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

3

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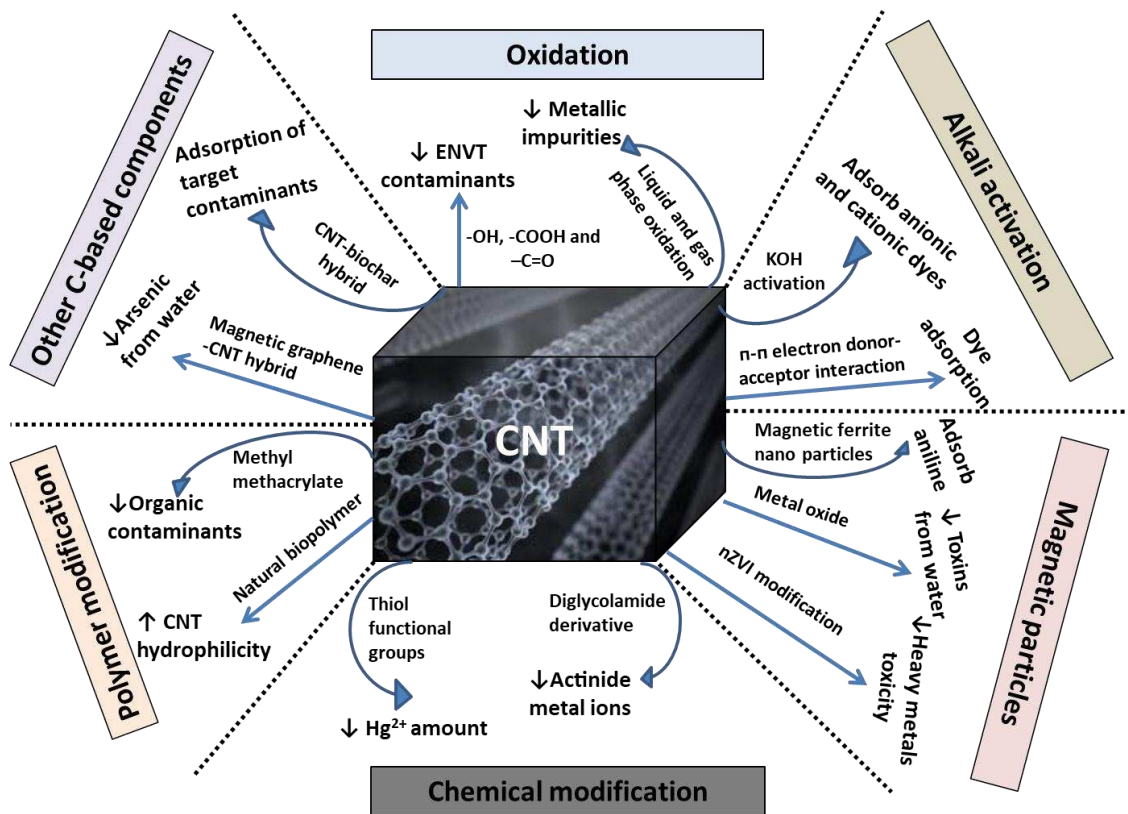
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26 **Highlights**

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

32

33 **Graphical abstract**



34

35

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67 **ABSTRACT**

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

87

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

90

91 **1. Introduction**

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

106 The search for effective and low-cost materials that can eliminate present and future harmful
107 contaminants and treat hazardous wastes in the environment is a scientific and technological
108 issue of paramount importance. Scientists around the world have been searching for various
109 materials - either of natural or synthetic origin - to fit into the purpose of environmental
110 remediation. However, conventional materials (e.g., zeolite, clay minerals, and agricultural/
111 industrial waste-based adsorbents) often experience drawbacks in practical applications,
112 including (i) poor contaminant removal capacity, (ii) lack of contaminant interaction
113 specificity, and (iii) environmental instability (Sud et al., 2008; Bhatnagar and Sillanpää, 2010;
114 Bhatnagar et al., 2011; Sarkar et al., 2012; Perego et al., 2013). Some adsorbents prepared from
115 industrial and municipal waste materials may also pose risks of secondary pollution (Bhatnagar

116 and Sillanpää, 2010). In this context, carbon materials, such as activated carbon and biochar,
117 occupy a unique position in the hierarchy of adsorbent materials for eliminating toxic
118 substances in air, water, and soil (Mohan et al., 2014; Ok et al., 2015). Activated carbon and
119 biochar may also encounter a number of problems when applied under the field conditions,
120 such as poor adsorption specificity and biofouling. In addition, over the last decade, carbon
121 nanotubes (CNTs) and graphene-based materials have seen an extensive use for environmental
122 remediation (Mauter and Elimelech, 2008; Apul and Karanfil, 2015; Perreault et al., 2015).

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

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

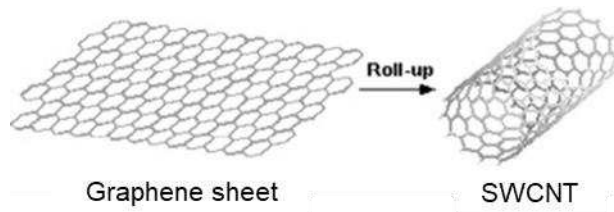
140 The current paper presents a critical review of existing literature on the interactions of
141 various contaminants with CNTs in water and soil environments. Some recent reviews focused
142 on CNT-based adsorption against specific types of contaminants in aqueous solutions (Gupta
143 et al., 2013;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

