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Designer carbon nanotubes for contaminant removal in water and wastewater: A critical review

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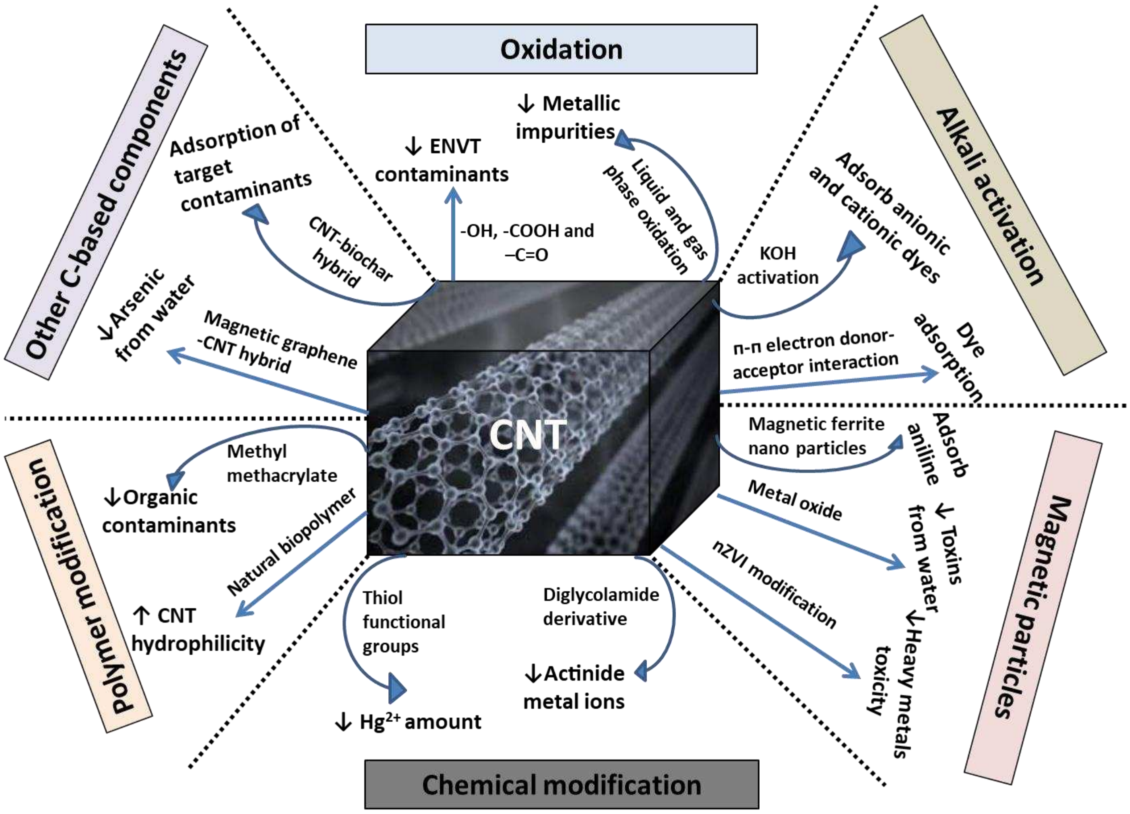
Highlights

- CNTs can be designed through specific functionalization or modification process.
- Designer CNTs can enhance contaminant removal efficiency.
- CNTs can facilitate recovery and regeneration of nanomaterials.
- CNTs hold potential applications in wastewater purification and desalination.
- Further research is needed to enhance commercial acceptance of CNTs.

Graphical abstract



Contents

ABSTRACT

The search for effective materials for environmental cleanup is a scientific and technological issue of paramount importance. Among various materials, carbon nanotubes (CNTs) possess unique physicochemical, electrical, and mechanical properties that make them suitable for potential applications as environmental adsorbents, sensors, membranes, and catalysts. Depending on the intended application and the chemical nature of the target contaminants, CNTs can be designed through specific functionalization or modification processes. Designer CNTs can remarkably enhance contaminant removal efficiency and facilitate nanomaterial recovery and regeneration. An increasing number of CNT-based materials have been used to treat diverse organic, inorganic, and biological contaminants. These success stories demonstrate their strong potential in practical applications, including wastewater purification and desalination. However, CNT-based technologies have not been broadly accepted for commercial use due to their prohibitive cost and the complex interactions of CNTs with other abiotic and biotic environmental components. This paper presents a critical review of the existing literature on the interaction of various contaminants with CNTs in water and soil environments. The preparation methods of various designer CNTs (surface functionalized and/or modified) and the functional relationships between their physicochemical characteristics and environmental uses are discussed. This review will also help to identify the research gaps that must be addressed for enhancing the commercial acceptance of CNTs in the environmental remediation industry.

Keywords: Carbon nanotubes; Surface functionalization/modification; Contaminants; Environmental remediation; Soil remediation; Desalination

1. Introduction

The earth is continuously being contaminated with numerous toxic substances from both natural and anthropogenic sources. Rapid population growth and increasing industrial development have caused the discharge of various toxic elements, compounds, and/or materials into the environment. Many new chemicals have been introduced for use without proper assessment of their environmental risks and human health impacts. The discharge of untreated industrial effluent into water and soil, the indiscriminate use of pesticides and fertilizers in agriculture, the unregulated use of harmful chemicals in consumer products, the lack of proper public sanitation systems in developing countries, the combustion of fossil fuels, the weathering of toxic elements from rocks and minerals, and the over-extraction of ground water are some of the primary causes of contamination of water, soil, and air. This environmental issue is worsening day by day as modern society faces ever increasing cases of deaths due to diseases, such as cancer. Although industrial and agricultural growth and the use of new chemicals are necessary to maintain human civilization, the scientific community has a huge responsibility to develop effective technologies for cleaning up the environment.

The search for effective and low-cost materials that can eliminate present and future harmful contaminants and treat hazardous wastes in the environment is a scientific and technological issue of paramount importance. Scientists around the world have been searching for various materials - either of natural or synthetic origin - to fit into the purpose of environmental remediation. However, conventional materials (e.g., zeolite, clay minerals, and agricultural/ industrial waste-based adsorbents) often experience drawbacks in practical applications, including (i) poor contaminant removal capacity, (ii) lack of contaminant interaction specificity, and (iii) environmental instability (Sud et al., 2008; Bhatnagar and Sillanpää, 2010; Bhatnagar et al., 2011; Sarkar et al., 2012; Perego et al., 2013). Some adsorbents prepared from industrial and municipal waste materials may also pose risks of secondary pollution (Bhatnagar and Sillanpää, 2010). In this context, carbon materials, such as activated carbon and biochar, occupy a unique position in the hierarchy of adsorbent materials for eliminating toxic substances in air, water, and soil (Mohan et al., 2014; Ok et al., 2015). Activated carbon and biochar may also encounter a number of problems when applied under the field conditions, such as poor adsorption specificity and biofouling. In addition, over the last decade, carbon nanotubes (CNTs) and graphene-based materials have seen an extensive use for environmental remediation (Mauter and Elimelech, 2008; Apul and Karanfil, 2015; Perreault et al., 2015).

In recent decades, CNTs have attracted the attention of scholars worldwide. These nanomaterials possess distinctive mechanical, electrical, thermal, and other properties that qualify them for applications in electronics, light sources, lightweight but high-strength polymer composites, sensors, nanoprobes in high-resolution imaging, nanoelectrodes, and hydrogen reservoirs (Baughman et al., 2002; De Volder et al., 2013).

This tiny crystalline form of active carbon also holds enormous potential in the field of environmental remediation, which has so far been less explored compared with other methods (Upadhyayula et al., 2009; Ren et al., 2011; Schnorr and Swager, 2011; Ersan et al., 2016). CNTs are emerging as one of the most promising remediation materials because of their large specific surface area, high porosity, light weight, and desirable interactions with a diverse range of contaminants (Ren et al., 2011; Gupta et al., 2013; Yu et al., 2014; Apul and Karanfil, 2015; Patiño et al., 2015). CNTs could outperform activated carbon in terms of practical applications in water treatment because of the nanoparticles' excellent self-assembling ability on supporting materials via chemical vapor deposition (Karwa et al., 2006), as well as their immobilization ability in membranes and filters (Hylton et al., 2008; Mishra and Ramaprabhu, 2010). On the other hand, CNTs may impose some unwanted impacts on environmental receptors (Cañas et al., 2008; Boncel et al., 2015; Chen et al., 2015; Vithanage et al., 2017).

The current paper presents a critical review of existing literature on the interactions of various contaminants with CNTs in water and soil environments. Some recent reviews focused on CNT-based adsorption against specific types of contaminants in aqueous solutions (Gupta et al., 2013; Yu et al., 2014; Apul and Karanfil, 2015; Patiño et al., 2015; Lee et al., 2016; Santhosh et al., 2016). However, information regarding the functional relationship between CNT modification/functionalization and environmental application of the designer products is still limited. Therefore, this review aims to highlight the preparation methods of various designer CNTs (surface functionalized and/or modified) and to assess the relationships between their physicochemical characteristics and environmental uses in a holistic approach.

2. CNT structure and types

CNTs are composed of enrolled cylindrical graphitic sheets (known as graphene sheets) in which carbon atoms are arranged in sp^2 hybridization at the corners of hexagons (Thostenson et al., 2001) (Fig. 1). The seamless cylinders give rise to an outer diameter from about 1 to 30 nm (Aqel et al., 2012). CNTs have nanometer-sized diameters but micrometer-sized lengths, which should yield a length-to-diameter ratio greater than 1,000 (Popov, 2004; Aqel et al., 2012). Previous studies have investigated the structural properties of CHTs (e.g., diameter, length, purity, defect, porosity, chirality, multi-wall vs. single-wall, straight vs. helical tubes, and individual vs. bundled structure) (Iijima and Ichihashi, 1993; Ajayan, 1999; Charlier, 2002; Wepasnick et al., 2010; Moradi et al., 2012). Two commercially available forms of CNTs, namely single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT), are commonly used as environmental adsorbents (Collins et al., 2000; Penza et al., 2004; 2007). Rolling of a single graphene layer into a cylindrical shape gives the SWCNT, while rolling of many concentric SWCNTs into a tubular shape produces the MWCNT (Iijima and Ichihashi, 1993). The interlayer distance in MWCNTs is nearly 0.33 nm, which is approximately the same as the distance between graphene layers in graphite (Aqel et al., 2012). Other CNT-related structures, which are less known for environmental applications, include nanobud (fullerene combined with CNT), graphenated CNT (graphitic foliates along the side wall of MWCNT), peapod (fullerene trapped inside CNT), torus (doughnut-shaped CNT), and cup-stacked CNT (stacked microstructure of graphene layers) (Ren et al., 2013).

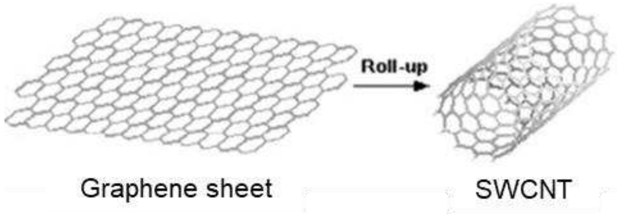


Fig. 1. Formation of CNT from graphene sheet (Aqel et al., 2012)

A number of techniques, including chemical vapor deposition (CVD), laser ablation, and arc discharge have been employed for CNT synthesis (Prasek et al., 2011). One of the most common routes of CNT synthesis is CVD through vapor deposition of the desired carbon precursor on a suitable catalyst surface (Endo et al., 2006; Prasek et al., 2011). CVD is attractive because it allows tailored control on the CNT architecture for a highly advanced field of electronics and optoelectronics while being easily scalable (Terranova et al., 2006). Transition metal nanoparticles, especially iron, cobalt, nickel, and yttrium, either alone or grafted on suitable supporting materials (e.g., silica, alumina, zeolite, and other metal oxides), are favorably selected for the nucleation and growth of CNTs (Harutyunyan et al., 2009). The role of CNTs in applications lies in the variables, such as architecture, carbon precursor, carbon feeding gas, temperature, pressure, density, and chemical environment (Terranova et al., 2006).

3. CNTs for various environmental applications

A range of physico-chemical properties of CNTs can be explored to employ the materials in environmental applications (e.g., adsorbent, membranes/filter, catalyst, oil spill sponge, and sensors) (**Fig. 2**).

