilicity, porosity, charge density and additional water channels) (Yin and Deng 2015) and improves antifouling properties (Manawi *et al.* 2016).

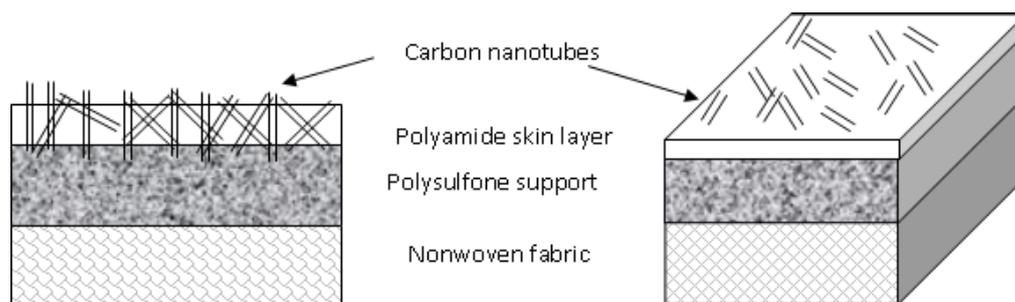


Fig. 6 The cross section of TFN membrane containing CNTs in the active layer

Modification of a membrane surface may be performed by direct imposition of the nano-material by means of 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 formation of TFN membrane (Yang *et al.* 2018, Kim *et al.* 2014, Shen *et al.* 2013, Wu *et al.* 2013, Park *et al.* 2010c, Wu *et al.* 2010a, Zhao *et al.* 2014, Zarrabi *et al.* 2016, Roy *et al.* 2011, Zhang and Chen 2011, Zheng *et al.* 2017, Inukai *et al.* 2015, Chang-chao *et al.* 2013). Preparation of membranes by introduction of 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). Modification of membrane surface requires relatively low amount of nano-material, what is economically beneficial and limits the impact of nano-material production on environment.

One of the most often used method 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 membrane preparation ultra-thin film formation is the most important (Adamczak *et al.* 2019). In Fig.6, 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 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 spread 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 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.

PA TFN membranes have been formed by immersion of polysulphone (PSf) substrates in piperazine (PIP) solution, and next solutions of MWCNTs-PMMA and trimesoyl chloride in toluene have been casted on the membrane's surface. As a result, an ultra-thin PA separation layer have been formed on PSf support due to interfacial reaction of TMC and PIP.

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 piperazine (PIP) aqueous solution in order to obtain TFN membranes via interfacial polymerization. The optimum concentration of MWCNTs have 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 characterized with better salt retention and stability in comparison with 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, polyethersulphone (PES) has been immersed in surfactant solution in order to increase pore size and hydrophilicity, while next CNTs functionalized with positive and negative functional groups have been filtered under vacuum through PES membranes. Finally, interfacial

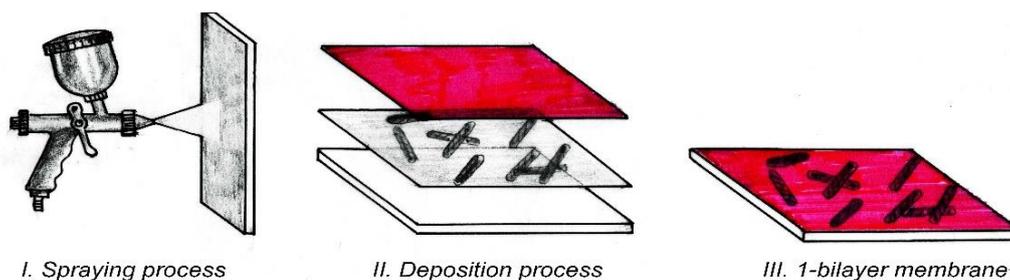


Fig. 7 The scheme of preparation of polyelectrolyte, multilayer membrane using spray-assisted layer-by-layer method (first layer: PSS/MWCNTs, second layer: PDDA), Liu *et al.* (2013)

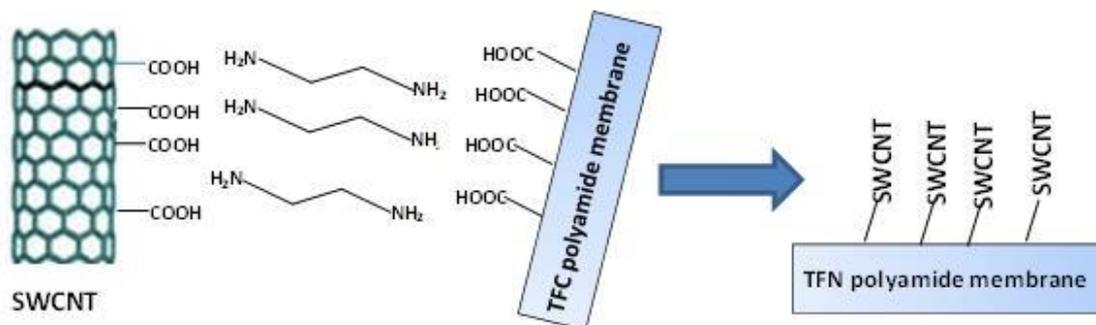


Fig. 8 The scheme of CNT immobilization on PA TFC membrane

polymerization between solution of methylene diamine (MPD) mixed with trimesoyl chloride (TMC) has been carried out on the surface of PS/CNTs membrane support. The obtained, CNTs base membranes have 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 have been uniformly distributed in ultrathin membrane skin layer.

Liu *et al.* (2013) have prepared PES/f-MWCNTs using spray-assisted layer-by-layer process. The negatively charged f-MWCNTs have been blended with poly(sodium 4-styrenesulfonate) (PSS), and next they have been deposited on 20 kDa PES substrate. Finally, positively charged poly(diallyldimethylammonium chloride) (PDDA) have also been sprayed onto first layer (Fig. 7) (Liu *et al.* 2013). The process has been repeated several times, hence several bi-layers of thin PSS/MWCNTs-PDDA film have been placed on PES support membrane. The first PSS/MWCNTs-PDDA layer has been 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 has 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 single-walled carbon nanotubes (SWCNTs). The prepared membranes have revealed excellent antimicrobial activity toward Gram-positive and Gram-negative bacteria (~80-90%), and they have exhibited ~2.5 logs virus removal efficiency. Moreover, the toxicity of PVK-SWCNTs has been tested

against fibroblast cells in order to evaluate possible application of these membranes for drinking water treatment. The results have not demonstrated any toxic effect of PVK-SWCNTs to fibroblast cells, while in case of pure SWCNTs it has been completely opposite (100%).

Tiraferri *et al.* (2011) have demonstrated the novel methods for functionalized with carboxylic group CNTs' immobilization on polyamide membrane skin layer, which involve strong covalent bonding (Fig. 8). Before modification, CNTs had been functionalized with carboxylic groups and next carboxylic groups of polyamide thin layer have been 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). 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 SWCNTs to minimize the onset of membrane biofouling during operation.