149

150 **2. CNT structure and types**

151 CNTs are composed of enroled cylindrical graphitic sheets (known as graphene sheets) in
152 which carbon atoms are arranged in sp^2 hybridization at the corners of hexagons (Thostenson
153 et al., 2001) (Fig. 1). The seamless cylinders give rise to an outer diameter from about 1 to
154 30 nm (Aqel et al., 2012). CNTs have nanometer-sized diameters but micrometer-sized lengths,
155 which should yield a length-to-diameter ratio greater than 1,000 (Popov, 2004; Aqel et al.,
156 2012). Previous studies have investigated the structural properties of CNTs (e.g., diameter,
157 length, purity, defect, porosity, chirality, multi-wall vs. single-wall, straight vs. helical tubes,
158 and individual vs. bundled structure) (Iijima and Ichihashi, 1993; Ajayan, 1999; Charlier, 2002;
159 Wepasnick et al., 2010; Moradi et al., 2012). Two commercially available forms of CNTs,
160 namely single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube
161 (MWCNT), are commonly used as environmental adsorbents (Collins et al., 2000; Penza et al.,
162 2004; 2007). Rolling of a single graphene layer into a cylindrical shape gives the SWCNT,
163 while rolling of many concentric SWCNTs into a tubular shape produces the MWCNT (Iijima
164 and Ichihashi, 1993). The interlayer distance in MWCNTs is nearly 0.33 nm, which is

165 approximately the same as the distance between graphene layers in graphite (Aqel et al., 2012).
166 Other CNT-related structures, which are less known for environmental applications, include
167 nanobud (fullerene combined with CNT), graphenated CNT (graphitic foliates along the side
168 wall of MWCNT), peapod (fullerene trapped inside CNT), torus (doughnut-shaped CNT), and
169 cup-stacked CNT (stacked microstructure of graphene layers) (Ren et al., 2013).



170

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

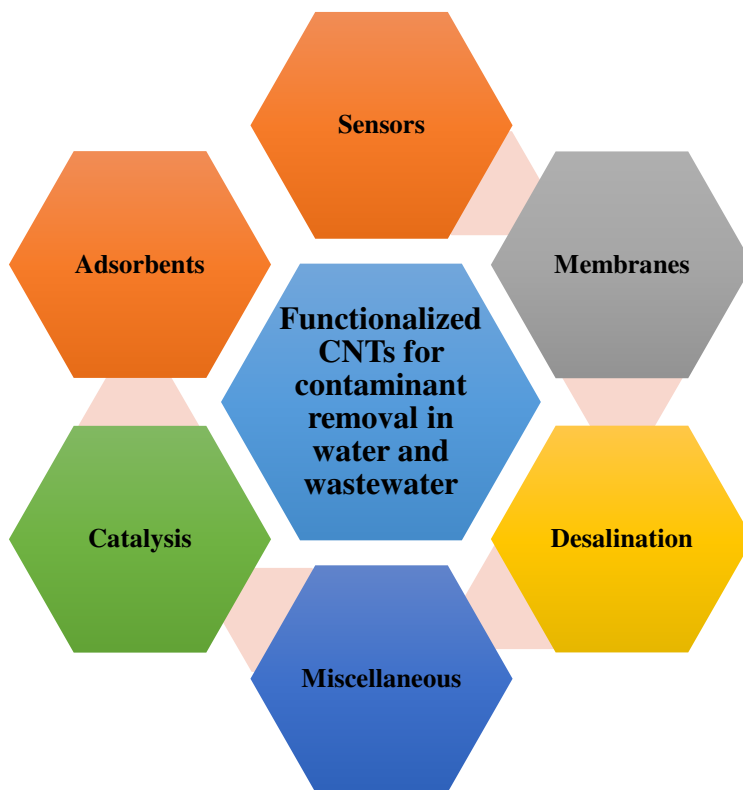
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173 A number of techniques, including chemical vapor deposition (CVD), laser ablation, and
174 arc discharge have been employed for CNT synthesis (Prasek et al., 2011). One of the most
175 common routes of CNT synthesis is CVD through vapor deposition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

184

185 **3. CNTs for various environmental applications**

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



189

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

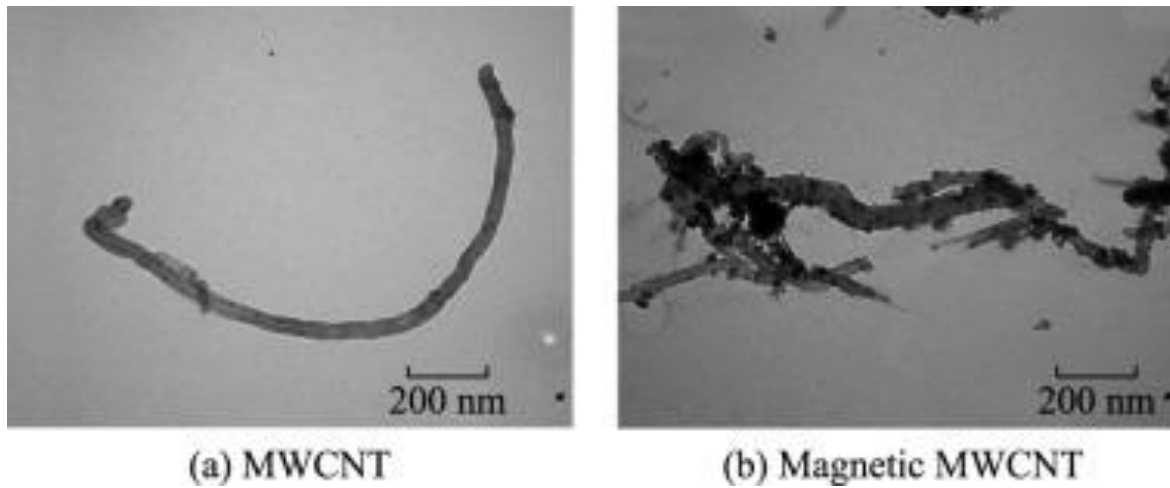
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192 *3.1. Adsorbents*