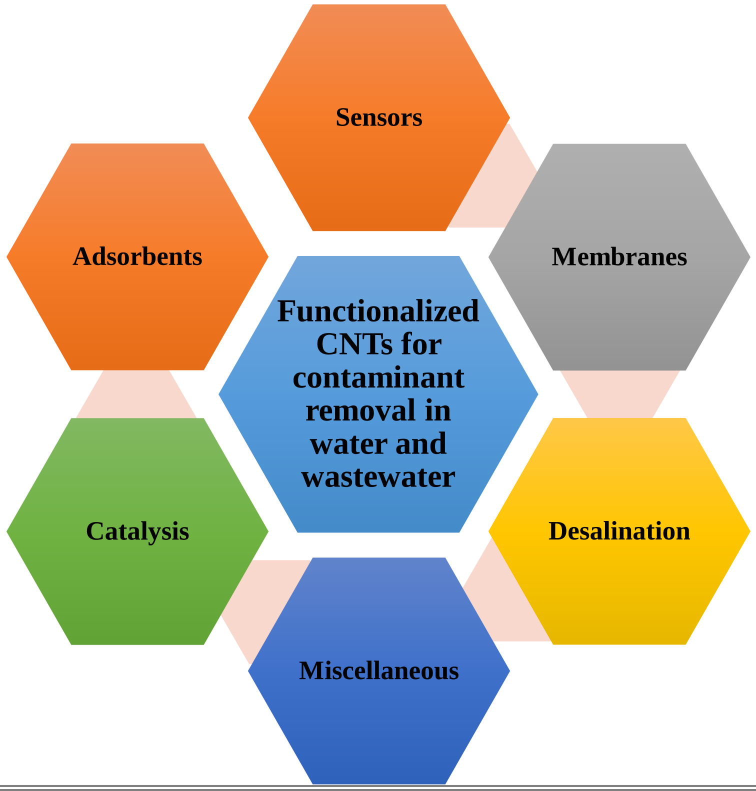
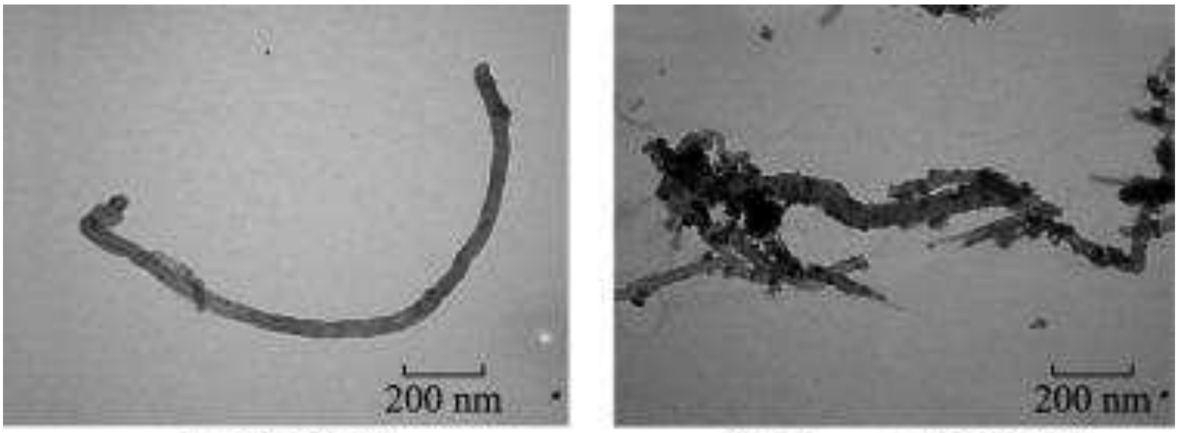


Fig. 2. Diverse classes of environmental applications of functionalized CNTs.

3.1. Adsorbents

The basic properties of CNTs (e.g., large specific surface areas and high chemical/thermal stabilities) make such materials attractive for adsorbing contaminants from water and wastewater. The adsorption properties of CNTs have been investigated against a series of toxic agents in water and wastewater, such as Pb, Cd, and 1,2-dichlorobenzene. For example, Hadavifar et al. (2014) reported the adsorption of Hg(II) from wastewater by amino- and thiol-functionalized MWCNTs. The above functional groups were introduced onto the CNT sidewalls by sequential reactions with ethylenediamine, cyanuric chloride, and sodium 2-mercaptoethanol. Adsorption isotherm and kinetic data were fitted by Langmuir and pseudo-second-order models, respectively. The thiol-functionalized MWCNTs generally removed Hg(II) more efficiently than amino-functionalized MWCTS from wastewater (Hadavifar et al., 2014).



(a) MWCNT (b) Magnetic MWCNT

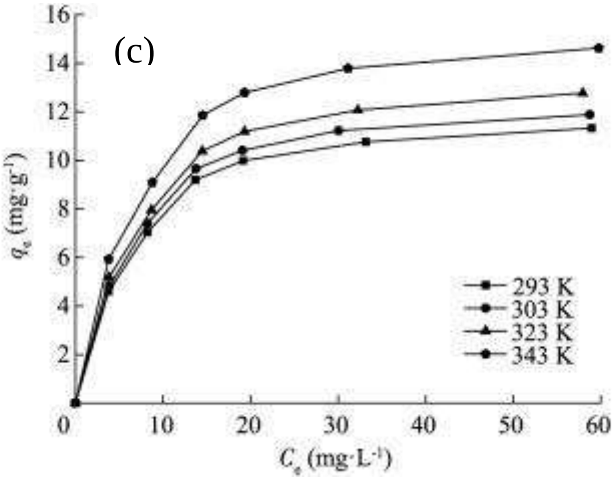


Fig. 3. (a, b) TEM images of (a) MWCNTs and (b) magnetic MWCNTs, and (c) adsorption isotherm of Cr(VI) for magnetic MWCNTs (Huang and Chen, 2014).

The removal of Cr(VI) by magnetic MWCNTs from wastewater was also investigated (Huang and Chen, 2014) (**Figs. 3 a and b).** An increase in the initial adsorbate concentration and prolonged contact time increased the Cr(VI) adsorption capacity of the magnetic MWCNTs. However, the adsorption capacity decreased with increasing adsorbent dosage. The pseudo-second-order model best explained the kinetic behavior of the adsorption process. The calculated value of the Gibbs free energy demonstrated a thermodynamically spontaneous, and endothermic adsorption process with an enthalpy deviation of 3.835 kJ mol^{-1}. Many studies have been conducted to confirm whether CNTs are highly effective adsorbents for eliminating various harmful substances in water and wastewater (section 4).

3.2. Membranes

High stability, considerable flexibility in use and large surface area enable the development of CNT membrane filters as highly effective treatment media for chemical and biological contaminants in water and wastewater (Jame Sadia and Zhou, 2016). For example, Liu et al. (2015) investigated electrochemically active CNT filters for eliminating organic pollutants from wastewater using a point-of-use treatment technology (**Fig. 4**). Since H_2O_2 alone could not remove phenolic species effectively from the system, H_2O_2 was activated anodically to generate radical species. With an average oxidation rate of 0.059 ± 0.001 mol h^{-1} m^{-2}, the removal efficiency of phenol was stable at 87.0 ± 1.8% continuously over 4 h. Such removal was influenced by the combined effects of several variables (e.g., electrode material, cathode potential, pH, flow rate, and dissolved oxygen) (Liu et al., 2015). This work demonstrated the potential of developing inexpensive filtration technology using CNTs to meet the ever-increasing demand of adequate clean water.

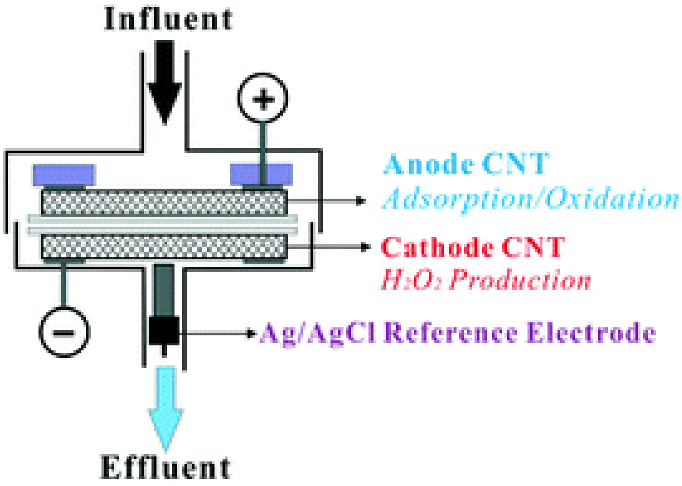


Fig. 4. Schematic of CNT-filter based electrochemical wastewater treatment system having in situ H_2O_2 generation assembly (Liu et al., 2015).

3.3. Catalysts

Among all options, the use of CNTs as a catalyst is also promising, especially for wastewater treatment. This potential is due to their mesoporous nature, exceptional mechanical strength, graphitic structure enabled support of specific metals, large surface area, and electrical/chemical/thermal characteristics. For example, Garcia et al. (2006) used different ruthenium (Ru) precursors and impregnation methods to prepare ruthenium/MWCNT catalysts. The MWCNT surface was subsequently treated with high strength aniline in wastewater using wet air oxidation. The Ru/MWCNT-COOH catalyst synthesized from 1,5-cyclooctadiene and 1,3,5-cyclooctatriene precursors yielded 100% conversion of aniline in about 45 min reaction time (Garcia et al., 2006). Stability of the catalyst was found to be directly linked with Ru loading and the strength of Ru-CNT interaction (Garcia et al., 2006). Recently, Jamie et al. (2016) reported the immobilization of a lipase enzyme (extracted from Candidia rugose) on modified MWCNTs and application of the CNT-biocatalyst for oily wastewater treatment. Surface oxidation level of MWCNTs, type of cross-linkers and their concentrations dominantly controlled the loading and subsequent catalytic activity of the

MWCNT-supported enzyme. The CNT-immobilized enzyme yielded approximately 93 times higher catalytic activity than the free enzyme (Jamie et al., 2016).

3.4. Sensors

Desirable properties of CNTs, including non-metallic nature, electronic transport, minute size per amount of material, and thermopower (voltages between junctions caused by interjunction temperature differences) can be exploited for environmental sensing applications (Jijun et al., 2002; Chakrapani et al., 2003; Penza et al., 2004; Kazachkin et al., 2008). As such, their applications have been validated from diverse fields or modes, including resistive sensors, capacitive sensors, chemical field effect transistors, gas ionization sensors, thermoelectric response, and CNT-aided optical (or acoustic) sensors. For example, Karimi-Maleh et al. (2014) prepared a highly sensitive electrochemical sensor using a ZnO/CNT nanocomposite to detect hydrazine in wastewater in the presence of phenol. The authors achieved simultaneous detection of hydrazine and phenol in wastewater at as low as 8.0 nmol L^{-1} concentrations using square wave voltammetry (SWV) technique (3σ) (Karimi-Maleh et al., 2014).

A selective Hg(II) sensor was developed by adsorbing cold mercury vapor on SWCNTs in industrial wastewater (Safavi et al., 2010). Various levels of Hg(II) adsorption on SWCNTs yielded differential impedances in the adsorbent material, and monitoring of these impedance values allowed to sense as low as 0.64 $\mu g\ mL^{-1}$ Hg(II) in different types of wastewater samples (Safavi et al., 2010). Recently, de Oliveira et al. (2015) investigated CNTs based on voltametric sensors to detect anthraquinone hair dyes in wastewater. Glassy carbon electrodes modified with MWCNTs (activated in the presence of sulfuric acid) performed the detection of anthraquinone in water samples at ultra-low concentration (2.7×10^{-9} mol L^{-1}) (de Oliveira et al., 2015). Likewise, a carbon paste electrode was prepared by modifying ZnO-CNT composite with 8,9-dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin for detecting hydroxylamine in water the presence of phenol and sulfite (Gupta et al., 2015). In water and wastewater samples, the nanocomposite showed 0.04, 0.1 and 0.3 μM detection limits for hydroxylamine, phenol and sulfite, respectively (Gupta et al., 2015). Overall, CNT-based sensors have exhibited good analytical performance, good sensitivity, and excellent stability for real world applications. Thus, the use of CNT-based sensors can be further extended to direct/real world applications in water and wastewater samples.