3.2.2 Modification by introduction of nano-material to polymeric membrane matrices

Membranes made of polymeric materials, especially of aromatic polyamides, but also of cellulose acetate, nylon, polyvinylidene fluoride, polysulphone, sulphonated polyether and non-polymeric materials (ceramic, metals) and their composites are used to filtrate of different solutions (Madhura *et al.* 2018, Bodzek 2019). The introduction of carbon nano-materials to polymeric membrane matrix influences on its structure and antibacterial properties as well as affects hydrophilicity, retention and mechanical strength (Daraei *et al.* 2013, Zhang *et al.* 2013, Ganesh *et al.* 2013, Aba *et al.* 2015, Chung *et al.* 2017, Lee *et al.* 2013, Yu *et al.* 2013, Xu *et al.* 2014, Zhao *et al.* 2013a, b).

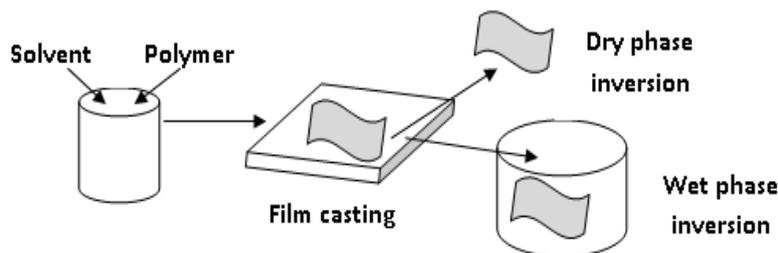


Fig. 9 The idea of preparation of polymeric membranes using phase inversion method

The method which is the most often used to introduce CNTs to polymeric membrane matrix is phase inversion process (Arockiasamy *et al.* 2012, Choi *et al.* 2006, Celik *et al.* 2011, Wu *et al.* 2010b, Brunet *et al.* 2008, Majeed *et al.* 2012, Shah and Murthy 2013, Yin *et al.* 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.

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.

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. 9). Among them, immersion precipitation is the most widely-used for polymeric membranes preparation. In refer to conventional membranes (without nano-material), surfaces of modified membranes characterize with denser pore structure, which results of 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 preparation of ultrafiltration or microfiltration membranes.

Zhang *et al.* (2013) have combined GO with oxidized carbon nanotubes (CNT) to modify ultrafiltration 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. The different ratios of GO and MWCNTs mixtures in total amount of 1 % wt. (mass of low-dimensional carbon materials/mass of polymer) have been first introduced into DMAc solvent, then the solution has been sonicated and next PVP (1 g) and PVDF (15 g) powders have been added. The casting solution has been next spread onto a clean glass plates with 200 μm gap and then immersed into coagulation bath (distilled water) for 30 min. The obtained membranes have been rinsed with distilled water before ultrafiltration tests. The presence of long and curled CNTs has allowed to prevent GO

aggregation, due to their tendency to bind with neighboring 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, water flux of GO-CNTs modified membranes in weight ratio equal 1:1 has increased by 252% in comparison with PVDF reference membrane.

Wu *et al.* (2010b) have prepared composite UF membrane by introducing MWCNTs to brominated poly (phenyl oxide) (BPPO) using wet phase inversion method with N-methyl-2-pyrrolidone (NMP) as a solvent and water as a coagulant. MWCNTs have been added to BPPO solution and the mixture has been sonicated. The obtained solution has been spread on a clean glass plate. Coagulation/precipitation of membrane has run in deionized water (DI) at 30°C for at least 24 hours in order to completely remove solvent and merge the formed membrane 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 has been prepared in N-methyl-2-pyrrolidone (NMP) and mixed with PSf. The prepared MWNTs/PSf blend membranes have been characterized with the use of a number of analytical methods, which included Fourier transform infrared (FTIR) spectroscopy, contact angle, scanning electron microscopy (SEM) and permeation tests. The surface of the MWNTs/PSf blend membranes has been found to be more hydrophilic than in case of pristine PSf membrane, because of the hydrophilic character of MWNTs. The morphology and permeation properties of the blend membranes have depend on the amount of MWNTs used. The pore size of the blend membranes has increased along with the contents of MWNTs up to 1.5%, in their content range 1.5-4% it has decreased, and at 4.0% of MWNTs, it has been smaller than pore size of pristine PSf membrane, but measured flux and rejection have been higher than ones measured for PSf membrane without MWNTs.

Brunet *et al.* (2008) have examined PSf ultrafiltration membranes prepared using carbon nanotube/polymer nanocomposites, according to the wet phase inversion method. The characteristics of membranes has covered surface roughness, contact angle, permeability and mechanical properties. A partial disaggregation of nanotubes has resulted in the appearance of individual nanotubes within the polymeric matrix, while some small

aggregates have nested in membrane's pores. The addition of MWCNTs (4wt.%) has not caused any disturbances in asymmetric membrane structure as well as in permeability and hydrophobicity, while the roughness of the membrane has increased. Surprisingly, the tensile strength of the composite membrane has not been improved, in opposite to expectations, while the elongation to failure has decreased because of insufficient nanotubes dispersion. The antibacterial effect has also been tested with two different methods, and neither of them has 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 synthesized the novel C/P membranes using phase inversion method, which have been next characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and contact angle measurements. 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 MWCNTs 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 7mgC/L, C/P blend membranes have shown higher flux and lower affinity to fouling than PES membranes. The filtration experiments have been followed by foulants desorption. It has been found that the amount of foulant desorbed from PE 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 preparation of polymer-nanotube composites have been made by mixing both, the nanotubes and a polymer in a suitably selected solvent, which has next been evaporated to obtain a composite film (Kilbride *et al.* 2002, Cadek *et al.* 2002, 2004, Coleman *et al.* 2004, Dalmás *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 of 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 has been prepared by dissolution and mixing of both polymers (1:1) in tetrahydrofuran at

room temperature. Modified MWCNTs (0.01-0.1wt.%) have been 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 have been dispersed in DMAc with ultrasounds, and next benzoyl peroxide has been added to the solution in order to improve dispersion and to assure better homogeneity of MWCNT's-PA solution. The obtained solution has been 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 has been 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%.

3.3 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 continuously develop and face a series of issued. Among the latter ones, one has to mention:

- 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 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 manufacture 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 on 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 losses and leakage to 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 ecotoxic effect of such membranes (Tiede *et al.* 2009).