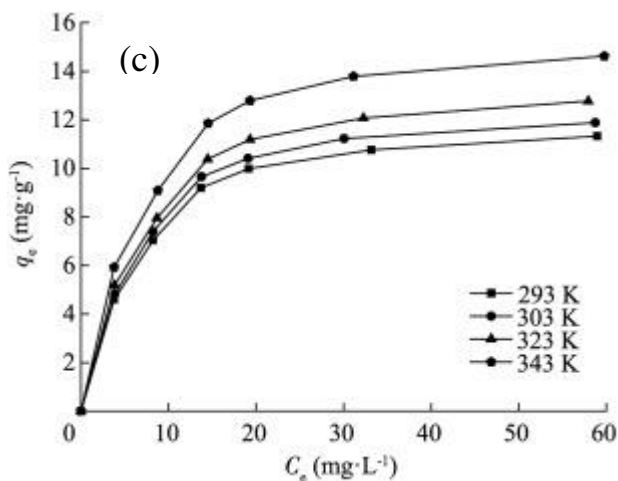
193 The basic properties of CNTs (e.g., large specific surface areas and high chemical/thermal
194 stabilities) make such materials attractive for adsorbing contaminants from water and
195 wastewater. The adsorption properties of CNTs have been investigated against a series of toxic
196 agents in water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

201 second-order models, respectively. The thiol-functionalized MWCNTs generally removed
202 Hg(II) more efficiently than amino-functionalized MWCTS from wastewater (Hadavifar et al.,
203 2014).

204



205



206

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

209

210 The removal of Cr(VI) by magnetic MWCNTs from wastewater was also investigated
211 (Huang and Chen, 2014) (**Figs. 3 a and b**). An increase in the initial adsorbate concentration
212 and prolonged contact time increased the Cr(VI) adsorption capacity of the magnetic
213 MWCNTs. However, the adsorption capacity decreased with increasing adsorbent dosage. The

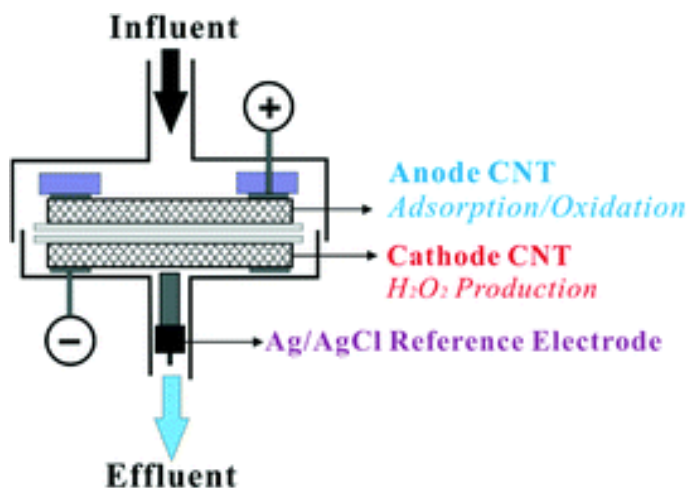
214 pseudo-second-order model best explained the kinetic behavior of the adsorption process. The
215 calculated value of the Gibbs free energy demonstrated a thermodynamically spontaneous, and
216 endothermic adsorption process with an enthalpy deviation of $3.835 \text{ kJ mol}^{-1}$. Many studies
217 have been conducted to confirm whether CNTs are highly effective adsorbents for eliminating
218 various harmful substances in water and wastewater (section 4).

219

220 3.2. Membranes

221 High stability, considerable flexibility in use and large surface area enable the development
222 of CNT membrane filters as highly effective treatment media for chemical and biological
223 contaminants in water and wastewater (Jame Sadia and Zhou, 2016). For example, Liu et al.
224 (2015) investigated electrochemically active CNT filters for eliminating organic pollutants
225 from wastewater using a point-of-use treatment technology (**Fig. 4**). Since H_2O_2 alone could
226 not remove phenolic species effectively from the system, H_2O_2 was activated anodically to
227 generate radical species. With an average oxidation rate of $0.059 \pm 0.001 \text{ mol h}^{-1} \text{ m}^{-2}$, the
228 removal efficiency of phenol was stable at $87.0 \pm 1.8\%$ continuously over 4 h. Such removal
229 was influenced by the combined effects of several variables (e.g., electrode material, cathode
230 potential, pH, flow rate, and dissolved oxygen) (Liu et al., 2015). This work demonstrated the
231 potential of developing inexpensive filtration technology using CNTs to meet the ever-
232 increasing demand of adequate clean water.

233



234

235 **Fig. 4.** Schematic of CNT-filter based electrochemical wastewater treatment system having *in*
 236 *situ* H₂O₂ generation assembly (Liu et al., 2015).

237

238 3.3. Catalysts

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

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

255

256 3.4. Sensors

257 Desirable properties of CNTs, including non-metallic nature, electronic transport, minute
258 size per amount of material, and thermopower (voltages between junctions caused by
259 interjunction temperature differences) can be exploited for environmental sensing applications
260 (Jijun et al., 2002; Chakrapani et al., 2003; Penza et al., 2004; Kazachkin et al., 2008). As such,
261 their applications have been validated from diverse fields or modes, including resistive sensors,
262 capacitive sensors, chemical field effect transistors, gas ionization sensors, thermoelectric
263 response, and CNT-aided optical (or acoustic) sensors. For example, Karimi-Maleh et al.
264 (2014) prepared a highly sensitive electrochemical sensor using a ZnO/CNT nanocomposite to
265 detect hydrazine in wastewater in the presence of phenol. The authors achieved simultaneous
266 detection of hydrazine and phenol in wastewater at as low as 8.0 nmol L^{-1} concentrations using
267 square wave voltammetry (SWV) technique (3σ) (Karimi-Maleh et al., 2014).