3.5. Oil spill sponges

The practical application of CNT-based materials in oil spill cleanup in sea water has been demonstrated in several studies. The management of oil spill in the sea can be more challenging than that of a land spill because oil spreads quickly over a large area with sea waves and wind. Owing to their rapid oil adsorption capacity, CNTs are considered an efficient material to control oil spills under oceanic conditions (Gui et al., 2010; Lee et al., 2011; Gui et al., 2013; Ge et al., 2016; Gupta and Tai, 2016; Kayvani Fard et al., 2016). Due to many advantageous properties (e.g., large surface area and porosity, super-hydrophobicity, high selectivity, chemical inertness, and easy recyclability), the suitability of CNTs for oil spill removal has been demonstrated successfully (Ge et al., 2016; Gupta and Tai, 2016). CNTs have thus been applied for oil spill removal as sponges (Gui et al., 2010), magnetic sponges (Ge et al., 2013; Gui et al., 2013; Nagappan and Ha, 2015), vertically aligned on solid support (e.g., steel) (Lee et al., 2011), and foam (Liu et al., 2013). The incorporation of magnetic attributes to CNTs or aligning them on solid surfaces has been proven effective in recovering spent materials by following spill cleanup. After recovering, the spent materials can be easily regenerated by heat treatment or solvent washing. However, a complete desorption of all adsorbed oil may not be possible because of the tight interaction between a portion of oils and the microporous network of CNTs.

4. Functionalization/modification of CNTs for environmental applications

Depending on the intended application and the chemical nature of the target contaminants, various functional groups can be generated or introduced on CNT surfaces (at tips and sidewalls) to effectively remove environmental contaminants. Non-polar organic contaminants show high affinity to CNTs due to the interactions of aromatic rings with the CNTs (Long and Yang, 2001). However, the CNT surfaces may require functionalization or modification to improve the affinity of CNTs towards hydrophilic ions or molecules. For example, CNTs can be functionalized through chemical oxidation by incorporating oxygen-containing functional groups (e.g., –OH, –COOH and –C=O) (Zhang et al., 2003; 2009), which is supposed to improve the material's affinity to heavy metal cations (Rao et al., 2007). A more complex modification of CNT surfaces is achievable by grafting guest molecules, which have high affinity toward a particular contaminant. For example, β-cyclodextrin grafted MWCNTs significantly improved the adsorption of Pb (Hu et al., 2010). Furthermore, polyaniline grafted MWCNTs demonstrated better removal of aniline and phenol (Shao et al., 2010), and alumina coated MWCNTs showed higher affinity toward heavy metal cations (Gupta et al., 2011b).

4.1. Oxidation

Surface oxidation has been the most common and easiest technique to create oxygen-containing –OH, –COOH and –C=O groups on CNT structures. Oxidation is typically performed under a refluxing condition in the presence of a single or a mixture of inorganic acids (e.g., HNO_3 and H_2SO_4) and an oxidizing agent (e.g., H_2O_2, $KMnO_4$, and NaOCl). Acid treatment is often carried out just after CNT synthesis to eliminate metallic impurities (e.g., the catalysts used for CNT synthesis) from products. After acid treatment, CNTs are either ready for direct environmental applications or have surface reaction sites that facilitate the grafting of guest moieties on the surface to incorporate additional functionalities (Chen et al., 2009c; Cho et al., 2010; Mishra et al., 2010; Fang and Chen, 2012; Wei et al., 2017). Gas-phase oxidation of CNT surfaces was also carried out through heat treatment (Nagasawa et al., 2000) or plasma treatment (Yu et al., 2011) under O_2 gas. However, liquid-phase oxidation is more extensively used for both removing metal impurities and functionalizing products. Gas-phase oxidation may sometimes burn the thinner structure of SWCNTs (Nagasawa et al., 2000). CNT oxidation in an O_2 or CO_2 environment can etch away the tube caps causing a layer-by-layer peeling of the outer layers, which may dramatically increase the surface area of the oxidized materials (Ajayan et al., 1993; Tsang et al., 1993). Liquid- or gas-phase oxidation can also clean impure amorphous carbon from synthesized CNTs and increase the number of effective reaction sites (Datsyuk et al., 2008).

Due to their intrinsic hydrophobic behavior, CNTs do no easily disperse in polar solvents such as water, making it difficult to use this material for cleaning up contaminants from wastewater. This issue can be solved by cutting the MWCNTs to a shorter length (several hundred nm) and/or creating hydrophilic functional groups on CNT surfaces through sonication in mixed acids (Saito et al., 2002; Avilés et al., 2009). In a comprehensive study, (Datsyuk et al., 2008) found that among two acidic treatments (HNO_3 and H_2SO_4-H_2O_2 mixture), nitric acid treatment under refluxing conditions achieved the highest degree of MWCNT functionalization (e.g., nanotube shortening and generation of additional defects in the graphitic network). On the other hand, basic oxidation in NH_4OH/H_2O_2 yielded better structural integrity of MWCNTs by facilitating the maximum removal of impurities (amorphous carbon and metal oxides) (Datsyuk et al., 2008). Acid functionalization can be accelerated by microwave irradiation for 20 to 40 min (Kuo and Lin, 2009; Addo Ntim and Mitra, 2011, 2012).

4.2. Alkali activation

One disadvantage of CNTs relative to activated carbon is their relatively low surface area, which may impose an adverse impact on contaminant adsorption. In addition, aggregation of nanoparticles may result in mesoporous structure of CNTs that contains interstices and grooves (Ma et al., 2012). This feature may induce strong affinitive interactions in CNTs and subsequently cause structural alterations (Ma et al., 2012). Activation of carbon materials, including CNTs, with alkali treatment can address this issue and effectively improve the surface area and pore volume (Foo and Hameed, 2011; Ma et al., 2012). The alkali activation of CNTs by Ma et al. (2012) involved heating a solid powdered mixture of MWCNTs and KOH at 750 °C for 1 h under an argon atmosphere in a horizontal tube furnace. After washing in concentrated HCl followed by deionized water, the dried powder successfully adsorbed dye compounds (both anionic and cationic) from aqueous solutions (Ma et al., 2012). Multiple interaction mechanisms, including hydrogen bonding, π–π electron-donor-acceptor interaction, electrostatic interaction, and mesopore-filling, resulted in effective dye adsorption on the alkali-activated MWCNTs (Ma et al., 2012). The alkali-activated CNTs were also successfully used to remove toluene, ethylbenzene, and m-xylene from aqueous solutions (Yu et al., 2012).

4.3. Modification with magnetic particles

CNTs used for removing environmental contaminants from aqueous media often undergo material regeneration and separation after remediation treatment. Filtration and/or high-speed centrifugation may be used to separate tiny nanoparticles from a solution, however, these techniques require a significant amount of energy and high cost. Thus, providing magnetic properties in a designer adsorbent to develop a cost-effective technology for separating spent adsorbents has gained increasing attention.

Simple homogeneous physical mixing of magnetic ferrite nanoparticles ($NiFe_2O_4$) prepared by sol-gel method with MWCNTs using an agate mortar was reported to provide the CNTs with magnetic properties (Abdel Salam et al., 2012). The composite mixture improved the adsorption of aniline from the solution and subsequently eased the separation of the spent adsorbent (Abdel Salam et al., 2012). However, such physical mixture of nanoparticles may result in unwanted nanoparticle mobility in the environment because the individual components are held together only by a weak attracting force. This operating problem can be addressed by grafting the magnetic component into the composite by using suitable reaction routes.

Incorporation of the magnetic attribute to CNTs through grafting may involve a multi-step sol-gel chemical reaction, in which magnetite (Fe_3O_4) particles were first synthesized and then coated with a silica layer (Guan et al., 2010). A separate sol solution of functionalized MWCNTs (MWCNT-OH) was also prepared by using methyltrimethoxysilane as the sol-gel precursor, poly(methylhydrosiloxane) as the deactivation reagent, and trifluoroacetic acid as the stabilizing agent. The final adsorbent was prepared by mixing the above-mentioned components in a conditioning environment under a nitrogen atmosphere (Guan et al., 2010). In another study, magnetic iron oxide nanoparticles were incorporated on MWCNTs that were covalently grafted with soluble starch (Chang et al., 2011). The resulting material improved the product's hydrophilicity and enhanced its affinity toward anionic dye compounds.

The synthesis of magnetite (Fe_3O_4) nanoparticles on oxidized MWCNTs can be achieved through a simple alkali precipitation method (Chen et al., 2009a; 2009b; Gong et al., 2009; Daneshvar Tarigh and Shemirani, 2013). The synthesis protocol involved the dispersion of the nanoparticles in a solution of iron and then the drop-wise addition of an alkali until the pH of the mixture became >10. A slightly elevated temperature (70 – 80 °C) and reaction under an inert environment were reported to provide a better yield of the oxidized iron nanoparticles.

Post-synthesis aging and/or heat treatment (~100 °C) was also beneficial. A mixed solution of ferric and ferrous forms of iron was also used to synthesize magnetite nanoparticles (Gupta et al., 2011a). Magnetic iron nanoparticle-decorated CNTs were found to remove arsenic (Mishra and Ramaprabhu, 2010), dye compounds (Qu et al., 2008), atrazine (Tang et al., 2012), and heavy metals (Wang et al., 2011) from contaminated waters.

4.4. Modification with nonmagnetic metal oxide

To achieve superior affinity toward contaminants, CNTs can be modified with various metal oxides. Transition metals, such as Fe, Zr, Ag, Ti, Ce, and bimetallic Pd-Fe (Xu et al., 2012), were successfully used for preparing metal oxide-CNT hybrids that adsorbed toxic elements (e.g., As, F, Cu, Cd, and 2,4-dichlorophenol) from water (Peng et al., 2005; Woan et al., 2009; Mishra and Ramaprabhu, 2010; Addo Ntim and Mitra, 2011; 2012; Ramamurthy et al., 2011; Venkata Ramana et al., 2013). The modification method is simple and often involves oxidative functionalization of the CNTs followed by alkali precipitation of the target metal oxide on surfaces of the nanotubes. The pre-functionalized CNTs are dispersed in the aqueous solution of the metal, and a strong alkali solution (5–7 M) is slowly added. The amount of alkali should be greater than the equivalent stoichiometric amount of the metal (final pH ≥ 10) to ensure that the oxidation reaction is complete. The metal oxide formation was facilitated by mild heating (85 °C) of the reaction mixture openly or under microwave irradiation (Addo Ntim and Mitra, 2011; 2012).

In most cases, the decoration of CNTs with metal oxide nanoparticles requires pre-treatment or functionalization of the CNT surfaces. However, this pre-treatment can be avoided by performing nanoparticle synthesis reaction and deposition with the aid of supercritical ethanol (An et al., 2007). A photo-reactive titania-MWCNT was successfully synthesized by the hydrolysis of titanium isopropoxide in supercritical ethanol at 270 °C for 2 h (An et al., 2007).

High-temperature annealing was not necessary to achieve the photo-reactivity; the composite was only vacuum-fired at 60 °C for 6 h. Non-magnetic Fe_2O_3 nano-catalysts were also decorated on MWCNTs by a simple impregnation of the CNTs with an aqueous $Fe(NO_3)_3$ solution followed by a 200 °C calcination for 4 h (Liao et al., 2009). The resulting catalysts were able to degrade phenolic contaminants (e.g., resorcinol and ortho-chlorophenol) in a H_2O_2-mediated Fenton reaction (Liao et al., 2009). The TiO_2-decorated MWCNTs were also used for the photocatalytic degradation of organic contaminants, such as 2,6-dinitro-p-cresol and 2,4-dinitrophenol, under solar irradiation (Wang et al., 2009a; 2009b).

4.5. Modification with zero-valent iron

Among manufactured nanoparticles, zero-valent iron (nZVI) has already received widespread attention for practical environmental remediation (Crane and Scott, 2012; Stefaniuk et al., 2016; Zou et al., 2016). Very high in-situ reactivity in the material is achieved at only a small synthesis cost, and this material is also easy to use in practical applications for contaminated groundwater remediation. Therefore, nZVI has been the most widely studied nanomaterial used for environmental remediation (Elliott and Zhang, 2001; Crane and Scott, 2012; Chekli et al., 2016). To prevent the oxidation and agglomeration of nZVI and prolong the material's reactivity, it was supported on various micro- and nano-particle supporting materials, including biochar (Mandal et al., 2017), clay minerals (Üzüm et al., 2009; Shi et al., 2011), and zeolite (Wang et al., 2010). Similarly, nZVI was also supported on CNTs and successfully used for removing hexavalent chromium (Lv et al., 2011), selenite (Sheng et al., 2016), azo dyes (Reza Sohrabi et al., 2015), and nitrobenzene (Jiao et al., 2016) from wastewater. The presence of other anions (even at high concentrations) did not affect the chromate reduction ability of designer materials (Lv et al., 2011). The decoration of MWCNTs with nZVI can significantly enhance the contaminant removal capacity of the material (Lv et al., 2011; Reza Sohrabi et al., 2015; Jiao et al., 2016; Sheng et al., 2016).