The combination of CNTs based membranes with other separation and treatment techniques like catalysis, adsorption and electrochemistry 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 as well as freestanding and composite CNTs membranes' properties. If currently defined issues are properly addressed, the capacity of CNTs containing membranes will also improve. Further research should also be focused on standardization of CNTs membranes manufacture methods, what will simplify commercialization of membranes dedicated to water and wastewater treatment at industrial scale/

4. The application of CNTs containing membranes in water and wastewater technology

4.1 Desalination

Water desalination is crucial technical solution dedicated to replenishment of fresh water at desert and coastal areas and in all regions with poor fresh water resources (Goh *et al.* 2016b, c). Conventional desalination methods, mainly RO and NF, cannot be widely applied due to high energy demand and costs (Yang *et al.* 2013a). In recent years a number of research on development of novel desalination techniques (Greenlee *et al.* 2009, Goh and Ismail 2015, Wang *et al.* 2017), i.e., membrane 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 diffusive 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 (Berezhkovskii and Hummer 2002)

4.1.1 Desalination with the use of high pressure driven processes

As it is discussed earlier, transport simulation models widely used in the research on water and salts transport in CNTs channels have shown, that water particles chain permeates fast and frictionless through hydrophobic core of CNTs (Ansari and Kazemi 2012, Hummer *et al.* 2001) due to formation of hydrogen bonds in the chain. A single chain of water particles (i.e. a series of water particles arranged in the form of a wire) may achieve high flow rate through CNTs of diameter as small as 0.83 nm if only proper pressure conditions are assured. Another important structural

Table 3 The efficiency of salt retention and flux of VA-CNT membrane (CNTs density CNT = $2,5 \times 10^{11} / \text{cm}^2$) based on molecular dynamic simulations (process parameters: TMP = 5.5 MPa, osmotic pressure = 2.4 MPa)

Rolled up index	Internal dia-meter (nm)	Retention (%)	Permeate flux ($\text{L}/\text{m}^2\text{h}$)	Improvement coefficient ^a
(5,5)	0.32	100	66.7	2.42
(6,6)	0.49	100	112.5	4.21
(7,7)	0.59	95	175.0	6.39
(8,8)	0.75	58	270.8	9.76

^aImprovement coefficient calculated in regard to commercial RO FILMTECH SW30H4-380 membranes

Table 4 Technical achievements reached by different CNTs membrane types

CNT membrane	VA-CNT membrane	Composite CNT membrane
Water flux, $\text{L}/\text{m}^2\text{-h-bar}$	10-15	4-6
Salt retention	BWRO ^b	BWRO ^b
Anti-fouling properties ^c	N.A.	30%
Type of membrane module	Frame plate (ab. 1m^2)	Spiral(8 in.)

^aAssumptions: for both CNT membranes inner diameter of CNT were 1 nm and pore density - $2,5 \times 10^{11} \text{ CNT}/\text{cm}^2$ (Holt *et al.* 2006), ^bSalt retention 93% at pressure 0.5–3.0 MPa, ^cBiofouling reduction brings high energy efficiency

feature, which is exhibited by CNTs as favorable water desalination material is the ability to retain dissolved salts. The research show, that CNTs diameter plays a 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 3) (Hoon *et al.* 2012). In general, molecular dynamics simulation carried out for VA-CNT membranes which possess the desalination capability comparable with RO membranes show that internal diameter of CNTs should be ca 0.6 nm (Hoon *et al.* 2012). However, currently available technologies do not allow for 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 particles 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 is found to decrease with the increase of ions concentration in aquatic solution. Fornasiero *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 and this tendency corresponds to Donnan equilibrium theory. By the increase of surface charge of a CNT membrane one may exclude

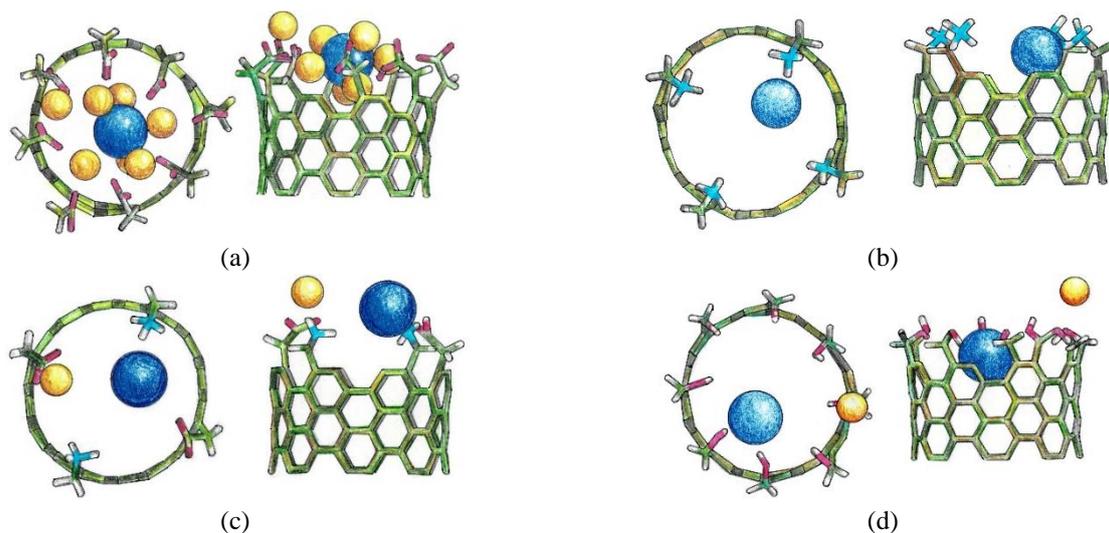


Fig. 10 Pictures illustrating functionalized CNTs pores entrances according to molecular dynamics simulations: (a) COO^- , (b) NH_3^+ , (c) combination of COO^- and NH_3^+ , and (d) OH^- (Corry 2011)

Table 5 The application of CNTs based membranes in water desalination

Materials	Feed/Operational conditions	Efficiency	Reference
CNTs-Cu nanolayer	Brackish water	The efficiency improvement with the increase of CNTs amount in the composite.	Park <i>et al.</i> 2014
Carboxylated CNTs	NaCl solution of concentration 3.4%	Stable membrane operation during long term operation. Water flux: 19.2 kg/m ² ·h	Bhadra <i>et al.</i> 2013
MWCNTs	KCl solution	Retention mechanism: electrostatic interactions between membrane charge and ions.	Fornasiero <i>et al.</i> 2008
CNTs	Saline water	CNTs increase membrane's surface porosity and hydrophilicity of surface and its permeability	de Lannoy <i>et al.</i> 2013
CNTs of zwitterionic structure	Saline water	High water flux and salt retention. Significant resistance to biofouling.	Chan <i>et al.</i> 2013
MWCNTs oxidized with HNO_3 and H_2SO_4	Saline water	Max. % separation was achieved at highest salt concentration in feed water	Tofighy <i>et al.</i> 2011
0.1% MWCNT/polyamide (PA)	NaCl solution (2,000 ppm, pH 7, 25 °C, TMP 16 bar)	Water flux: 28.05 L/m ² ·h, NaCl retention >90%	Zhao <i>et al.</i> 2014
MWCNT/PA aromatic (15 mg MWCNT/gPA)	NaCl solution (4,000 ppm and 20 °C, TMP 3.9 MPa)	Water flux: 0.71 L/m ² h bar, NaCl retention: 76%	Shawky <i>et al.</i> 2011
0.1% MWCNT/polyamide (PA)	NaCl solution (2,000 ppm, 25 °C, TMP 1.6 MPa)	Water flux: 71 L/m ² ·h, Retention: 98%	Zhang <i>et al.</i> 2011
PES/0.45% MWCNT	Na_2SO_4 , MgSO_4 and NaCl solutions (200 ppm, TMP 4 bar, pH = 7.0, 25°C)	Pure water flux: 23.7 L/m ² ·h, Salts retention: Na_2SO_4 - 65%, MgSO_4 - 45% and NaCl-20%	Vatanpour <i>et al.</i> 2014