268 A selective Hg(II) sensor was developed by adsorbing cold mercury vapor on SWCNTs in
269 industrial wastewater (Safavi et al., 2010). Various levels of Hg(II) adsorption on SWCNTs
270 yielded differential impedances in the adsorbent material, and monitoring of these impedance
271 values allowed to sense as low as $0.64 \mu\text{g mL}^{-1}$ Hg(II) in different types of wastewater samples
272 (Safavi et al., 2010). Recently, de Oliveira et al. (2015) investigated CNTs based on voltametric
273 sensors to detect anthraquinone hair dyes in wastewater. Glassy carbon electrodes modified
274 with MWCNTs (activated in the presence of sulfuric acid) performed the detection of
275 anthraquinone in water samples at ultra-low concentration ($2.7 \times 10^{-9} \text{ mol L}^{-1}$) (de Oliveira et
276 al., 2015). Likewise, a carbon paste electrode was prepared by modifying ZnO-CNT composite
277 with 8,9-dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin for detecting

278 hydroxylamine in water the presence of phenol and sulfite (Gupta et al., 2015). In water and
279 wastewater samples, the nanocomposite showed 0.04, 0.1 and 0.3 μM detection limits for
280 hydroxylamine, phenol and sulfite, respectively (Gupta et al., 2015). Overall, CNT-based
281 sensors have exhibited good analytical performance, good sensitivity, and excellent stability
282 for real world applications. Thus, the use of CNT-based sensors can be further extended to
283 direct/real world applications in water and wastewater samples.

284

285 *3.5. Oil spill sponges*

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

303

304 **4. Functionalization/modification of CNTs for environmental applications**

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

319

320 *4.1. Oxidation*

321 Surface oxidation has been the most common and easiest technique to create oxygen-
322 containing $-OH$, $-COOH$ and $-C=O$ groups on CNT structures. Oxidation is typically
323 performed under a refluxing condition in the presence of a single or a mixture of inorganic
324 acids (e.g., HNO_3 and H_2SO_4) and an oxidizing agent (e.g., H_2O_2 , $KMnO_4$, and $NaOCl$). Acid
325 treatment is often carried out just after CNT synthesis to eliminate metallic impurities (e.g., the
326 catalysts used for CNT synthesis) from products. After acid treatment, CNTs are either ready
327 for direct environmental applications or have surface reaction sites that facilitate the grafting

328 of guest moieties on the surface to incorporate additional functionalities (Chen et al., 2009c;
329 Cho et al., 2010; Mishra et al., 2010; Fang and Chen, 2012; Wei et al., 2017). Gas-phase
330 oxidation of CNT surfaces was also carried out through heat treatment (Nagasawa et al., 2000)
331 or plasma treatment (Yu et al., 2011) under O₂ gas. However, liquid-phase oxidation is more
332 extensively used for both removing metal impurities and functionalizing products. Gas-phase
333 oxidation may sometimes burn the thinner structure of SWCNTs (Nagasawa et al., 2000). CNT
334 oxidation in an O₂ or CO₂ environment can etch away the tube caps causing a layer-by-layer
335 peeling of the outer layers, which may dramatically increase the surface area of the oxidized
336 materials (Ajayan et al., 1993; Tsang et al., 1993). Liquid- or gas-phase oxidation can also
337 clean impure amorphous carbon from synthesized CNTs and increase the number of effective
338 reaction sites (Datsyuk et al., 2008).

339 Due to their intrinsic hydrophobic behavior, CNTs do not easily disperse in polar solvents
340 such as water, making it difficult to use this material for cleaning up contaminants from
341 wastewater. This issue can be solved by cutting the MWCNTs to a shorter length (several
342 hundred nm) and/or creating hydrophilic functional groups on CNT surfaces through
343 sonication in mixed acids (Saito et al., 2002; Avilés et al., 2009). In a comprehensive study,
344 (Datsyuk et al., 2008) found that among two acidic treatments (HNO₃ and H₂SO₄-H₂O₂
345 mixture), nitric acid treatment under refluxing conditions achieved the highest degree of
346 MWCNT functionalization (e.g., nanotube shortening and generation of additional defects in
347 the graphitic network). On the other hand, basic oxidation in NH₄OH/H₂O₂ yielded better
348 structural integrity of MWCNTs by facilitating the maximum removal of impurities
349 (amorphous carbon and metal oxides) (Datsyuk et al., 2008). Acid functionalization can be
350 accelerated by microwave irradiation for 20 to 40 min (Kuo and Lin, 2009; Addo Ntim and
351 Mitra, 2011, 2012).

352

353 *4.2. Alkali activation*

354 One disadvantage of CNTs relative to activated carbon is their relatively low surface area,
355 which may impose an adverse impact on contaminant adsorption. In addition, aggregation of
356 nanoparticles may result in mesoporous structure of CNTs that contains interstices and grooves
357 (Ma et al., 2012). This feature may induce strong affinitive interactions in CNTs and
358 subsequently cause structural alterations (Ma et al., 2012). Activation of carbon materials,
359 including CNTs, with alkali treatment can address this issue and effectively improve the
360 surface area and pore volume (Foo and Hameed, 2011; Ma et al., 2012). The alkali activation
361 of CNTs by Ma et al. (2012) involved heating a solid powdered mixture of MWCNTs and
362 KOH at 750 °C for 1 h under an argon atmosphere in a horizontal tube furnace. After washing
363 in concentrated HCl followed by deionized water, the dried powder successfully adsorbed dye
364 compounds (both anionic and cationic) from aqueous solutions (Ma et al., 2012). Multiple
365 interaction mechanisms, including hydrogen bonding, π - π electron-donor-acceptor interaction,
366 electrostatic interaction, and mesopore-filling, resulted in effective dye adsorption on the
367 alkali-activated MWCNTs (Ma et al., 2012). The alkali-activated CNTs were also successfully
368 used to remove toluene, ethylbenzene, and m-xylene from aqueous solutions (Yu et al., 2012).
369