4.6. Specific chemical derivatization or modification

Several specific chemical derivatizations or modifications of CNTs were reported to improve the material's affinity toward specific contaminant elements or compounds. Carboxyl-functionalized SWCNTs (SWCNT-COOH) were derivatized with thiol functional groups by reacting with ethanol-dissolved cysteamine hydrochloride (Bandaru et al., 2013). The reaction was conducted in the presence of N-hydroxysuccinimide and a coupling agent (e.g., 1-ethyl-(3-3-dimethylaminopropyl) carbodiimide) (Bandaru et al., 2013). Such derivatization processes may improve the dispersibility of CNTs in aqueous solutions and its affinity toward heavy metal cations, including Hg. Bandaru et al. (2013) reported that thiol-derivatized SWCNTs adsorbed a three-fold and four-fold greater amount of Hg^{2+} than unmodified SWCNTs and activated carbon, respectively. Similarly, adsorption of actinide ions was achieved by modifying MWCNTs with a ligand, such as a diglycol amide derivative (Deb et al., 2012). The biodegradation or biocompatibility of the resulting CNT adsorbent was engineered by selecting an appropriate ligand. The spent material can be easily incinerated and disposed of due to the organic component in the adsorbent. Other chemical compounds, such as β-cyclodextrin (Fuhrer et al., 2011), iodide/sulfur (Gupta et al., 2014), amino compounds (Vuković et al., 2011; Ji et al., 2012; Hamdi et al., 2015), tannic acid (Tong et al., 2011), and ethylenediamine (Vuković et al., 2010), were also used to modify CNT surfaces. The cyclodextrin molecules were also grafted on CNTs along with magnetic nanoparticles with the aid of plasma technology (Hu et al., 2010; 2011a) or polyaniline (Shao et al., 2010; 2012). Tannic acid-modified MWCNTs were reported to be excellent adsorbents of rare earth elements (e.g., La, Tb, and Lu) (Tong et al., 2011).

4.7. Modification with polymers

Various types of polymers are often used to modify CNTs and other adsorbents for improving their adsorption affinity toward a particular element or compound. For example, dendrimers are a unique class of polymers that successfully modify the surface of MWCNTs (Eskandarian et al., 2014). The adsorbent was prepared by reacting carboxyl-functionalized MWCNTs with poly(propyleneimine) dendrimer in aqueous media and the dendrimers were used to adsorb single- and multi-component organic dye solutions (Eskandarian et al., 2014).

A plasma technique was also adopted for grafting methyl methacrylate on CNTs (Shao et al., 2011). Poly(methyl methacrylate) is known to adsorb organic contaminants, however it sediments rapidly in aqueous solutions, which may compromise its adsorption capacity. This issue was tackled by grafting poly(methyl methacrylate) molecules on CNT surfaces, thereby preventing the sedimentation of the active ingredient. Thus, the designer material successfully removed 4,4′-dichlorinated biphenyl from the aqueous solutions (Shao et al., 2011).

Natural biopolymers can also be used to enhance the hydrophilic nature and improve biocompatibility of CNTs in environmental applications. For example, Yan et al. (2012b) reported the covalent grafting of guar gum onto MWCNT surfaces. During an attempt to incorporate magnetic Fe_3O_4 nanoparticles into the designer material, it was found that the biopolymer facilitated a better dispersion of the Fe_3O_4 nanoparticles on the adsorbent surfaces through a supramolecular interaction between its hydroxyl groups and the metal ions; this significantly improved the adsorption of aqueous dye contaminants (Yan et al., 2012b).

4.8. CNT immobilization

CNTs are highly resistant to degradation and may impart toxicity to environmental organisms. Therefore, they should be removed from treated water. The limitation of the techniques used to separate these small particles from water may obstruct their widespread use as adsorbents in environmental remediation. This can somehow be tackled by immobilizing CNTs in polymer-carrying electrospun fibrous membranes, in alginate composites or on large particles. For example, Dai et al. (2016) fabricated a laccase-carrying electrospun fibrous membrane by co-electrospinning a poly(D,L-lactide)/laccase/MWCNT mixture. The total removal (synergistic adsorption and degradation) of the target species (e.g., 2,4-dichlorophenol, bisphenol A, and triclosan) by the fabricated material reached 92.6, 95.5, and 99.7%, respectively, with 81.7, 90.5, and 85.6% contributions from the enzyme-catalyzed degradation of the respective contaminants (Dai et al., 2016). Li et al. (2010) immobilized CNTs by injecting a homogeneous dispersion of CNTs and sodium alginate into a solution of calcium chloride, with Ca^{2+} serving as the bridging agent. The authors successfully used the resulting material to remove Cu^{2+} from the water. Similarly, a composite fiber containing calcium alginate-MWCNT was obtained via wet spinning method, and the resulting material was used to remove dye compounds (both cationic and anionic) from aqueous media (Sui et al., 2012a). In a novel approach, MWCNTs were inserted into the cavities of diatomite and subsequently supported onto flexible polyurethane foams (Yu and Fugetsu, 2010). The composite material was able to effectively remove organic dye compounds from contaminated water (Yu and Fugetsu, 2010). In a similar approach, a sponge-like natural vermiculite-CNT hybrid was synthesized by intercalating CNTs into the exfoliated vermiculite for oil adsorption (Zhao et al., 2011). Several other clay minerals (e.g., smectite and palygorskite), which are naturally occurring, inexpensive, and non-toxic, have enormous potential to be developed as composite CNT adsorbents. The clay minerals themselves have well known environmental applications due to their high surface reactivity (Sarkar et al., 2012). Combining this feature with CNT composites is expected to promote the development of advanced environmental adsorbents and simultaneously restrict the unwanted mobility of CNTs from the materials (Sarkar et al., 2015).

4.9. Modification with other carbon based adsorbents

Hybrid adsorbent materials containing CNTs as a major component have also been used to remove/treat environmental contaminants. A self-assembled graphene–CNT hybrid was prepared by autoclaving a mixed dispersion of pre-exfoliated graphene oxide and MWCNTs in ethanol/water (1:1 v/v) at 200 °C for 6 h (Ai and Jiang, 2012). Sui et al. (2012b) reported the synthesis of graphene–CNT hybrid aerogels in a green process, in which graphene oxide was reduced to graphene by Vitamin C in the presence of HCl. The authors (Sui et al., 2012b) synthesized hybrid aerogels by mixing graphene and MWCNTs under heat treatment and then drying the mixture with supercritical CO_2. Free-standing adsorbent papers were prepared from a mixture of different types of CNTs and graphene. These materials were then used successfully to adsorb both metal cations and nonpolar organic compounds (Dichiara et al., 2014b; 2015b). The prepared nanocomposites thus demonstrated up to four fold and 50% greater adsorption of Cu^{2+} from aqueous solutions than those of activated carbon and CNTs alone, respectively (Dichiara et al., 2015b). A similar material prepared from SWCNTs and graphene nanoplatelets exhibited 25% improvement in adsorption of organic contaminants (e.g., 1-pyrenebutyric acid, 2,4-dichlorophenoxyacetic acid, and diquat dibromide) in comparison with either component of the nanocomposites alone (Dichiara et al., 2014b). Similarly, CNT-biochar hybrid materials were prepared in two steps: (i) dip-coating of CNTs on a biochar feedstock in the presence or absence of a surfactant and (ii) slow pyrolysis of dip-coated dried feedstock (for 1 h at 600 °C) under an N_2 environment (Inyang et al., 2014; 2015). The loading of CNTs in these composites was arbitrary. Future research may focus on optimizing the mixing ratio of individual components to achieve the best adsorption of a target contaminant. Care should also be taken to restrict the unwanted mobility of CNTs. The carbon-CNT hybrid material can also be magnetized by incorporating iron oxides. While Vadahanambi et al. (2013) used such a magnetic graphene-CNT hybrid material for removing arsenic from water, Wang et al. (2014) used it for adsorbing cationic dyes (i.e., methylene blue).

5. Contaminant treatment by CNTs

The key strategies for treating contaminants by CNTs mainly include adsorption and degradation/detoxification. In both cases, the reactivity of CNTs is often improved by modification or functionalization of the material. Designer CNTs can be prepared to target a specific contaminant element or compound for remediation. Designing CNTs with certain surface engineering may also facilitate the separation of the materials following the contaminant treatment process. **Fig. 5** depicts the potential avenues of CNT modification and their possible applications in environmental contaminant mitigation. The incorporation of a magnetic component into CNTs is one of the common approaches used for nanoparticle separation (Abdel Salam et al., 2012). With or without such modifications, CNTs have been reported to remediate several groups of contaminants, including emerging pollutants, phenolics, polycyclic aromatic hydrocarbons (PAHs), dyes, pesticides, chlorinated organics, and heavy metals. For example, Glomstad et al. (2016) reported that with decreasing oxygen-containing functional groups and increasing surface areas, SWCNTs and MWCNTs adsorbed a greater amount of phenanthrene in the presence of aqueous natural organic matter while significantly reducing the toxicity of the contaminant to freshwater algae Pseudokirchneriella subcapitata.

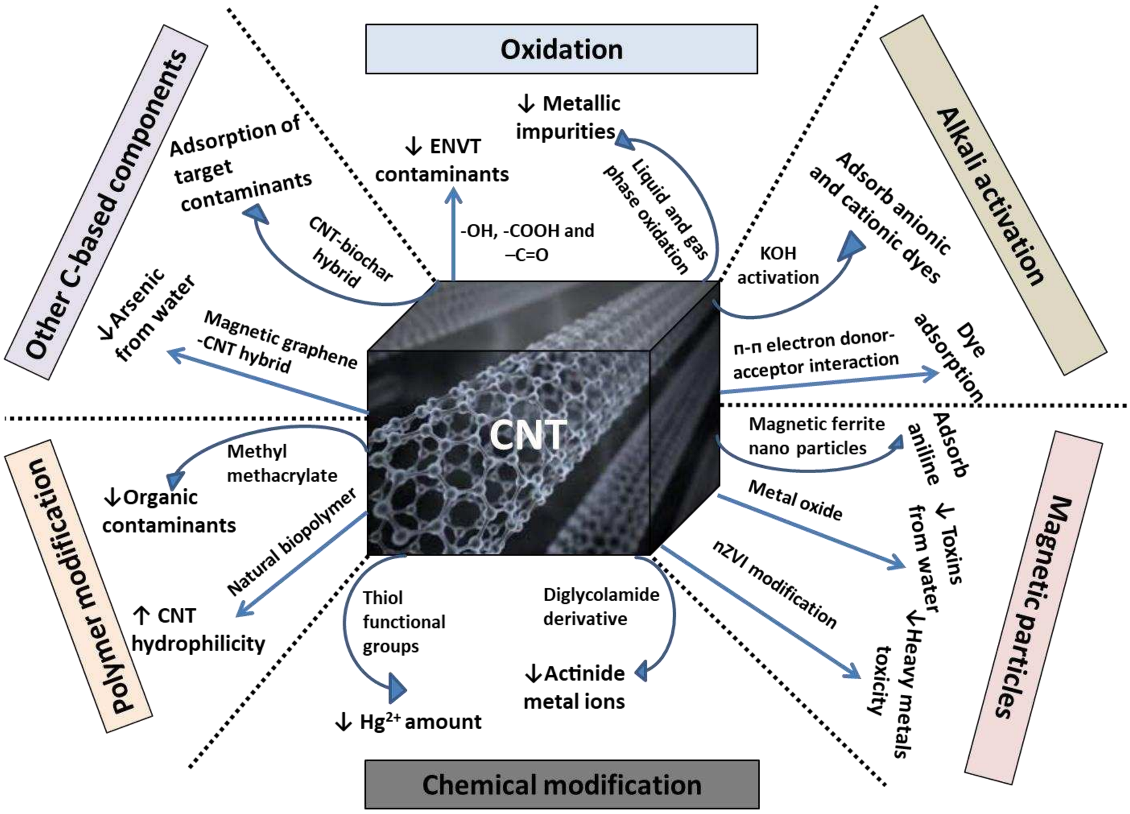


Fig. 5. Schematic diagram representing different modification processes of CNTs for contaminant removal from water and wastewater (C: Carbon; CNT: Carbon nanotube; ENVT: Environmental; Hg: Mercury; KOH: Potassium hydroxide).