even sodium ions, even though they diameter us 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 (Vatanpour *et al.* 2017), including better selectivity toward anions and cations (Joseph *et al.* 2003). It has been found, that CNTs functionalized with both, positive and negative functional groups, as for example $-\text{COO}^-$ and $-\text{NH}_3^+$ 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. 10) (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 case of CNTs due to the decrease of neutral and smooth internal structures of modified nanotubes in comparison with non-modified ones. Still f-CNTs characterize with significantly higher water fluxes than commercially available polymeric desalination membranes.

In Table 4 the summary of technical achievements in regard to efficiency reached by different CNTs membrane types 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 measured for brackish water (BW) RO

Table 6 The review of research on water desalination with the use of f-CNT membranes

Salt type	CNT membranes			CNTs share g/cm ² or %wt./cm ²	Removal mechanism	Additional remarks	Reference	
	Membrane type	^a R (%)	Matrix					^b IC
NaCl	E-CNTs	99%	PVDF	35000 mg/L	2g/9.3 cm ²	Chemical interactions	Very high water permeability.	Lee <i>et al.</i> 2017
	Amine-functi onalized MWCNTs	20%	PES	200 mg/L	0.045 wt.%/19.6 cm ²	Electrostatic interaction Donnan effect	Strong BSA antifouling properties, high flux and NaCl retention.	Vatanpour <i>et al.</i> 2014
	COOH-MW CNTs	> 90%	PSf	584 mg/L	2% w/v/18.1 cm ²	Electrostatic interaction Complexation	Strong antifouling and antioxidative properties.	Zhao <i>et al.</i> 2014
	COOH-MW CNTs	98.5%	Poly-amide	2000 mg/L	0.025%/36 cm ²	Surface complexation	Very high water permeability and BSA antifouling properties.	Vatanpour and Zoqi 2017
	Oxidized CNTs	> 98%	PSf	2000 mg/L	0.4g/3.3×68 cm ²	Surface complexation, electrostatic interaction	Excellent DOM antibiofouling properties.	Kim <i>et al.</i> 2014
	Acid modified MWCNTs-n Ag	88.1%	PSf	2000 mg/L	5.0wt%/0.01764 cm ²	Chemical interactions	High permeability and retention and antibiofouling properties.	Kim <i>et al.</i> 2012
	Sulphonated MWCNT-O H	96.8%	PES	1000 mg/L	1g/12.56 cm ²	Electrostatic interaction/ Donnan effect	Strong NOM antifouling properties.	Zheng <i>et al.</i> 2017
Na ₂ SO ₄	PMMA-MW NTs	>99%	PSf	2000 mg/L	0.67g/19.62 cm ²	N/A	Significantly increase in selectivity and permeability.	Shen <i>et al.</i> 2013
	Amine-functi onalized MWCNTs	65%	PES	200 mg/L	0.045 %wt./19.6 cm ²	Electrostatic interaction/ Donnan effect	High water flux and Na ₂ SO ₄ retention, strong BSA antifouling efficiency.	Vatanpour <i>et al.</i> 2014
	f-MWCNTs- nAg/TFN	95.6%	PSf	2000 mg/L	5.0 wt.%/0.01764 cm ²	Chemical interactions	Antibiofouling properties. High salt retention and water flux.	Kim <i>et al.</i> 2012
MgSO ₄	amine-functi onalized MWCNTs	45%	PES	200 mg/L	0.045wt%/19.6 cm ²	Electrostatic interaction/Donn an effect	High water permeability and strong BSA antifouling properties.	Vatanpour <i>et al.</i> 2014

^aR – efficiency of salt rejection,%. ^bIC - initial concentration, mg/L. N/A represent not available

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 time higher than the flux of BWRO membranes (Ratto *et al.* 2010).

The main advantage of CNTs membranes is low affinity to fouling in comparison with commercial RO and NF membranes. CNTs nanoparticles cause inactivation of bacteria cells by attacking their cellular walls (Kang *et al.* 2007, Li *et al.* 2008a). In refer to MWCNTs, SWCNTs (or DWCNTs) reveal better antifouling and antibiofouling efficiency and decrease the surface available for bacteria growth (Jia *et al.* 2005, Rodrigues and Elimelech 2010), when compared with commercial NF and RO membranes. The next feature of CNTs 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 Tables 5 and 6 the summary of results of research on water desalination with the use of SWCNTs and MWCNTs membranes is given.

Pendergas and Hoek (2011) have presented theoretical prognosis for VA-CNT and RO membranes application in desalination (Fig. 11a) using data available for VA-CNT and popular saline water (SW) RO membranes. The X-axis represents fractional CNTs content in the membrane at maximum CNTs density equal ca. 2.5×10¹¹/cm² established on the basis of several transmission electron microscopy (TEM) images, while the Y axis shows average water permeability and the highest value (4 times higher) is exhibited by CNTs of (6,6) type (Corry 2008). Moreover, if functionalization of CNT is applied, the high retention at simultaneous high water flux can be obtained (Fig. 11b). Hence, it may be concluded that the application of CNTs membrane as an alternative for conventional RO membranes in water desalination is advantageous due to potential overcome of limits of conventional water treatment systems (Cohen-Tanugi and Grossman 2012, Müller 2013).