370 *4.3. Modification with magnetic particles*

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

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

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

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

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

407

408 *4.4. Modification with nonmagnetic metal oxide*

409 To achieve superior affinity toward contaminants, CNTs can be modified with various metal
410 oxides. Transition metals, such as Fe, Zr, Ag, Ti, Ce, and bimetallic Pd-Fe (Xu et al., 2012),
411 were successfully used for preparing metal oxide-CNT hybrids that adsorbed toxic elements
412 (e.g., As, F, Cu, Cd, and 2,4-dichlorophenol) from water (Peng et al., 2005; Woan et al., 2009;
413 Mishra and Ramaprabhu, 2010; Addo Ntim and Mitra, 2011; 2012; Ramamurthy et al., 2011;
414 Venkata Ramana et al., 2013). The modification method is simple and often involves oxidative
415 functionalization of the CNTs followed by alkali precipitation of the target metal oxide on
416 surfaces of the nanotubes. The pre-functionalized CNTs are dispersed in the aqueous solution
417 of the metal, and a strong alkali solution (5–7 M) is slowly added. The amount of alkali should
418 be greater than the equivalent stoichiometric amount of the metal (final pH \geq 10) to ensure that
419 the oxidation reaction is complete. The metal oxide formation was facilitated by mild heating
420 (85 °C) of the reaction mixture openly or under microwave irradiation (Addo Ntim and Mitra,
421 2011; 2012).

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

427 High-temperature annealing was not necessary to achieve the photo-reactivity; the composite
428 was only vacuum-fired at 60 °C for 6 h. Non-magnetic Fe₂O₃ nano-catalysts were also
429 decorated on MWCNTs by a simple impregnation of the CNTs with an aqueous Fe(NO₃)₃
430 solution followed by a 200 °C calcination for 4 h (Liao et al., 2009). The resulting catalysts
431 were able to degrade phenolic contaminants (e.g., resorcinol and ortho-chlorophenol) in a
432 H₂O₂-mediated Fenton reaction (Liao et al., 2009). The TiO₂-decorated MWCNTs were also
433 used for the photocatalytic degradation of organic contaminants, such as 2,6-dinitro-p-cresol
434 and 2,4-dinitrophenol, under solar irradiation (Wang et al., 2009a; 2009b).

435

436 *4.5. Modification with zero-valent iron*

437 Among manufactured nanoparticles, zero-valent iron (nZVI) has already received
438 widespread attention for practical environmental remediation (Crane and Scott, 2012;
439 Stefaniuk et al., 2016; Zou et al., 2016). Very high in-situ reactivity in the material is achieved
440 at only a small synthesis cost, and this material is also easy to use in practical applications for
441 contaminated groundwater remediation. Therefore, nZVI has been the most widely studied
442 nanomaterial used for environmental remediation (Elliott and Zhang, 2001; Crane and Scott,
443 2012; Chekli et al., 2016). To prevent the oxidation and agglomeration of nZVI and prolong
444 the material's reactivity, it was supported on various micro- and nano-particle supporting
445 materials, including biochar (Mandal et al., 2017), clay minerals (Üzüm et al., 2009; Shi et al.,
446 2011), and zeolite (Wang et al., 2010). Similarly, nZVI was also supported on CNTs and
447 successfully used for removing hexavalent chromium (Lv et al., 2011), selenite (Sheng et al.,
448 2016), azo dyes (Reza Sohrabi et al., 2015), and nitrobenzene (Jiao et al., 2016) from
449 wastewater. The presence of other anions (even at high concentrations) did not affect the
450 chromate reduction ability of designer materials (Lv et al., 2011). The decoration of MWCNTs

451 with nZVI can significantly enhance the contaminant removal capacity of the material (Lv et
452 al., 2011; Reza Sohrabi et al., 2015; Jiao et al., 2016; Sheng et al., 2016).

453

454 *4.6. Specific chemical derivatization or modification*

455 Several specific chemical derivatizations or modifications of CNTs were reported to
456 improve the material's affinity toward specific contaminant elements or compounds. Carboxyl-
457 functionalized SWCNTs (SWCNT-COOH) were derivatized with thiol functional groups by
458 reacting with ethanol-dissolved cysteamine hydrochloride (Bandaru et al., 2013). The reaction
459 was conducted in the presence of N-hydroxysuccinimide and a coupling agent (e.g., 1-ethyl-
460 (3-(3-dimethylaminopropyl) carbodiimide) (Bandaru et al., 2013). Such derivatization
461 processes may improve the dispersibility of CNTs in aqueous solutions and its affinity toward
462 heavy metal cations, including Hg. Bandaru et al. (2013) reported that thiol-derivatized
463 SWCNTs adsorbed a three-fold and four-fold greater amount of Hg²⁺ than unmodified
464 SWCNTs and activated carbon, respectively. Similarly, adsorption of actinide ions was
465 achieved by modifying MWCNTs with a ligand, such as a diglycol amide derivative (Deb et
466 al., 2012). The biodegradation or biocompatibility of the resulting CNT adsorbent was
467 engineered by selecting an appropriate ligand. The spent material can be easily incinerated and
468 disposed of due to the organic component in the adsorbent. Other chemical compounds, such
469 as β -cyclodextrin (Fuhrer et al., 2011), iodide/sulfur (Gupta et al., 2014), amino compounds
470 (Vuković et al., 2011; Ji et al., 2012; Hamdi et al., 2015), tannic acid (Tong et al., 2011), and
471 ethylenediamine (Vuković et al., 2010), were also used to modify CNT surfaces. The
472 cyclodextrin molecules were also grafted on CNTs along with magnetic nanoparticles with the
473 aid of plasma technology (Hu et al., 2010; 2011a) or polyaniline (Shao et al., 2010; 2012).
474 Tannic acid-modified MWCNTs were reported to be excellent adsorbents of rare earth
475 elements (e.g., La, Tb, and Lu) (Tong et al., 2011).