5.1. Emerging contaminants

Modern manufacturing processes and industrial effluents discharge more than 80,000 synthetic chemicals into the environment every year (Naidu et al., 2016). Among the synthetic and naturally occurring chemicals, emerging contaminants are defined as those that have been newly observed in the environment. Tackling the issue of emerging contaminants is extremely challenging owing to the lack of (a) precise analytical methods for identifying contaminants, (b) certified reference materials for several of these chemicals, (c) information on their fate, toxicity, and behavior in the environment, (d) data of their environmental and human health limits, and (e) knowledge about their long-term (chronic) health impacts (Naidu and Wong, 2013; Naidu et al., 2016). Therefore, continuous efforts are needed to find effective materials for cleaning up these contaminants.

Among emerging contaminants, pharmaceuticals and personal care products (PPCPs) are of widespread public concern because their fate and mobility in the environment are largely unknown (Yang et al., 2017). Some of the specific compounds in this group include ibuprofen (an anti-inflammatory drug) and triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol, a disinfectant). CNTs were successfully used to adsorb these compounds from aqueous media (Cho et al., 2011). Given their large specific surface areas, SWCNTs showed better adsorption of both ibuprofen and triclosan than MWCNTs. Oxidation of the CNT surface resulted in a reduction of PPCP adsorption (Cho et al., 2011).

Many synthetic antibiotic compounds are considered to be emerging contaminants in the environment. They are often only partially eliminated from the effluents of drug manufacturing industries or public sewage systems. Therefore, a residual amount of these compounds can reach the surface or groundwater. Although they can be present at low concentrations, such small concentrations can also potentially develop resistance in soil and water microbial species. When compared with an activated carbon and a synthetic carbon xerogel, an MWCNT sample adsorbed almost the same amount of ciprofloxacin as activated carbon and about 40% less than a xerogel (Carabineiro et al., 2011). Following a strong oxidation treatment (7 M HNO_3), the adsorption capacities of the activated carbon and xerogel were drastically reduced, whereas the adsorption by CNT was unaffected. However, a thermal treatment (900 °C) following the oxidation enhanced the ciprofloxacin absorption performance of the activated carbon and xerogel, but not that of the CNTs (Carabineiro et al., 2011). The combined oxidation and thermal treatment increased the surface basicity of the materials and thus enhanced the adsorption of the negatively charged antibiotic compound. Therefore, the removal of antibiotic compounds by CNTs largely depends on the type of compounds themselves (cationic or anionic).

The type of CNTs (whether single- or multi-walled) can significantly affect the material's affinity for emerging contaminants. For example, the adsorption of perfluorooctane sulfonate (PFOS) was greater for SWCNTs than for MWCNTs (Chen et al., 2011b). PFOS and perfluorooctanoic acid (PFOA) are present in fire-extinguishing aqueous film-forming foam (AFFF), and in recent years, they have emerged as some of the most concerning contaminants because of their high concentration, wide global distribution, extremely high environmental persistence, and potential for bioaccumulation (Arias Espana et al., 2015). CNTs demonstrated a considerably fast adsorption equilibrium (as quick as 2 h) toward PFOS in comparison with biomass-derived chars (384 h) and ash (48 h) because of the greater number of available reaction sites in the cylindrical external surfaces of CNTs and the strong hydrophobic type interaction mechanism (Chen et al., 2011b). Deng et al. (2012b) found that hydrophobic interactions dominated the accumulation of perfluorinated compounds (PFCs) on CNTs. The adsorption affinity of PFCs increased with the compounds' increasing C-F chain lengths, and the functionalization of CNTs with oxygen-containing groups caused a reduction in PFC adsorption (Deng et al., 2012b).

Among emerging inorganic contaminants, perchlorate (ClO_4^-) anions have received widespread attention because of their disruptive effect on iodine uptake by mammals, which leads to a number of diseases, such as thyroid disorder, neurological damage, and anemia (Dasgupta et al., 2008; Sijimol et al., 2015). CNTs, especially the double-walled ones (DWCNTs) with oxygen-containing functional groups, were found to remove perchlorate from aqueous media (Fang and Chen, 2012). Perchlorate removal by various CNTs was in the order: DWCNTs-oxidized > DWCNTs > SWCNTs > MWCNTs. Fang and Chen (2012) also proposed a combined electrostatic interaction and hydrogen bonding mechanism for the adsorption. However, these mechanisms should be further examined by conducting adsorption tests under different pH values, ionic strengths, organic matter concentrations, and temperatures.

Roxarsone (3-nitro-4-hydroxyphenylarsonic acid) is an organoarsenic compound used to prevent and control parasites in poultry farming. The compound itself is not highly toxic, but following degradation (which is quite fast under ambient environmental conditions), it can produce extremely toxic inorganic arsenic species (Arai et al., 2003). Removal of roxarsone using MWCNTs was evaluated by Hu et al. (2012). The authors suggested the suitability of using MWCNTs for roxarsone remediation depending on both batch and static column test results. The adsorption capacity reached 13.5 mg g^{-1}, which decreased markedly with rising ionic strength and pH of the contaminant solutions. A π–π electron–donor–acceptor (EDA) interaction was suggested to control the roxarsone adsorption reaction on the CNT surfaces (Hu et al., 2012).

Magnetic particles decorated with surface-functionalized CNTs can also be used to retain/concentrate emerging contaminants from aqueous media. For example, Guan et al. (2010) used MWCNT functionalized magnetic particles to extract estrogen from solutions. Indiscriminate disposal of medications is the main source of estrogen into the household sewerage systems. As is apparent from the complex synthesis procedure of magnetic CNT adsorbents (Guan et al., 2010), these materials may be inappropriate for treating high volumes of contaminated wastewater owing to the high cost involved, but they can be efficient in developing an analytical separation technique (separating media) for emerging contaminants. A detection limit for diethylstilbestrol, estrone, and estriol estrogens as low as 0.2 ng mL^{-1} was achieved by using a magnetically modified CNT material (Guan et al., 2010). **Table 1** summarizes the examples of cases in which CNTs (with or without surface modification) were used for removing various emerging contaminants from the environment.

Table 1

Removal of emerging contaminants by CNTs with or without surface modification.

CNT type	Modification	Target contaminant	Test method	Removal capacity	Remarks	Reference
SWCNTs and MWCNTs	Reflux with 70% w/w HNO_3	Ibuprofen (IBU) and triclosan (TCS)	Batch adsorption isotherm	For SWCNT, IBU at pH 7: 232 mg g^{-1}; TCS at pH 7: 558 mg g^{-1}	SWCNT adsorbed more IBU and TCS than MWCNT; IBU adsorption was greater at pH 4 whereas TCS adsorption was greater at pH 7; CNT surface oxidation reduced the adsorption.	(Cho et al., 2011)

MWCNTs	HNO_3 (7 M) oxidation and heat treatment (350 – 900 °C) under inert atmosphere (N_2)	Ciprofloxacin (CPX)	Batch adsorption isotherm and kinetics	About 150 mg g^{-1}	CNT adsorbed more CPX than activated carbon and carbon xerogel, but the oxidation and heat treatment did not impact the adsorption capacity of CNT.	(Carabineiro et al., 2011)
SWCNTs and MWCNTs	As received.	Perfluorooctane sulfonate (PFOS)	Batch adsorption kinetics	SWCNT: 237 mg g^{-1}	SWCNT adsorbed more PFOS than MWCNT.	(Chen et al., 2011b)
SWCNTs and MWCNTs	Functionalized by –OH and –COOH groups	Perfluorinated compounds (PFCs)	Batch adsorption isotherm	For SWCNT, Freundlich constants (K_F) for perfluorohexane acid,	SWCNT adsorbed more PFCs than MWCNT; adsorption	(Deng et al., 2012b)

				perfluorobutane acid, perfluorooctanoate, PFOS, perfluorobutane sulfonate and perfluorohexane sulfonate are 0.05, 0.07, 0.26, 1.61, 5.89 and 157, respectively.	increased with increasing C-F chain lengths; functionalization reduced adsorption.	
SWCNTs and MWCNTs	Reflux with 65% HNO3	Perchlorate (ClO_4^-)	Batch adsorption isotherm	As high as 3.55 mg g^{-1}	DWCNTs adsorbed more ClO_4^- than SWCNT and MWCNT; oxygen-containing functional groups improved adsorption.	(Fang and Chen, 2012)

MWCNTs	As received.	Roxarsone	Batch equilibrium adsorption and column adsorption	As high as 13.5 mg g^{-1}	Adsorption markedly decreased with increasing pH and ionic strength.	(Hu et al., 2012)
SWCNTs	In the presence of natural organic matter (NOM)	Bisphenol A (BPA) and 17β-estradiol (E2)	Batch adsorption and partition coefficient determination	Presence of NOM: 8 mg L^{-1} SWCNT: 10 mg L^{-1}	BPA and E2 adsorption ranged from 7.3% to 95% depending upon the solution pH and the absence and presence of NOM and SWCNTs	(Heo et al. 2012)

MWCNTs	Surface oxidized MWCNT containing 0.85, 2.16 and 7.07% oxygen	Atrazine [2-chloro-4-ethylamino-6-isopropylamino-s-triazine]	Adsorption kinetics, isotherm and thermodynamics	Pseudo second order model; adsorption of atrazine MWCNTs-O (0.85%): 17.35, MWCNTs-O (2.16%): 16.65 and MWCNTs-O (7.07%): 10.50 mg g^{-1}	Atrazine adsorption affinity decreased when the surface oxygen content increased	(Chen et al., 2009c)
MWCNTs	As prepared and oxidized	Diuron (pesticide)	Adsorption studies	Adsorption of diuron by As-prepared MWCNT: 28.37, and oxidized MWCNT: 29.82 mg g^{-1}	Diuron adsorption was pH dependent and favorable under neutral and basic conditions	(Deng et al., 2012a)

SWCNTs and MWCNTs	As received (presence of Cu^{2+})	Tetracycline	Batch adsorption studies	Freundlich coefficient for SWCNT: 1,150 and for MWCNT: 240 $mmol^{1-n}\ L^{n}\ kg^{-1}$	Tetracycline adsorption on MWCNTs (larger mesoporous interstices) was higher than SWCNT by the presence of Cu^{2+}	(Ji et al., 2010a)
MWCNTs	Coated with magnetic Fe_3O_4 followed by amino functionalization	Tetrabromobisphenol A	Batch adsorption studies	As high as 33.7 mg g^{-1}	The composite also adsorbed Pb(II) (75 mg g^{-1})	(Ji et al., 2012)

MWCNTs	Carboxyl functionalization	Mixture of four linear alkylbenzene sulfonates compounds	Batch adsorption studies	Up to 168 mg g^{-1}	Hydrophobic interaction and hydrogen bond formation enabled the adsorption	(Guan et al., 2017)

5.2. Heavy metals, metalloids and radionuclides

The affinity of CNTs towards heavy metals and metalloids was improved by oxidative modification (Cho et al., 2010; Yu et al., 2011), incorporation of magnetic iron oxides (Chen et al., 2009a; Addo Ntim and Mitra, 2011; Gupta et al., 2011a; Daneshvar Tarigh and Shemirani, 2013), coating with non-magnetic metal oxides (Zhao et al., 2010), thiol derivatization (Bandaru et al., 2013), and sulfur functionalization (Gupta et al., 2014). Among the synthetic iron oxides, a mixture of goethite (α-FeO(OH)), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4) was capable of removing trace quantities of heavy metal from water (Addo Ntim and Mitra, 2011). The mechanism of heavy metal adsorption by CNT-based materials is dependent on the employed modification/functionalization treatments (Gupta et al., 2016; Ihsanullah et al., 2016). Generally, metal oxide-CNT composites adsorb heavy metals and metalloids through a synergistic effect of chemisorption and physisorption (Addo Ntim and Mitra, 2011). The adsorption affinity also highly depend on the ionic radius, hydration energy, and hydrolysis potential of the specific contaminant element (Hu et al., 2011b). For example, under similar experimental conditions, Pb(II) removal by iron oxide-coated MWCNTs was greater than Cu(II) (Hu et al., 2011b). The presence of organic co-contaminants also affected the adsorption of heavy metals by CNTs. For example, Cd(II) removal by oxidized MWCNTs was enhanced by the coexistence of 1-naphthol, but the removal of 1-naphthol was independent of the coexistence of Cd(II) in the same system (Yang et al., 2012a). This result was mainly due to the difference in the adsorption mechanisms of the two contaminants on functionalized MWCNTs. While high pH conditions may favor inner-sphere complexation during metal adsorption, low pH may favor outer-sphere complexation and/or ion exchange (Yang et al., 2012a). The adsorption of organic contaminants such as 1-naphthol can take place through π–π bond formation between MWCNT structure and the contaminant's aromatic rings (Yang et al., 2012a).