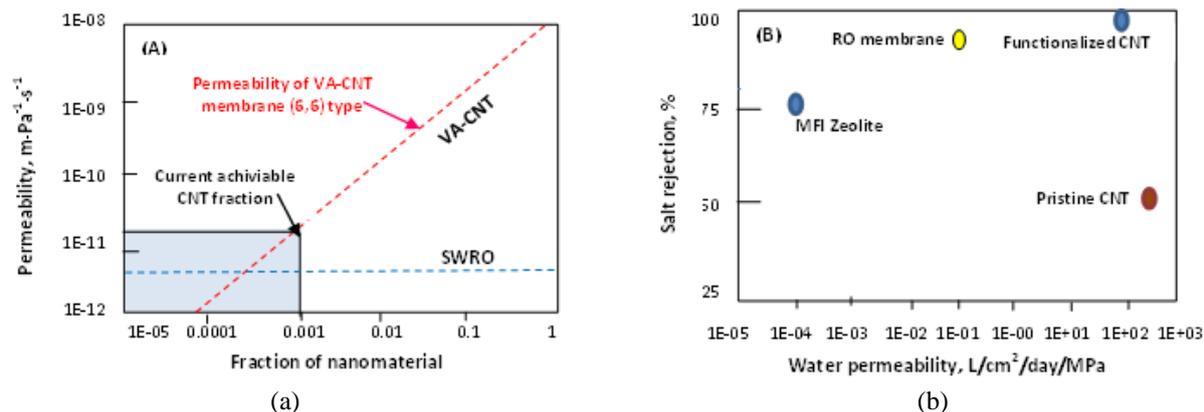


Fig. 11 (a) Simulation of VA-CNT performance in comparison with currently applied polymeric (P) SWRO, (b) capability of functionalized CNTs and conventional membranes

4.1.2 Desalination with the use of diffusive membrane techniques

Forward osmosis (FO) is novel desalination technology of promising prospective and low energy demand (Voutchkov 2018). FO, however, possesses some disadvantages related with manufacturing of membranes of high capacity and minimal internal concentration polarization (Wang *et al.* 2013b). The internal concentration polarization in FO process is caused by diffusion of salt to porous membrane support, what results in significant decrease in permeate flux (Zhao and Zou 2011). Hence, researches on the introduction of CNTs to membranes used in FO process are carried out and they are focused on the increase of capacity and decrease of internal concentration polarization, including simulation research (Jia *et al.* 2010) and experimental investigations (Wang *et al.* 2013b, Amini *et al.* 2013, Dumée *et al.* 2013, Goh *et al.* 2013b). The experimental research on the use of conventional polyamide (TFC) FO membranes modified with MWCNTs functionalized with amine group (0.01-0.1wt.%) by means of interfacial polymerization have been run (Amini *et al.* 2013). It was observed that introduction of less than 0.1wt.% (optimum 0.05wt.%) of MWCNTs to nano-composite FO membrane resulted in 2.5 times higher permeate flux from $35.7 \text{ L}/\text{m}^2\text{h}$ for TFC membrane to $96.7 \text{ L}/\text{m}^2\text{h}$ for TFN membrane. It can be assumed that MWCNTs form nanochannels, which enhance water permeability, which functionalization with amine increases membrane's hydrophilicity (Amini *et al.* 2013).

Goh *et al.* (2013b) have made glass fiber membranes with polyethyleneimine-poly(amide-imide), which contained MWCNTs immobilized within membrane structure using vacuum filtration. The results of tests on the membrane use in FO have showed, that modified membranes reached the flux of $13.4 \text{ L}/\text{m}^2\text{h}$, which was 44% higher than flux measured for membranes, which did not contain MWCNTs.

Dumée *et al.* (2013) have manufactured TFN FO membranes using interfacial polymerization method. The membranes comprised of a dense polyamide layer (PA) on self-supporting bucky-papers (BP) made from CNTs functionalized with hydroxyl groups. The obtained, hydrophilic support characterized with low water contact angle ($<20^\circ$), higher water uptake capacity (17 wt.%) and

large porosity ($>90\%$), what made them a promising material in comparison to polysulphone (PSf) support commonly used as a support in RO TFC.

In opposite to high pressure driven membrane desalination techniques, i.e., NF and RO, direct contact membrane distillation (DCMD) characterizes with a potentially low energy and high rejection route to the desalination of highly contaminated or saline waters. However, membranes, which are currently used in MD, synthesized from polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF) are not sufficiently porous, exhibit low flux and are more expensive than membranes dedicated to RO. Hence, it is important to seek for alternatives either techniques or modification enabling the improvement of process efficiency, especially in the field of membranes properties and structure. It has been found that nanocomposite or bucky paper CNT membranes characterize with high desalination efficiency when applied in MD process, what has been confirmed by laboratory scale research (Khalid *et al.* 2015, Zarrabi *et al.* 2016, Dumée *et al.* 2010).

Dumée *et al.* (2010, 2011) have prepared bucky-paper (BP) and composite membranes containing CNTs, and they used them in MD process. Self-supporting BP-CNT membranes have been prepared by means of vacuum filtration through $0.2 \mu\text{m}$ polyethersulphone (PES) support followed by flaking of the imposed layer. The obtained membranes have characterized with high porosity (90%), hydrophobicity (contact angle 113°), heat flux ($2.7 \text{ kW}/\text{m}^2\text{h}$), salt retention equal 99% and distillate flux $12 \text{ kg}/\text{m}^2\text{h}$ (seawater $35 \text{ g NaCl}/\text{L}$). In comparison with polytetrafluoroethylene (PTFE) membranes, the porosity was 20% higher, but salt retention and flux were the same (Dumée *et al.* 2010). On the other hand, composite CNT membranes have exhibited higher stability, capacity and salt retention than freestanding BP membranes. Bhadra *et al.* (2013) have used MWCNTs functionalized with $-\text{COOH}$ groups to prepare freestanding CNT membrane dedicated to membrane distillation (MD). The use of functionalized MWCNTs with increased polarity and interaction between membrane surface and water vapor, what resulted in the increase of capacity of MD based desalination. Distillate flux equal $19.2 \text{ kg}/\text{m}^2\cdot\text{h}$ measured for MWCNT membrane

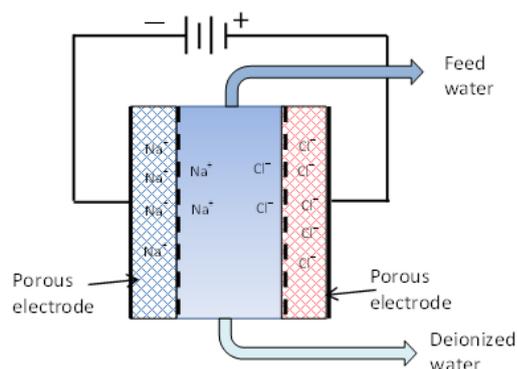


Fig. 12 An illustration of capacitive deionization device

was higher than the flux obtained for conventional PVDF membranes.