476

477 *4.7. Modification with polymers*

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

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

490 Natural biopolymers can also be used to enhance the hydrophilic nature and improve
491 biocompatibility of CNTs in environmental applications. For example, Yan et al. (2012b)
492 reported the covalent grafting of guar gum onto MWCNT surfaces. During an attempt to
493 incorporate magnetic Fe₃O₄ nanoparticles into the designer material, it was found that the
494 biopolymer facilitated a better dispersion of the Fe₃O₄ nanoparticles on the adsorbent surfaces
495 through a supramolecular interaction between its hydroxyl groups and the metal ions; this
496 significantly improved the adsorption of aqueous dye contaminants (Yan et al., 2012b).

497

498 *4.8. CNT immobilization*

499 CNTs are highly resistant to degradation and may impart toxicity to environmental
500 organisms. Therefore, they should be removed from treated water. The limitation of the

501 techniques used to separate these small particles from water may obstruct their widespread use
502 as adsorbents in environmental remediation. This can somehow be tackled by immobilizing
503 CNTs in polymer-carrying electrospun fibrous membranes, in alginate composites or on large
504 particles. For example, Dai et al. (2016) fabricated a laccase-carrying electrospun fibrous
505 membrane by co-electrospinning a poly(D,L-lactide)/laccase/MWCNT mixture. The total
506 removal (synergistic adsorption and degradation) of the target species (e.g., 2,4-
507 dichlorophenol, bisphenol A, and triclosan) by the fabricated material reached 92.6, 95.5, and
508 99.7%, respectively, with 81.7, 90.5, and 85.6% contributions from the enzyme-catalyzed
509 degradation of the respective contaminants (Dai et al., 2016). Li et al. (2010) immobilized
510 CNTs by injecting a homogeneous dispersion of CNTs and sodium alginate into a solution of
511 calcium chloride, with Ca^{2+} serving as the bridging agent. The authors successfully used the
512 resulting material to remove Cu^{2+} from the water. Similarly, a composite fiber containing
513 calcium alginate-MWCNT was obtained via wet spinning method, and the resulting material
514 was used to remove dye compounds (both cationic and anionic) from aqueous media (Sui et
515 al., 2012a). In a novel approach, MWCNTs were inserted into the cavities of diatomite and
516 subsequently supported onto flexible polyurethane foams (Yu and Fugetsu, 2010). The
517 composite material was able to effectively remove organic dye compounds from contaminated
518 water (Yu and Fugetsu, 2010). In a similar approach, a sponge-like natural vermiculite-CNT
519 hybrid was synthesized by intercalating CNTs into the exfoliated vermiculite for oil adsorption
520 (Zhao et al., 2011). Several other clay minerals (e.g., smectite and palygorskite), which are
521 naturally occurring, inexpensive, and non-toxic, have enormous potential to be developed as
522 composite CNT adsorbents. The clay minerals themselves have well known environmental
523 applications due to their high surface reactivity (Sarkar et al., 2012). Combining this feature
524 with CNT composites is expected to promote the development of advanced environmental

525 adsorbents and simultaneously restrict the unwanted mobility of CNTs from the materials
526 (Sarkar et al., 2015).

527

528 *4.9. Modification with other carbon based adsorbents*

529 Hybrid adsorbent materials containing CNTs as a major component have also been used to
530 remove/treat environmental contaminants. A self-assembled graphene–CNT hybrid was
531 prepared by autoclaving a mixed dispersion of pre-exfoliated graphene oxide and MWCNTs
532 in ethanol/water (1:1 v/v) at 200 °C for 6 h (Ai and Jiang, 2012). Sui et al. (2012b) reported the
533 synthesis of graphene–CNT hybrid aerogels in a green process, in which graphene oxide was
534 reduced to graphene by Vitamin C in the presence of HCl. The authors (Sui et al., 2012b)
535 synthesized hybrid aerogels by mixing graphene and MWCNTs under heat treatment and then
536 drying the mixture with supercritical CO₂. Free-standing adsorbent papers were prepared from
537 a mixture of different types of CNTs and graphene. These materials were then used successfully
538 to adsorb both metal cations and nonpolar organic compounds (Dichiara et al., 2014b; 2015b).
539 The prepared nanocomposites thus demonstrated up to four fold and 50% greater adsorption of
540 Cu²⁺ from aqueous solutions than those of activated carbon and CNTs alone, respectively
541 (Dichiara et al., 2015b). A similar material prepared from SWCNTs and graphene nanoplatelets
542 exhibited 25% improvement in adsorption of organic contaminants (e.g., 1-pyrenebutyric acid,
543 2,4-dichlorophenoxyacetic acid, and diquat dibromide) in comparison with either component
544 of the nanocomposites alone (Dichiara et al., 2014b). Similarly, CNT-biochar hybrid materials
545 were prepared in two steps: (i) dip-coating of CNTs on a biochar feedstock in the presence or
546 absence of a surfactant and (ii) slow pyrolysis of dip-coated dried feedstock (for 1 h at 600 °C)
547 under an N₂ environment (Inyang et al., 2014; 2015). The loading of CNTs in these composites
548 was arbitrary. Future research may focus on optimizing the mixing ratio of individual
549 components to achieve the best adsorption of a target contaminant. Care should also be taken

550 to restrict the unwanted mobility of CNTs. The carbon-CNT hybrid material can also be
551 magnetized by incorporating iron oxides. While Vadahanambi et al. (2013) used such a
552 magnetic graphene-CNT hybrid material for removing arsenic from water, Wang et al. (2014)
553 used it for adsorbing cationic dyes (i.e., methylene blue).