Similar to the mechanisms of heavy metal/metalloid removal, CNT-based materials were also reported to efficiently remediate various radionuclides. However, such studies are still rarely reported in the literature. **Table 2** lists the studies in which CNTs were used for heavy metal, metalloid, and radionuclide removal following various modifications/functionalizations. Despite the significant potential of using these modified/functionalized materials, no consensus has been reached with regard to the obtained results. For example, for the same heavy metal cation, different authors reported different removal capacities by employing specific modification processes. This indicates that extensive research is required and large-scale experiments should be conducted to confirm the results.

Table 2

Removal of heavy metals and radionuclides by CNTs with or without surface modification.

CNT type	Modification	Target contaminant	Test method	Removal capacity	Remarks	Reference
MWCNTs	Coated with iron oxide (Fe-MWCNT)	Trace level arsenic from drinking water	Kinetics and adsorption isotherm	As (III) and As (V) adsorption capacities of Fe-MWCNT were 1723 and 189 μg g^{-1}, respectively	Negatively charged As species may adsorb onto positively charged modified MWCNT sites	(Addo Ntim and Mitra, 2012)
SWCNTs	Thiol-derivatized SWCNT (SWCNT-SH) synthesized with HNO_3	Mercury, Hg (II)	Adsorption and desorption studies	Maximum Hg (II) adsorption with SWCNT-SH: 131 mg g^{-1}	Strong chemisorption between Hg (II) and thiol groups on derivatized SWCNT surfaces	(Bandaru et al., 2013)

MWCNTs	Iron oxide magnetic composite	Nickel [Ni(II)] and strontium [Sr(II)]	Batch adsorption studies	Ni(II) adsorption: ~80% (pH 8) and Sr(II) adsorption: ~95% (pH 10.4)	Ni(II) and Sr (II) on MECNT-iron oxide magnetic is highly dependent on pH. Ni(II) adsorption increased from 10% (pH 3.5) to 80% (pH 8.0)	(Chen et al., 2009a)
MWCNTs	Oxidation using chemical vapor deposition	Sr(II) and europium [Eu (III)]	Adsorption experiment	Sr(II) adsorption: ~36% and Eu(III) adsorption: ~96%	Increasing pH enhanced Sr(II) and Eu(III) adsorption, while increasing ionic strength decreased adsorption	(Chen et al., 2008)
MWCNTs	Diglycolamide functionalized MWCNT (DGA-MWCNTs)	Uranium from aqueous solution	Adsorption studies	Maximum Uranium adsorption by DGA-MWCNTs: 133.74 mg g^{-1}	Adsorption is favored at higher adsorbent concentration and higher temperature	(Deb et al., 2012)

MWCNTs	Oxidized with HNO_3	Cesium [Cs(I)] from aqueous solution	Batch method	About 13 mg g^{-1}	Low ionic strength, high pH and low initial Cs(I) concentration favored adsorption	(Yavari et al., 2011)
MWCNTs	Alumina coated CNT (Al_2O_3-MWCNT)	Lead ions from aqueous solution	Adsorption experiment	Al_2O_3-MWCNT increased lead absorption from 20% to 99% compared to MWCNTs	Lead adsorption increased when pH increased from 3 to 7	(Gupta et al., 2011b)
MWCNTs	Sulfur functionalized MWCNT with CS_2	Mercury [Hg(II)] from aqueous solution	Batch method	Maximum Hg(II) adsorption capacity by S-MWCNT: 151.5 mg g^{-1}	The material also effectively adsorbed Hg(0) vapor from CFL bulbs.	(Gupta et al., 2014)

MWCNTs	Magnetic nano-iron oxide coated MWCNT	Chromium [Cr(III)] from aqueous solution	Batch and fixed bed reactor	>90% Cr(III) removed from a 20 mg L^{-1} solution with 50 mg adsorbent at pH 6	In fixed bed mode, Cr(III) removal capacity increased with decreasing flow rate; the composite material performed better than activated carbon	(Gupta et al., 2011a)
MWCNTs	Magnetic iron oxide coated MWCNT	Lead [Pb(II)] and copper [Cu(II)] from wastewater	Batch method	Adsorption capacity of Pb(II): 10 – 31 mg g^{-1}; and Cu(II): 3 – 9 mg g^{-1}	Adsorption of metals depended on the ionic radius, hydration energies and hydrolysis of their hydroxides	(Hu et al., 2011b)
MWCNTs	Titanium dioxide (TiO_2) incorporated MWCNT	Lead [Pb(II)] from aqueous solution	Batch method	As high as 137 mg g^{-1}	Very fast and spontaneous adsorption	(Zhao et al., 2010)

MWCNTs	O_2-plasma-oxidized MWCNT	Lead [Pb(II)] from aqueous solution	Batch method	54 mg g^{-1}	Adsorption capacity was comparable to that of activated carbon	(Yu et al., 2011)
MWCNTs	Silver nanoparticles deposited MWCNT	Copper [Cu(II)] and cadmium [Cd(II)] from aqueous solution	Batch method	Cu(II): 58 mg g^{-1} Cd(II): 55 mg g^{-1}	Optimum adsorption of Cu(II) and Cd(II) was observed at pH 6 and 7, respectively	(Venkata Ramana et al., 2013)
MWCNTs	As received	Chromium [Cr(III)]	Batch method	2.07 mmol g^{-1}	Cr(III) is bound by surface carboxyl groups	(Manilo et al., 2017)

5.3. Organic dyes

Organic dye compounds are discharged into the environment from many industries (e.g., textile, cosmetics, and paper manufacturing processes). The wide occurrence of dyes in bodies of water raises concerns over their adverse effects on the ecosystem and human health. Compared with traditional adsorptive materials, CNTs exhibit remarkable affinity for organic dyes. Various CNT-based materials may be adopted for dye removal without further treatment (**Table 3)**.

Table 3

Treatment performance for the removal of selected dyes using different CNTs.

Dye contaminants	Adsorbent	Modification method	Surface area (m^2 g^{-1})	Capacity (q$_m$[a])/removal efficiency	References
Reactive blue 4; Acid red 183	MWCNTs	Untreated	217	69; 45	(Wang et al., 2012)
Acid blue 161	MWCNTs	Untreated	233	91.68%	(Geyikçi, 2013)
Acid red 18	MWCNTs	Untreated	270	166.67	(Shirmardi et al., 2012)
Alizarin red S; morin	MWCNTs	Untreated	NA [b]	161.29; 26.247	(Ghaedi et al., 2011)

Reactive blue 29	SWCNTs	Untreated	700	496	(Jahangiri-Rad et al., 2013)
Methyl orange	MWCNTs	Oxidized and microwave method	NA	306	(Mahmoodian et al., 2015)
Congo red	MWCNTs	Untreated	40	352.11	(Zare et al., 2015b)
Amido black 10B	MWCNTs	Functionalized by cysteamine composite (MWCNT-COOH-Cysteamine)	NA	131	(Sadegh et al., 2016)
Maxilon blue	MWCNTs	Untreated	NA	260.7	(Alkaim et al., 2015)
Methylene blue and neutral red	MWCNTs	Fe_2O_3 nanoparticles	114	MB: 42.3 and NR: 77.5	(Qu et al., 2008)

Congo red	MWCNTs	Impregnation with chitosan hydrogel beads	237.76	450.4	(Ruiz-Hitzky et al., 2011)
Direct red 23 (DR 23)	MWCNTs	Magnetic MWCNT Fe_3-C nanocomposites	38.7	85.5	(Yang et al., 2016)
Methylene blue and neutral red	MWCNTs	Grafted with guar gum (GG) and iron oxide nanoparticles	NA	MB: 61.92 NR: 89.85	(Yan et al., 2012b)
Reactive Red M-2BE	MWCNTs	Untreated	180.9	335.7	(Machado et al., 2011)
Acid blue 161 (AB 161)	MWCNTs	Untreated	233	458.33	(Ruiz-Garcia et al., 2013)
Reactive blue 4 (RB4) and acid red 183 (AR183)	MWCNTs	Untreated	217	RB4: 58.8 AR183: 45.3	(Wang et al., 2012)

Basic Red 46 (BR 46)	SWCNTs	Pristine and oxidized	~400	SWCNTs: 38.35 Oxidized: 49.45	(Moradi, 2013)
Reactive Red 120 (RR 120)	SWCNTs	Untreated	>700	426.49	(Walker et al., 2004)
Reactive blue 29 (RB 29)	SWCNTs	Untreated	700	496	(Dawson et al., 1998)
Malachite green	MWCNTs	Untreated	270	142.85	(Shirmardi et al., 2013)
Methylene blue, neutral red and brilliant cresyl blue	MWCNTs	Magnetic CNT-iron oxide composite	61.7	MB: 11.86 NR: 9.77 BCB: 6.28	(Gong et al., 2009)

Methyl orange and methylene blue	MWCNTs	Soluble starch coated magnetic iron oxide nanocomposite	132.6	MO: 135.6 MB: 93.7	(Chang et al., 2011)
Methylene blue	MWCNTs	Graphene-coated CNT hybrid using graphene oxide	78.9	87.97	(Ai and Jiang, 2012)

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[a] q_m = maximum adsorption capacity (mg g^{-1}).

[b] NA = not available

Functionalization of CNTs can enhance adsorption ability of organic dyes (Zare et al., 2015a). Among the various modification methods, oxidized MWCNTs are the most effective in removing methylene orange and methylene blue from water matrixes (Ghaedi et al., 2012; Mahmoodian et al., 2015). A new magnetic MWCNT-κ-carrageenan-Fe_3O_4 nanocomposite was successfully prepared to effectively remove crystal violet (Duman et al., 2016). The new nanocomposite can also be used in CNT modification to increase the adsorption capacity of cationic dyes. Sadegh et al. (2016) showed that an adsorbent synthesized by CNT modification, namely, MWCNT-COOH-cysteamine, could significantly enhance the removal of Amido black 10B (AB 10B). The adsorption capacity of AB 10B using MWCNT-COOH and MWCNT-COOH-cysteamine improved from 50.1 mg g^{-1} to 90 mg g^{-1} (80% increase) and 131 mg g^{-1} (162% increase), respectively. In addition, having large surface area, SWCNTs demonstrated good adsorption properties. An excellent adsorption capacity of 496 mg g^{-1} was obtained for the removal of Blue 29 (RB 29) (Jahangiri-Rad et al., 2013).

5.4. Pesticides

The widespread application of pesticides in agriculture has alarmingly contaminated our soil and water resources. CNTs showed potential for effective removal of several types of pesticides (**Table 4**). Deng et al. (2012a) reported that the adsorptive removal of diuron by as-prepared and oxidized MWCNTs was most favored at pH ≥ 7.0. An oxidative modification of CNTs increased the product's surface area and pore volume, which resulted in higher diuron removal performance. The uptake of pesticides (chlordane and *p,p'*- dichlorodiphenyldichloroethylene) in roots and shoots of lettuce crop was reduced by 88% and 78%, respectively, with the use of non-functionalized CNTs, while the same were reduced by 57% and 23%, respectively, with the use of amino-functionalized CNTs (Hamdi et al., 2015). Therefore, CNTs and their types may significantly influence pesticide availability to plants. Investigations into electronically sorted (i.e., semiconducting or metallic types) SWCNTs for the removal of 1-pyrenebutyric acid, diquat dibromide and 2,4-dichlorophenoxyacetic acid from aqueous media revealed that the semiconducting SWCNTs were capable of adsorbing up to 70.6% greater pesticides than the metallic SWCNTs (Rocha et al., 2017). The lack of electron density around the semiconducting SWCNTs would have favored high pesticide adsorption (Rocha et al., 2017). By contrast, the adsorption of pesticides by CNTs is mostly restricted in batch systems, and only a few studies have tested these materials in continuous flow experiments (Dichiara et al., 2015a). The uptake of diquat dibromide in a fixed bed system by SWCNTs and MWCNTs was not as high as in a batch system, but the former allowed the complete removal of the contaminant over time (Dichiara et al., 2015a). Multiple mechanisms (i.e., hydrophobic interaction, π–π binding, and micropore filling) were identified for the adsorption of diquat dibromide by CNTs (Dichiara et al., 2015a). Thus far, information on pesticide removal with the application of CNTs is not as extensive as the data on other organic contaminants.