CNTs allow also for the improvement of transportation and separation properties of membranes used not only in RO, FO or MD, but they also are used in desalination processes, which are based on electrochemical methods, especially in capacitive deionization (CDI). CDI is the water deionization technology, in which electrical potential difference is applied over two electrodes often made of porous carbon. Such the arrangement makes anions (negatively charged ions) to be removed from water and stored in positively polarized electrode (anode). Similarly, cations (positively charged ions) are stored in negatively polarized electrode (cathode) (Anderson *et al.* 2010). The CDI experiments, the apparatus consists of two electrodes, which for a capacitor across which the voltage enabling the adsorption of ions of opposite polarity from the treated water is applied (Fig. 12). When the applied potential is reversed, the adsorbed ions are released in the form of concentrated brine solution. Physical properties of electrodes used to ions adsorption significantly influence on CDI process dynamics (Anderson *et al.* 2010). The electrodes materials needs to characterized with large surface to enable accumulation of ions, high electrical conductivity and capacity and reasonable porosity guaranteeing adsorption of ions in electrodes structure (Anderson *et al.* 2010, Pan *et al.* 2009). It has been shown that carbon based materials characterize with such properties and has been proved to be used for future CDI applications as electrodes in the form of carbon aerogels (Xu *et al.* 2008), carbon plates (Hou *et al.* 2012) or carbon nanotubes (Pan *et al.* 2009, Liu *et al.* 2014, Hou *et al.* 2014, Wimalasiri and Zou 2013, Yan *et al.* 2012). It is very importing considering that CDI is regarded as potential, energy efficient technology for brackish water desalination and serious alternative for RO and distillation. The main difference between these processes relies on the fact that CDI extract salts ions from the solution, while RO and distillation extract water.

In literature, several polymeric composite materials, which contain CNTs or other nanomaterials, are discussed in regard to their use in CDI process. Such materials are found to improve CDI electrodes conductivity, pores volume, mesoporosity (pores sized 5-20 nm), ions electrosorption, desalination effectiveness, efficient and fast

desorption of ions and, finally, energy consumption (Pan *et al.* 2009, Liu *et al.* 2014, Hou *et al.* 2014, Wimalasiri and Zou 2013, Yan *et al.* 2012). The most of results indicates that addition of CNTs to polymers or other electrodes-forming materials based on carbon nanostructure offers promising opportunities for CDI process.

Wimalasiri and Zou (2013) have investigated the capacity of CDI with the use of SWCNTs containing electrodes combined with graphene nanosheets. The composite SWCNT-graphene electrode has characterized with more beneficial properties than electrodes, which contained only graphene sheets. The placement of SWCNTs between graphene nanosheets has created diffusion channels, which enhanced ions transport, increased pores density, created mesopores network, increased electrode conductivity and, in overall, allowed to achieve high efficiency of salts removal up to 98%.

In another research, Hou *et al.* (2014) have prepared MWCNT/poly(vinyl alcohol) composite (MW-CNT/PVA) further used as electrode for CDI. The obtained results have shown, that in comparison with electrodes made from active carbon, SWCNT/PVA composite exhibited two times higher electrosorption capacity, larger surface for ions electrosorption and lower energy consumption. Similar CDI electrodes improvements have been made by combining conductive polymer, specifically polypyrrole with CNTs, what gave the composite CNT/polypyrrole of increased adsorption capacity in comparison with one of only CNT (Wang *et al.* 2014). Yan *et al.* (2012) have combined polyaniline with SWCNTs and observed the improvement in mesopores volume and electrochemical properties of composite in regard to materials made only from polyaniline or only SWCNTs, while the capacity of salt rejection increased by 12% in comparison with SWCNTs electrode.

Liu *et al.* (2014) and Li *et al.* (2008b) have proposed the introduction of CNTs to polymeric, ion exchange membranes in order to use them in CDI process. Ion exchange membranes prevent the attraction of counter-charged ions to electrodes during their regeneration. Liu *et al.* (2014) have combined CNTs electrodes with anionic polymer – diallyl-dimethyl-ammonium chloride (DADMAC) – and with cationic polymer – polyethylene imine and investigated the effectiveness of the developed membranes. The results of tests have indicated on the improvement of mesoporosity and microstructure of CNT layer. The ion-exchangeable polymeric fraction of the composite membrane allowed for the salt removal efficiency increase up to 93% in comparison with 25% established for electrodes made only from CNTs.

4.2 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 7). The large adsorption capacity in regard to inorganic substances revealed by f-CNTs is related with large specific surface and highly porous and empty structure of nanotubes as well as functional groups presence on CNTs surface and favorable

Table 7 The summary of selected research on removal of heavy metals and arsenic with the use of f-CNTs and F-CNTs containing membranes

Metal type	Membrane/adsorbent containing CNTs			Removal mechanism	Comments	Reference	
	Nanomaterial type	R, AC	C ₀				
As(III)	MWCNT-ZrO ₂	2mg/g	0.1mgL ⁻¹	100mg/10mL	Chemisorption/ Physical sorption	As (III) adsorption capacity is not related with pH.	Ntim and Mitra 2012
	MWCNT-Fe ₂ O ₃	1.73mg/g	0.1 mgL ⁻¹	10mg/10mL	Electrostatic interaction	Adsorbents for water treatment.	Ntim and Mitra 2011
As(V)	MWCNT-ZrO ₂	5mg/g	0.1 mgL ⁻¹	100mg/10mL	Chemisorption/ Physical sorption	As(V) adsorption capacity is not related with pH.	Ntim and Mitra 2012
	MWCNT-Fe ₂ O ₃	0.18mg/g	0.1 mgL ⁻¹	10mg/10mL	Electrostatic interaction	MWCNTs modification can be used to preparation membranes/ adsorbents for water treatment.	Ntim and Mitra 2011
Cr(III)	CNTs modified with acid	0.5 mg/g	1 mgL ⁻¹	120,000 mg/500mL	Electrostatic interaction	Cr removal efficiency increase with CNTs amount increase.	Atieh <i>et al.</i> 2010
Cr(VI)	Functionalized MWCNTs	95%	0.1 mgL ⁻¹	100mg/10mL	Ion exchange, Diffusion	Cr(VI) regeneration can be achieved in alkaline environ.	Pillay <i>et al.</i> 2009
Pb(II)	Oxidized MWCNTs	95 %	10 mgL ⁻¹	3,000mg/100mL	Chemical, electrostatic, hydrophobic and π - π interactions	High efficiency of heavy metals ions removal from wastewater.	Li <i>et al.</i> 2011
Cd(II)	Functionalized MWCNTs	> 85%	100 mgL ⁻¹	1,000mg/4mL	N/A	Excellent capacity of heavy metals removal.	Wang <i>et al.</i> 2012
Zn(II)	Functionalized MWCNTs	99%	1.1 mL ⁻¹	90mg/100mL	Electrostatic interaction	The possibility of the use in heavy metals removal.	Mubarak <i>et al.</i> 2013
Cu(II)	Functionalized MWCNTs	97%	100 mgL ⁻¹	1,000mg/4mL	N/A	Excellent capacity of metals removal.	Wang <i>et al.</i> 2012
Co(II)	Oxidized MWCNTs	70 mg/g	1,200 mgL ⁻¹	50mg/25mL	Chemical interactions	Promising material for removal of heavy metals.	Tofighy and Mohammadi 2011
Ni(II)	Oxidized MWCNTs	49.26 mg/g	10-200 mgL ⁻¹	20mg/50mL	Electrostatic interaction	Greater adsorption ability than raw MWCNTs in water.	Kandah and Meunier 2007