554

555 **5. Contaminant treatment by CNTs**

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

572

587 2013; Naidu et al., 2016). Therefore, continuous efforts are needed to find effective materials
588 for cleaning up these contaminants.

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

597 Many synthetic antibiotic compounds are considered to be emerging contaminants in the
598 environment. They are often only partially eliminated from the effluents of drug manufacturing
599 industries or public sewage systems. Therefore, a residual amount of these compounds can
600 reach the surface or groundwater. Although they can be present at low concentrations, such
601 small concentrations can also potentially develop resistance in soil and water microbial species.
602 When compared with an activated carbon and a synthetic carbon xerogel, an MWCNT sample
603 adsorbed almost the same amount of ciprofloxacin as activated carbon and about 40% less than
604 a xerogel (Carabineiro et al., 2011). Following a strong oxidation treatment (7 M HNO₃), the
605 adsorption capacities of the activated carbon and xerogel were drastically reduced, whereas the
606 adsorption by CNT was unaffected. However, a thermal treatment (900 °C) following the
607 oxidation enhanced the ciprofloxacin absorption performance of the activated carbon and
608 xerogel, but not that of the CNTs (Carabineiro et al., 2011). The combined oxidation and
609 thermal treatment increased the surface basicity of the materials and thus enhanced the
610 adsorption of the negatively charged antibiotic compound. Therefore, the removal of antibiotic

611 compounds by CNTs largely depends on the type of compounds themselves (cationic or
612 anionic).

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

628 Among emerging inorganic contaminants, perchlorate (ClO_4^-) anions have received
629 widespread attention because of their disruptive effect on iodine uptake by mammals, which
630 leads to a number of diseases, such as thyroid disorder, neurological damage, and anemia
631 (Dasgupta et al., 2008; Sijimol et al., 2015). CNTs, especially the double-walled ones
632 (DWCNTs) with oxygen-containing functional groups, were found to remove perchlorate from
633 aqueous media (Fang and Chen, 2012). Perchlorate removal by various CNTs was in the order:
634 DWCNTs-oxidized > DWCNTs > SWCNTs > MWCNTs. Fang and Chen (2012) also
635 proposed a combined electrostatic interaction and hydrogen bonding mechanism for the

636 adsorption. However, these mechanisms should be further examined by conducting adsorption
637 tests under different pH values, ionic strengths, organic matter concentrations, and
638 temperatures.

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

649 Magnetic particles decorated with surface-functionalized CNTs can also be used to
650 retain/concentrate emerging contaminants from aqueous media. For example, Guan et al.
651 (2010) used MWCNT functionalized magnetic particles to extract estrogen from solutions.
652 Indiscriminate disposal of medications is the main source of estrogen into the household
653 sewerage systems. As is apparent from the complex synthesis procedure of magnetic CNT
654 adsorbents (Guan et al., 2010), these materials may be inappropriate for treating high volumes
655 of contaminated wastewater owing to the high cost involved, but they can be efficient in
656 developing an analytical separation technique (separating media) for emerging contaminants.
657 A detection limit for diethylstilbestrol, estrone, and estriol estrogens as low as 0.2 ng mL^{-1} was
658 achieved by using a magnetically modified CNT material (Guan et al., 2010). **Table 1**
659 summarizes the examples of cases in which CNTs (with or without surface modification) were
660 used for removing various emerging contaminants from the environment.

661 **Table 1**

662 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, increased with perfluorooctanoate, increasing C-F chain PFOS, perfluorobutane lengths; sulfonate and functionalization perfluorohexane reduced adsorption. sulfonate are 0.05, 0.07, 0.26, 1.61, 5.89 and 157, respectively.

SWCNTs and MWCNTs	Reflux with 65% Perchlorate (ClO_4^-) HNO ₃	Batch adsorption isotherm	As high as 3.55 mg g ⁻¹	DWCNTs adsorbed (Fang and more ClO_4^- than Chen, 2012) SWCNT and MWCNT; oxygen-containing functional groups improved adsorption.
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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; atrazine adsorption of MWCNTs-O (0.85%): 17.35, MWCNTs-O (2.16%): 16.65 and MWCNTs-O (7.07%): 10.50 mg g ⁻¹	Atrazine adsorption (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 (Deng et al., 2012a)

SWCNTs	As received	Tetracycline	Batch adsorption	Freundlich coefficient	Tetracycline	(Ji et al.,
and	(presence of Cu ²⁺)		studies	for SWCNT: 1,150 and	adsorption on	2010a)
MWCNTs				for MWCNT: 240	MWCNTs (larger	
				mmol ¹⁻ⁿ L ⁿ kg ⁻¹	mesoporous	
					interstices) was	
					higher than SWCNT	
					by the presence of	
					Cu ²⁺	
MWCNTs	Coated with	Tetrabromobisphenol	Batch adsorption	As high as 33.7 mg g ⁻¹	The composite also	(Ji et al.,
	magnetic Fe ₃ O ₄	A	studies		adsorbed Pb(II) (75	2012)
	followed by amino				mg g ⁻¹)	
	functionalization					

MWCNTs	Carboxyl functionalization	Mixture of four linear alkylbenzene sulfonates compounds	Batch adsorption studies	Up to 168 mg g ⁻¹	Hydrophobic interaction hydrogen bond formation enabled the adsorption	(Guan et al., 2017)
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664 5.2. *Heavy metals, metalloids and radionuclides*