6. CNT-based water treatment technologies

6.1. Drinking water purification

Compared with many conventional adsorbents commonly used in advanced water treatment processes, CNTs have larger specific surface area. Generally SWCNTs hold a larger surface area than MWCNTs. Surface oxygen content, which is another parameter that influences the contaminant removal performance of CNTs, may be increased through oxidation process. The adsorption capacity can also be increased up to 70% at an appropriate pH value. Enhanced performance is also achieved with neutral PPCP molecules (e.g., triclosan and ibuprofen) than their ionized forms (Wang et al., 2015). The presence of NOM and inorganic salts in the influent may affect the adsorption process (Upadhyayula et al., 2009; Jung et al., 2015). In-depth studies about detailed adsorption mechanisms of multi-pollutants, pilot or full-scale operation of CNT processes, and commercial application of CNTs for drinking water purification processes are still rare. Information on endocrine-disrupting compounds (EDCs) and PPCPs adsorption using CNTs are inadequate as well (Ren et al., 2011). **Table 4** summarizes the treatment performance of selected EDCs and PPCPs in either synthetic water or water treatment plant effluent using different types of CNTs from recent studies. CNT properties (e.g., surface area, charge, and functional groups) and operating parameters (e.g., pH, contact time, initial concentration, and temperature) play a vital role in determining the treatment capacity of EDCs and PPCPs in CNT-based adsorption systems (Agnihotri et al., 2006; Shi et al., 2010; Ahmed et al., 2012; Wang et al., 2015). Adsorption rate and capacity were related to the physicochemical properties of organic pollutants (e.g., molecular size, shape, hydrophobicity, and charge properties) (Cho et al., 2011; Joseph et al., 2011a; Ncibi and Sillanpää, 2015). Wang et al. (2015) reported that SWCNTs and MWCNTs can effectively remove triclosan, acetaminophen, and ibuprofen. However, in their study, the performance ranged from approximately 10% to 95% owing to various factors. The removal efficiency increased with increasing aromatic ring numbers in the compounds (e.g., ibuprofen < triclosan).

Table 4

Treatment performance for the removal of selected EDCs and PPCPs using different CNTs.

EDC and PPCP contaminants	Adsorbent	Surface area ($m^2 g^{-1}$)	Source water	Capacity/removal efficiency/comment	References
Wide-spectrum antibiotics					
Ciprofloxacin	SWCNTs	576.7	Synthetic water	724 [a]	(Ncibi and Sillanpää, 2015)
Oxytetracycline	SWCNTs	576.7	Synthetic water	554 [a]	(Ncibi and Sillanpää, 2015)

Sulfadimethoxine	MWCNTs	174	Synthetic water	1300-1500 [b]	(Xia et al., 2013)
Sulfamethoxazole	MWCNTs	300	Synthetic water	10^2-10^3 [b]	(Ji et al., 2009)
Tylosin	MWCNTs	157-422	Synthetic water	11,300-33,900 [b]	(Ji et al., 2010b)
Ofloxacin	MWCNTs	117-228	Synthetic solution	80% adsorption	(Peng et al., 2012)
Norfloxacin	MWCNTs	160	Aqueous solution	84.7 [c]	(Yang et al., 2012b)
Sulfadimethoxine (SDM), sulfamethizole (SMZ),	MWCNTs	179	Aqueous solution	SDM: 9.68 [d] SMZ: 6.98 [d]	(Wei et al., 2017)

sulfamethazine (SMT) and sulfamethoxazole (SMX)				SMT: 1.25 ^{d} SMX: 1.53 ^{d}	
Hormones					
17-β-estradiol (E2)	SWCNTs	NA ^{e}	Synthetic water	115 ^{c}	(Zaib et al., 2012)
17α-ethinyl estradiol	SWCNTs	407	Synthetic water	35.6-35.7 ^{c}	(Joseph et al., 2011b)
Bisphenol A (BPA) and 17β-estradiol (E2)	SWCNTs	NA	Synthetic water	BPA: 122 ^{c}; E2: 162 ^{c}	(Heo et al., 2012)
Bisphenol A (BPA)	SWCNTs and MWCNTs	338-467	Synthetic wastewater	SWCNT: 55.5 ^{c} MWCNT: 19.4 ^{c}	(Renshaw et al., 2011)
NSAIDs ^{f}					

Diclofenac	MWCNTs	162	WTP effluent	22.3 [c]	(Sotelo et al., 2012)
Ibuprofen	SWCNTs and MWCNTs	1020,283	WTP effluent	10-95% removal	(Wang et al., 2015)
Bactericide/disinfectant					
Triclosan (TCS)	SWCNTs and MWCNTs	1020,283	WTP effluent	10-95% removal	(Wang et al., 2015)
Triclosan	MWCNTs	281	NA	157.7 [c]	(Navarro et al., 2008)
Triclosan	SWCNT	NA	NA	Triclosan interacts via chemical process with semiconductor (8,0) SWCNT, and via physical process with both	(Castro et al., 2017)

				semiconductor (8,0) and metallic (5,5) SWCNTs	
Pesticides/herbicides					
Isoproturon	MWCNTs	162	WTP effluent	8.1 [c]	(Sotelo et al., 2012)
Atrazine	SWCNTs	407	Synthetic water	4.97 [c]	(Jung et al., 2015)
Diuron	MWCNTs	258.6 to 427.5	Aqueous solution	As prepared: 42.6 [c] Oxidized: 49.2 [c]	(Deng et al., 2012a)
Dicholbenil	MWCNTs	83-558	Synthetic solution	17.5 [c]	(Chen et al., 2011a)

Phenoxy acid herbicide (4-chloro-2-methylphenoxyacetic acid)	SWCNTs	94-541	Synthetic solution	25.7 [c]	(Boularbah et al., 2006)
2,4-D	Regenerated SWCNT-graphene composite	NA	Aqueous solution	124 [c]	(Dichiara et al., 2014a)
Diquat dibromide	MWCNTs	233	Aqueous solution	83-87% [g]	(Dichiara et al., 2015a)
	SWCNTs	407		85-87% [g]	
	SWCNT-OH	407		57-61% [g]	

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[a] Adsorption capacity from Brouers–Sotolongo model

[b] Distribution coefficient (L kg^{-1}) calculated from Freundlich model

[c] q_m = maximum adsorption capacity calculated from Langmuir model (mg g^{-1})

[d] K_F = Capacity factor (mg g^{-1})/(m^3 mg^{-1}) for Freundlich model

[e] NA = not available

[f] NSAIDs = Nonsteroidal anti-inflammatory drugs

[g] Utilization efficiency of the adsorbent in a fixed bed process

Biological contaminants are one of the major contaminants present in surface water and in water treatment plants (Upadhyayula et al., 2009; Smith and Rodrigues, 2015). The structural and functional properties of CNTs impart their highly affinitive interactions with biological contaminants. Compared with conventional adsorbents, CNTs possess superior bacterial inactivation efficiency and viral/bacterial spore adsorption capacity due to their larger surface areas (Lu and Su, 2007; Brady-Estévez et al., 2008). CNTs demonstrate immense potential in antimicrobial applications, particularly in drinking water purification (**Table 5**).

Table 5

Treatment performance for the removal of biological contaminants using different CNTs.

Biological contaminants	Adsorbent	Surface area (m^2 g^{-1})	Capacity/removal efficiency/comment	References
NOM				
DOC and AOC	SWCNTs	507	22–26 ^{a}	(Lu and Su, 2007)
Humic acid	CNTs	NA ^{b}	81-96 ^{a}	(Skandari et al., 2016)
Colloidal NOM and humic substances	SWCNTs	407	80-100%	(Ajmani et al., 2014)
Humic acid, Nordic lake fulvic acid, Waskish peat fulvic acid	MWCNTs	NA	10-40%	(Neiva et al., 2014)
Standard Suwannee River NOM (SR-NOM)	MWCNTs	NA	NOM adsorbed 0.033-0.104 mg C mg^{-1}	(Hyung et al., 2007)

Tannic acid (TA)	SWNCTs and MWCNTs	58-541	Adsorption of TA increased with decreasing CNT diameter	(Lin and Xing, 2008)
Trihalomethane (THM), dihaloacetonitrile (DHAN) and total N-nitrosamine (TONO) precursor	SWCNTs and MWCNTs	92-837	Adsorption varied with CNT type and dose, with TONO precursors having the highest percent removals (up to 97%)	(Needham et al., 2016)
Bacteria				
E. coli	SWCNTs	407	3.18×10^{12} CFU mL^{-1}	(Brady-Estévez et al., 2008)
E. coli and B. subtilis	PVK- SWCNTs	NA	>90% inactivation	(Ahmed et al., 2012)
E. coli DH5α	MWCNTs-Ag	NA	96% inactivation	(Su et al., 2013)
E. coli K12	SWCNTs	407	(79±9)% inactivation	(Brady-Estévez et al., 2008)

Streptococcus mutants	MWCNTs (surface modified)	250	Viable cells reduced by 7.5 log	(Bai et al., 2011)
Agrobacterium	MECNTs	88	Biodegradation efficiencies is 54.2%	(Xia et al., 2010)
Escherichia coli (E.coli) K12 and Staphylococcus aureus (S.aureus) SH 1000	SWCNTs	NA	CNT aggregation: 6.54×10^{-9} and 8.98×10^{-9} (E. Coli); 1.00×10^{-7} and 1.66×10^{-7} cm^2 s^{-1}	(Upadhyayula et al., 2008)
Viruses				
MS2 bacteriophage	SWCNTs	407	10^7-10^8 PFU mL^{-1}	(Brady-Estévez et al., 2008)
Influenza virus (H3N2)	CNTs	NA	detective limitation> 3.4 PFU mL^{-1}	(Ahmed et al., 2016)

MS2 bacteriophage	SWNCTs	407	10^6-10^7 PFU mL^{-1}	(Brady-Estévez et al., 2010)
MS2 bacteriophage (ATCC 15597-B1) along with host E. Coli	MWCNTs	NA	5.8 to 7.4 log inactivation	(Rahaman et al., 2012)
MS2 bacteriophage	SWCNTs	NA	9.3 and 9.8 PFU mL^{-1} limit detection	(Prieto-Simón et al., 2015)
Swine influenza virus (SIV) H1N1	SWCNTs	NA	Virus detection limit: 180 $TCID_{50}$ mL^{-1}	(Lottermoser, 2015)
Biological toxins				
Microcystin-LR	MWCNTs	NA	detective limitation 0.05-20 μg L^{-1}	(Han et al., 2013)

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[a] q_m = Maximum adsorption capacity (mg g^{-1})

[b] NA = Not available

6.2. Water desalination

As a result of urban climate warming, the salinity levels of both land and sea water are constantly increasing. Therefore, appropriate water desalination technologies should be developed. CNTs, which feature low energy consumption and antimicrobial functions, have been introduced for this application. In addition, CNTs can attract polar water molecules and reject salts and pollutants (Goh et al., 2013). **Table 6** summarizes some successful cases of membrane desalination processes employing CNTs.

Table 6

Desalination performance of different CNT membrane types (modified from Daer et al. (2015)).