AC - adsorption capacity of a contaminant % and mg/g, R – percentage removal efficiency, C₀ – initial concentration

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 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 research have shown that the ability of heavy metals adsorption on f-CNTs is usually higher than in case of non-functionalized CNTs. Usman *et al.* (2017) have stated that high adsorption of metal ions exhibited by CNT membranes functionalized with for example 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 (Lu and Chiu 2006) (Fig. 13). In general, cations adsorption is better at alkaline pH

due to increase negative charge density of f-CNTs surface and at acidic pH the removal of contaminants is not satisfactory (Ihsanullah *et al.* 2016a, b, c). Vuković *et al.* (2010), while investigating removal of Cd from aqueous solution with the use of MWCNTs functionalized by oxidation of ethylene diamines addition have found that 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 on 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.

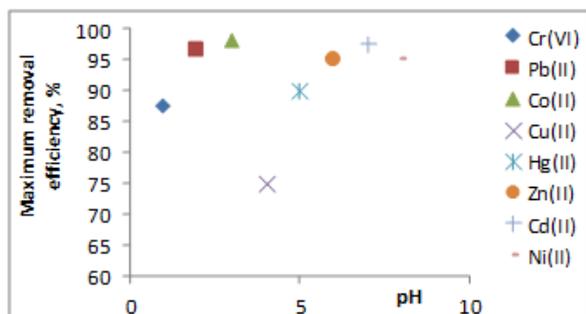


Fig. 13 Maximum efficiency of heavy metals removal using f-CNTs in regard to pH (Lu and Chiu 2006, Kabbashi *et al.* 2009, Chen *et al.* 2012, Al-Khaldi *et al.* 2013, Ihsanullah *et al.* 2016a, b, c)

4.3 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: 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, EDCs 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 with 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 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 on 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 8.

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 increase 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 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 groups on CNTs surface 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 in hybrid rGO/MWCNT membrane has been used to purify drinking water and enable retaining of a wide range of organic compounds, including humic and fulvic, and also organic acids dyes, proteins, organophosphates, 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 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 has ranged within 10-95% and it has increased with the increase of a number of aromatic rings (AAP \approx 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 on PPCP removal by up to 70%. The greater efficiency has been 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 favourable PPCPs-CNTs interactions.

In Fig. 14 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 (Kaminska *et al.* 2016) is presented. The permeate flux established for PAN-CNTs membranes has been about 80% higher than that for an unmodified PAN membrane. The increase of the amount of SWNTs 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% has surprisingly adversely affected recovery levels, while the permeate flux has kept the increasing tendency (Fig. 16).

Recently, a new methodology for the preparation of an enzymatically active MWCNT BP for organophosphate bioremediation has been developed (Mechrez *et al.* 2014). This

Table 8 The summary of selected research on the removal of organic compounds using f-CNTs and f-CNTs containing membranes

Contaminant type	Membrane/adsorbent containing CNTs				Removal mechanisms	Comments	Reference
	Nanomaterial type ^a R,	AC	Initial concentration	CNTs amount			
PhACs and PCP	CNT based nanocomposite	45%	0.1 mg L ⁻¹	22g/m ²	Chemical adsorption	High removal rate of PhACs and PCPs from water solutions.	Wang <i>et al.</i> 2016a
	CNT based nanocomposite	95%	1 mg L ⁻¹	22g/m ²	Electrostatic interaction, hydrogen bonding, π - π interaction	The increase of removal rate with increasing aromatic rings number.	Wang <i>et al.</i> 2015b
Humic acid	MWCNTs coated with calcium	90.2%	20 mg L ⁻¹	0.5 g/L	Chemical adsorption	Excellent removal efficiency and regeneration (after 5 process cycles R>89.2%)	Li <i>et al.</i> 2017
	Functionalized bucky-paper CNT	>93%	5 mg L ⁻¹	0.05g/20 mm	Physical interaction/surface complexation	Excellent NOM adsorption and significant water flux increase.	Yang <i>et al.</i> 2013b
Dye (brilliant blue)	Calcium alginate/MWCNTs-COOH	98.2%	6-50 mg L ⁻¹	5 wt.%	Physical interaction	Higher rejection coefficient of low molecular weight organic substances.	Guo <i>et al.</i> 2016
	Magnetic MWCNTs	98.8%	1-37 mg L ⁻¹	0.5g/L	Electrostatic attraction and Van der Waals forces	Excellent dyes removal in comparison with other methods.	Gong <i>et al.</i> 2009
Methylene blue	Magnetic MWCNTs	99.16%	1-37 mg L ⁻¹	0.5g/L	Electrostatic attraction and Van der Waals forces	Excellent dyes removal in comparison with other methods.	Gong <i>et al.</i> 2009
BSA	Dodecylamine-Functionalized MWCNTs	N/A	200 mg L ⁻¹	0.5 wt.%/42cm ²	N/A	Resistant to proteins fouling. Higher permeate flux.	Khalid <i>et al.</i> 2015
	CNTs of polyelectrolyte type	99.9%	1 mg L ⁻¹	N/A	Electrostatic interaction	Better antifouling features of the membrane.	Liu <i>et al.</i> 2013
Phenols	CNTs impregnated with Al ₂ O ₃	99.4%	2 mg L ⁻¹	0.25g	Ionic exchange	High affinity to phenols removal according to Langmuir adsorption model.	Ihsanullah <i>et al.</i> 2015b
Polychlorinated biphenyls	MWCNTs grafted by β -cyclodextrin	> 96%	4.14 mg L ⁻¹	N/A	π - π interactions, steric hindrance effect	Higher adsorption capability than in case of pristine MWCNTs.	Shao <i>et al.</i> 2010
Atrazine	MWCNTs	> 35 mg/g	0.87-26.04mg L ⁻¹	0.002g/20ml	N/A	High atrazine adsorption	Yan <i>et al.</i> 2008

^aAC - adsorption capacity of contaminants % and mg/g, ^aR – percentage removal efficiency

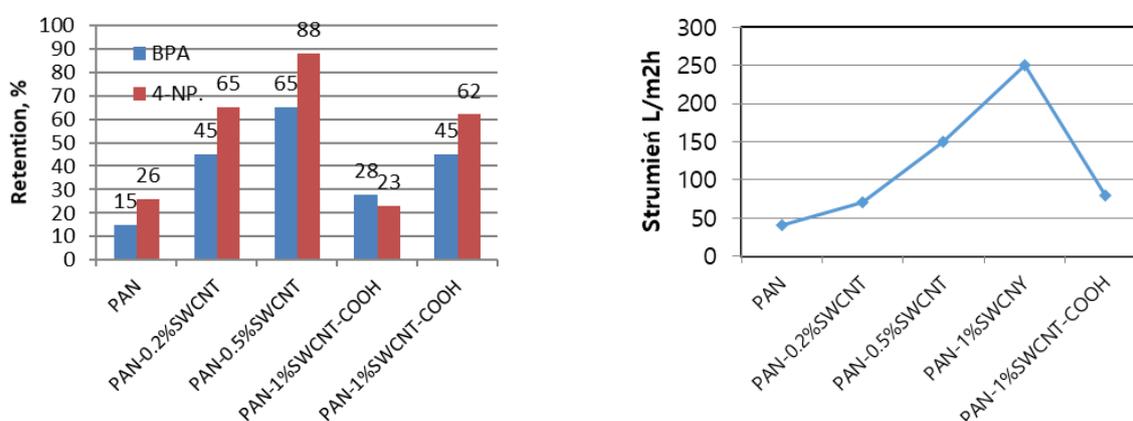


Fig. 14 The effect of SWCNT amount in PAN on wastewater flux (at 0.5 bar) and the removal of bisphenol A (BPA) and 4-nonylphenol (4-NP) by composite PAN/SWCNT membranes (Kaminska *et al.* 2016)

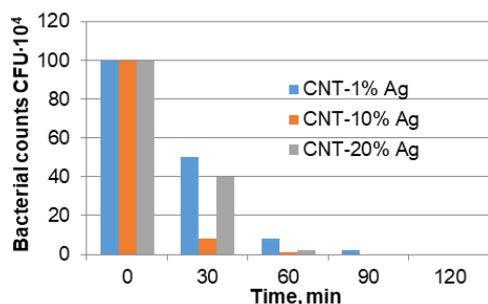


Fig. 15 The effect of time on the amount of bacteria remaining in the filtrate (expressed as colony forming units (CFU)) after passage across Ag/MWCNT membranes with different shares of Ag (Roy *et al.* 2012)

novel BP has been prepared using carboxylated MWCNTs (MWCNTs-COOH), and dispersed solution of MWCNTs has been 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) has subsequently been covalently immobilized onto the nanotube surface. To demonstrate its bioremediation features, an aqueous solution of methyl paraoxon, a model organophosphate contaminant, has been filtered using the OPH/MWNT BP. A significant decrease in the concentration of methyl paraoxon has been achieved due to its in situ hydrolysis by the immobilised enzyme during the filtration process.

4.4 Removal of microorganisms

Pathogenic microorganisms, which most often appear in water and wastewater include bacteria, viruses and protozoa (Bodzek *et al.* 2019). 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 9).

Brady-Estévez *et al.* (2008, 2010) has been one of the first, who demonstrate the antimicrobial properties of BPs, and their ability to efficient removal of bacteria and viruses from contaminated water. During their experiments, they examined BPs prepared from dimethylsulfoxide 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 is 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 efficient 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 on 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 9 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 SWCNT BPs 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 BPs can be comparably effective in removal of microbial 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 with 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 microorganisms inactivation. For example, Ihsanullah *et al.* (2015c) have obtained CNTs membranes of different nanosilver content (1, 10 and 20wt.%) 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.15 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. The ability of removal of microorganisms from water during its treatment is assigned to toxic effect of Ag-CNTs nanoparticles

5. Conclusions

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 removal of a variety of organic and inorganic contaminant as well as microorganisms.

Inactivation of bacteria and viruses on f-CNT membranes may be achieved by CNTs due to their ability of destruction of microorganisms cellular walls, what may be

Table 9 List of publications related to the removals of microorganism by f-CNT membranes

Micro-organism kind	Membrane/adsorbent with CNTs			Load of CNTs	Removal mechanism	Comments	References
	Type of complex	Retention	Initial counts of microorganism in the suspension				
<i>Escherichia coli</i> (<i>E. coli</i>)	Silver doped-CNT membrane	100%	1×10^6 CFU/mL	19.8 g/600mL	Physical interaction	High anti-biofouling. Can be used for water purification.	(Ihsanullah <i>et al.</i> 2015c)
	Nano-hybrid CNT-Ag	89.3%	10^6 CFU/mL	0.004 g/mL	N/A	High potential to inactivate a large number of pathogenic microbes from wastewaters	(Nie <i>et al.</i> 2017)
	Nano-composite Chitosan/CNT	3.62 log	$1.5 \times 10^8 - 5.0 \times 10^8$ CFU/mL	5 wt%	Physical interaction and complexing	Very high efficiency of deactivation of microorganisms after a short time of contact.	(Morsi <i>et al.</i> 2017)
	A-MWCNTs	N/A	$10^6 - 10^9$ CFU/mL	0.02 g/100 mL	Electrostatic repulsion/sieve mechanism	CNTs dispersion is responsible for antibacterial effects.	(Chi <i>et al.</i> 2016)
<i>Staphylococcus aureus</i>	MWCNTs-(C ₁₈) interaction with microwave	100%	3.5×10^7 CFU/mL	1g/250 mL	Polarization	Microwave interaction with f-CNTs is an innovative approach that can be used to water disinfection.	(Al-Hakami <i>et al.</i> 2013)
	Nano-hybrid CNT-Ag	95%	10^6 CFU/mL	0,004 g/mL	N/A	Demonstrating high potential to inactivate large number of pathogenic microbes in waste water.	(Nie <i>et al.</i> 2017)
	Chitosan/CNTs nanocomposite	5.2 log reduction	$1.5 \times 10^8 - 5.0 \times 10^8$ CFU/mL	5 wt%	Physical interaction and complexation	Superior antimicrobial capacity in short contact time.	(Morsi <i>et al.</i> 2017)
<i>Aspergillus flavus</i>	Chitosan/CNTs nanocomposite	4.3 log reduction	$1.5 \times 10^8 - 5.0 \times 10^8$ CFU/mL	5 wt%	Physical interaction and complexation	Superior antimicrobial capacity in short contact time.	(Morsi <i>et al.</i> 2017)

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 to 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 dimeters, what decreases retention of salts during treatment of brackish or seawater. Thus, for efficient water desalination further research on manufacture of CNTs of lower diameters are 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 exists a lot of solution on the potential use of f-CNTs membranes in this field, but these are tested only in 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 preparation in industrial scale, elaboration of additional procedures of CNTs introduction to existing and novel membranes, monitoring and measure 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 significant 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 treatment of real water and wastewater during long term operation are required, while such are 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 (Wang *et al.* 2018). Such lower materials costs, in combination with breakthrough research results indicate on the possible, industrial use of f-CNTs 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 to water and wastewater treatment can be obtained only through 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 determination of capacity and selectivity of CNTs membranes at real and demanding process conditions.

Integration of conventional technologies with CNTs based processes allowing for the development of advanced water and wastewater treatment systems.

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