CNT membrane type	Feed water	Operation conditions	Removal capacity	References
CNTs (forward osmosis)	0.58 M aqueous NaCl solution (feed), 1.74 M aqueous NaCl solution	300 K and 1 atm	100% salt rejection	(Jia et al., 2010)
MWCNT-COOH/ polyvinylidene fluoride	3.4% aqueous NaCl solution	24 mL min^{-1} feed flow, 1 L min^{-1} dry air in SGMD arrangement, 60–90 °C	99% salt rejection	(Bhadra et al., 2013)
Polyaniline polymer/SWCNT for capacitive deionization electrodes	100 μS cm^{-1} aqueous NaCl solution	20 mL min^{-1} feed flow rate, 1.2 V voltage	78.4% salt removal efficiency, 100% regeneration rate	(Yan et al., 2012a)

0.1% MWCNT/polyamide polymer	Aqueous NaCl solution	2000 mg L^{-1}, pH 7, 25 °C, transmembrane pressure 16 bar	28.05 L m^2 h water flux and N 90% salt rejection	(Zhao et al., 2014)
Polyethersulfone/0.045% MWCNT	200 mg L^{-1} each of Na_2SO_4, $MgSO_4$, and NaCl	4 bar, pH (7.0 ± 0.1), 25 ± 1 °C	Rejection of Na_2SO_4 (65%), $MgSO_4$ (45%), and NaCl (20%)	(Vatanpour et al., 2014)
MWCNT/polyethyleneimine-poly (amide–imide) hollow fiber forward osmosis	Deionized water (feed water)	0.5 M $MgCl_2$ solution (draw solution), 1 bar	87.8% $MgCl_2$ rejection	(Goh et al., 2013)
MWCNT/aromatic polyamide (PA) (15 mg MW-CNT/g PA)	Aqueous NaCl solution	(4000 ppm and 20 °C) 3.9 MPa	76% salt rejection	(Shawky et al., 2011)

MWCNT/carbonized nanofibrous membranes	Monochloroacetic acid (feed volume: 15 mL of 80 mg L^{-1})	Voltage: 14 to 18 kV and solution flow rate: 0.6 and 1.2 mL h^{-1}	Removal efficiency: 85%, rejection coefficient: 9%	(Asensio et al., 2013b)
Zwitterion functionalized CNT/polyamide nanocomposite membrane	1000 mg L^{-1} of Na^{+} (or ~2500 mg L^{-1} NaCl or 43.5 mM)	Water and ion flux pressure drop: 3.65 MPa (530 psi)	The rejection ratio is 20% for CNTs having five carboxylic acid groups	(Asensio et al., 2013a)
CNT-Bucky-papers/vacuum filtration in 99.8% pure propane-2-ol	Synthetic seawater (35 g L^{-1} NaCl solutions)	Hydrophobic membrane (contact angle 113°), highly porous (90%), thermal conductivity of 2.7 kW m^{-2} h	99% salt rejection and a flux rate of ∼12 kg m^{-2} h	(Aciego Pietri and Brookes, 2009)
Polyvinyl chloride/MWCNT-co-copper nanolayer composite nanoparticles	0.5M NaCl solution	Flux: 6.10 (mol m^{-2} S) 10^{5} and electrical resistance: 19 Ω cm^{2}	Ionic permeability and flux increased from 0.5 to 8 wt% in prepared membrane	(Sanderson et al., 2015)

Vertically aligned-CNT (VA-CNT)	Colloidal silica, dextran, NaCl and Na_2SO_4	Pure water permeability for the VA-CNT 400 L m^{-2} h bar	The ratios of irreversible fouling to total resistance for VA-CNT: 68.8%	(Naidu, 2013)
CNT-film synthesized on macroporous surface of α-alumina support by chemical vapor deposition (CVD) of cyclohexanol and ferrocene	10,000, 20,000 and 30,000 mg L^{-1} of NaCl	Oxidized CNT membrane by HNO_3 and H_2SO_4 was very effective for salty water desalination	Maximum separation% was obtained at the highest feed concentration, temperature and flow rate (30,000 mg L^{-1}, 45 °C, and 500 L h^{-1}, respectively)	(Zanuzzi et al., 2009)
Honeycomb-CNT membrane (HC-CNT)	500 mM NaCl	CNT diameter had a marginal effect on the desalination of this new technology.	Increased salt rejection (95%) by applying an electric field of 0.8 V nm^{-1}.	(Castillejo and Castelló, 2010)

Carbon nanotube immobilized membrane (CNIM)	3.4 wt% NaCl solutions	Permeate flux reached up to 19.2 kg m^{-2} h for 3.4% NaCl concentration	More than 99% of the salt reduction was achieved, and the conductivity of the produced fresh water in the range of 1–2.5 μs cm^{-1}	(Abdelhafez et al., 2014)

Corry (2008) reported the size difference effect of CNT-based membranes on the performance of water desalination and developed models of the transport behavior of water molecules. The results showed that membranes comprising sub-nanometer diameter CNTs achieved a higher performance of water desalination when CNTs were used in reverse osmosis (RO). The use of hollow CNTs in membrane desalination with high removal performance was also reported (Goh et al., 2013). Water molecules can travel through CNT-based membranes without much impedance, which makes the membranes applicable under high flux conditions. The increased hydrophobicity of MWCNTs (e.g., functionalized polyamide polymer) can enable frictionless water migration across the membranes made of the nanotubes (Shawky et al., 2011; Zhao et al., 2014).

Modification of the CNT pores to selectively sense and reject contaminants can be achieved without even causing a significant damage to the inner surface characteristics of the nanotubes (Cohen-Tanugi and Grossman, 2012). A membrane developed by supporting oxidized CNTs on macroporous α-alumina was able to retain salinity-causing ions even at high temperatures (Tofighy et al., 2011). This could be achieved through the combined effects of ion retention and unimpeded water permeation across the CNT-membrane. The concentration of ions in the feed water may significantly influence the desalination efficiency of the membrane (Corry, 2011; Bhadra et al., 2013). However, owing to the easy water permeation property of the CNT-membrane, the effect of ion concentration may be largely overcome (Daer et al., 2015). In addition, specially-aligned CNTs may generate desirable channels in the membrane enabling a highly efficient desalination performance, and can act as “gatekeepers” for a size controlled separation process (Das et al., 2014). In terms of energy consumption, CNT membranes are a more cost-effective desalination technology than RO and forward osmosis (FO) (Fritzmann et al., 2007; Jia et al., 2010; Elimelech and Phillip, 2011; Goh et al., 2013). Despite its relatively short research history, CNT-based desalination technologies are developing at a fast pace, and have seen many pilot to full-scale deployments in water treatment plants worldwide.

7. Interaction of CNTs with environmental colloids

Numerous environmental remediation technologies frequently require the remediation materials to be directly introduced into the contaminated soil, air, or water. At the same time, the behaviors of nano-sized engineered remediation materials in the environment are not fully known, and these materials can be harmful to the native ecology of the application site. This has sparked a debate as to whether CNTs are risk-free for remediation purposes. One can logically assume that CNT mobility through porous media (e.g., soil) may be restricted if they are grafted on large micro-particles (e.g., clay minerals). The clay minerals themselves are inert and naturally abundant in the environment.

Only a limited number of studies have investigated the role of environmental micro-nanoparticles such as clay minerals on the fate and availability of CNTs. The effect of clay minerals may largely depend on the type of surfactants used to obtain a stable suspension of CNTs. For example, MWCNT suspensions stabilized by cetyltrimethylammonium bromide were easily agglomerated by montmorillonite and kaolinite, whereas the same suspension stabilized by sodium dodecyl sulfate was unaffected by these clay minerals (Han et al., 2008). Two mechanisms were suggested to explain the effect of clay minerals on CNT agglomeration behaviors either when clay minerals removed the surfactants from the solution and the MWCNT surface or when surfactant molecules formed bridges between clay minerals and MWCNTs (Han et al., 2008). In a surfactant-free environment, the affinity of MWCNTs toward clay minerals followed the order of: smectite < kaolinite < shale under a given electrolyte concentration (Na^+) (Zhang et al., 2012). As the negative surface charge of smectite was greater than that of kaolinite, the latter imparted a lower repulsive force to the negatively charged

MWCNTs and more efficiently agglomerated them as compared to kaolinite (Zhang et al., 2012). By contrast, shale attracted CNTs through hydrophobic interactions due to the higher concentration of organic matter (Zhang et al., 2012). Environmental conditions (e.g., ionic strength) would significantly influence the above interactions. For example, a higher concentration of electrolytes or electrolytes with a higher valent cation would promote the rapid agglomeration of CNTs in the presence of any clay minerals (Saleh et al., 2008; Zhang et al., 2012; Schwyzer et al., 2013).

The interaction of CNTs with environmental macro or nanoparticles might also influence the former's adsorption capacity towards contaminant species. For example, Chen et al. (2017) recently reported that SiO_2 or Al_2O_3 nanoparticles inhibited the adsorption of sulfamethoxazole by MWCNTs. The increasing particle size of SiO_2 nanoparticles significantly affected sulfamethoxazole adsorption capacity, whereas Al_2O_3 provided a reverse effect in terms of their particle sizes (Chen et al., 2017). These results were probably due to the variable hetero-aggregation behavior of the nanoparticles with CNTs depending on their dissimilar surface change properties. Further research is needed to investigate the aggregation behavior of CNTs in the presence of different macro and nanoparticles in the environment so as to optimize their contaminant remediation ability.

8. Economic assessment

Cost can be an important obstacle to the practical applications of CNT-based materials for environmental remediation. Hundreds of thousands of liters of wastewater are produced every year, and thousands of hectares of soils are contaminated in various countries. Remediating such a huge volume of contaminated water and soil requires a large amount of CNTs. Some industrial-scale productions of CNTs have recently started, but this technology remains inaccessible to many environmental cleanup companies. Generally, MWCNTs are cheaper than

SWCNTs (Apul and Karanfil, 2015; Jia and Wei, 2017). The price of commercial CNTs falls in the ranges of $0.6 to $25 per g of MWCNTs and $25 to $300 per g of SWCNTs depending on the purity level and tube diameter of the products, as well as on the type of functionalization undertaken in their preparation (www.cheaptubes.com; accessed on 07 May 2017). Thus, MWCNTs are more frequently used than SWCNTs in environmental applications. However, SWCNTs show better performance than MWCNTs in some environmental sensing applications. MWCNTs might offer additional indirect benefits because they are usually less toxic to non-target microorganisms in the environment than SWCNTs (Shrestha et al., 2013; 2015). Nonetheless, the development of technologies for large-scale production of high quality CNTs (possibly from renewable carbon and catalyst precursors) (Gournis et al., 2002; Bakandritsos et al., 2005; Su, 2009) requires further research to make CNT-based environmental remediation technologies accessible. The cost of CNT-based water/wastewater treatment technologies also depends on (i) the cost/complexity of CNT functionalization, (ii) the type of water treatment (i.e., batch vs. continuous flow process), (iii) the need for solid/liquid separation (e.g., magnetic CNTs can be easily recovered), and (iv) the recycling cost and efficiency (i.e., CNTs typically exhibit higher regeneration capability). Contaminant concentration in effluents can be one of the most critical factors in determining whether to employ a batch or fixed bed treatment process to achieve an efficient and cost effective treatment (Dichiara et al., 2015c). Empirical models can be used to choose the most appropriate treatment process (either batch or fixed bed) that would minimize the adsorbent loading and ultimately achieve the targeted removal of contaminants (Dichiara et al., 2015c). Further research is needed to optimize the process parameters for cutting costs in CNT-based water treatment technologies.

9. Conclusions and future research direction

CNTs exhibit excellent physicochemical, mechanical, thermal, and electrical properties that can be maximized for applications in environmental adsorbents, sensors, membranes, and catalysts. Designer CNTs, which are prepared through various functionalization or modification processes, demonstrate remarkable enhancement in contaminant removal efficiency and offer easy nanomaterial recovery and regeneration. CNTs can be functionalized/modified via oxidation, alkali activation, incorporation of magnetic properties, grafting of metal and metal oxide catalysts, hybridizing with other carbon nanomaterials, and derivatization with special chemical molecules. CNT-based materials can interact with diverse organic, inorganic, and biological contaminants, including heavy metals, radionuclides, pharmaceutical compounds, pesticides, dyes, hydrocarbons, and harmful microorganisms. The mechanism of contaminant removal through CNTs can be engineered in terms of their surface functionalization or modification type. In general, CNTs adsorb organic contaminants through hydrophobic interaction, π–π binding and micropore filling, and polar species through the formation of specific chemical bonds with the aid of surface functional groups and micropore filling. Some practical applications of CNTs in wastewater purification and desalination through membrane technology have been reported. However, the high cost of the materials, their complex interactions with environmental colloids and microorganisms, and the lack of pilot- and industrial-scale studies impede the widespread uptake of CNT-based water treatment technologies. The commercial acceptance of CNT in the environmental remediation industry might be improved by undertaking the following future research:

- More pilot- and large-scale studies to test the remediation performance of various CNT-based materials.
- Optimization of various process parameters for the application of CNT materials under diverse environmental conditions.
- Optimization of CNT modification and functionalization method.

- Development and testing of new CNT-based remediation technologies.
- Cost-effective synthesis of CNTs from renewable resources.

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