665 The affinity of CNTs towards heavy metals and metalloids was improved by oxidative
666 modification (Cho et al., 2010; Yu et al., 2011), incorporation of magnetic iron oxides (Chen
667 et al., 2009a; Addo Ntim and Mitra, 2011; Gupta et al., 2011a; Daneshvar Tarigh and
668 Shemirani, 2013), coating with non-magnetic metal oxides (Zhao et al., 2010), thiol
669 derivatization (Bandaru et al., 2013), and sulfur functionalization (Gupta et al., 2014). Among
670 the synthetic iron oxides, a mixture of goethite (α -FeO(OH)), hematite (α -Fe₂O₃), maghemite
671 (γ -Fe₂O₃), and magnetite (Fe₃O₄) was capable of removing trace quantities of heavy metal from
672 water (Addo Ntim and Mitra, 2011). The mechanism of heavy metal adsorption by CNT-based
673 materials is dependent on the employed modification/functionalization treatments (Gupta et
674 al., 2016; Ihsanullah et al., 2016). Generally, metal oxide-CNT composites adsorb heavy metals
675 and metalloids through a synergistic effect of chemisorption and physisorption (Addo Ntim
676 and Mitra, 2011). The adsorption affinity also highly depend on the ionic radius, hydration
677 energy, and hydrolysis potential of the specific contaminant element (Hu et al., 2011b). For
678 example, under similar experimental conditions, Pb(II) removal by iron oxide-coated
679 MWCNTs was greater than Cu(II) (Hu et al., 2011b). The presence of organic co-contaminants
680 also affected the adsorption of heavy metals by CNTs. For example, Cd(II) removal by
681 oxidized MWCNTs was enhanced by the coexistence of 1-naphthol, but the removal of 1-
682 naphthol was independent of the coexistence of Cd(II) in the same system (Yang et al., 2012a).
683 This result was mainly due to the difference in the adsorption mechanisms of the two
684 contaminants on functionalized MWCNTs. While high pH conditions may favor inner-sphere
685 complexation during metal adsorption, low pH may favor outer-sphere complexation and/or
686 ion exchange (Yang et al., 2012a). The adsorption of organic contaminants such as 1-naphthol
687 can take place through π - π bond formation between MWCNT structure and the contaminant's
688 aromatic rings (Yang et al., 2012a).

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

698

699 **Table 2**

700 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 $\mu\text{g g}^{-1}$, respectively	Negatively charged species may adsorb onto positively charged modified MWCNT sites	As (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 and [Sr(II)]	[Ni(II)] and strontium	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 chemical deposition	using vapor (III)]	Sr(II) europium [Eu and	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 aqueous solution	from	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)]	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 ₂ O ₃ -MWCNT)	Lead ions from aqueous solution	Adsorption experiment	Al ₂ O 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 from aqueous solution	[Pb(II)]	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 and cadmium from aqueous solution	[Cu(II)] [Cd(II)]	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)

702 5.3. *Organic dyes*

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

709

710 **Table 3**

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

Dye contaminants	Adsorbent	Modification method	Surface area ($\text{m}^2 \text{g}^{-1}$)	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 ₂ O 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 nanocomposites	MWCNT Fe ₃ -C 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)

712

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

714 ^b NA = not available

715

716 Functionalization of CNTs can enhance adsorption ability of organic dyes (Zare et al.,
717 2015a). Among the various modification methods, oxidized MWCNTs are the most effective
718 in removing methylene orange and methylene blue from water matrixes (Ghaedi et al., 2012;
719 Mahmoodian et al., 2015). A new magnetic MWCNT- κ -carrageenan-Fe₃O₄ nanocomposite
720 was successfully prepared to effectively remove crystal violet (Duman et al., 2016). The new
721 nanocomposite can also be used in CNT modification to increase the adsorption capacity of
722 cationic dyes. Sadegh et al. (2016) showed that an adsorbent synthesized by CNT modification,
723 namely, MWCNT-COOH-cysteamine, could significantly enhance the removal of Amido
724 black 10B (AB 10B). The adsorption capacity of AB 10B using MWCNT-COOH and
725 MWCNT-COOH-cysteamine improved from 50.1 mg g⁻¹ to 90 mg g⁻¹ (80% increase) and 131
726 mg g⁻¹ (162% increase), respectively. In addition, having large surface area, SWCNTs
727 demonstrated good adsorption properties. An excellent adsorption capacity of 496 mg g⁻¹ was
728 obtained for the removal of Blue 29 (RB 29) (Jahangiri-Rad et al., 2013).

729

730 5.4. Pesticides

731 The widespread application of pesticides in agriculture has alarmingly contaminated our soil
732 and water resources. CNTs showed potential for effective removal of several types of pesticides
733 (**Table 4**). Deng et al. (2012a) reported that the adsorptive removal of diuron by as-prepared
734 and oxidized MWCNTs was most favored at pH \geq 7.0. An oxidative modification of CNTs
735 increased the product's surface area and pore volume, which resulted in higher diuron removal
736 performance. The uptake of pesticides (chlordane and *p,p'*-dichlorodiphenyldichloroethylene)
737 in roots and shoots of lettuce crop was reduced by 88% and 78%, respectively, with the use of
738 non-functionalized CNTs, while the same were reduced by 57% and 23%, respectively, with
739 the use of amino-functionalized CNTs (Hamdi et al., 2015). Therefore, CNTs and their types
740 may significantly influence pesticide availability to plants. Investigations into electronically

741 sorted (i.e., semiconducting or metallic types) SWCNTs for the removal of 1-pyrenebutyric
742 acid, diquat dibromide and 2,4-dichlorophenoxyacetic acid from aqueous media revealed that
743 the semiconducting SWCNTs were capable of adsorbing up to 70.6% greater pesticides than
744 the metallic SWCNTs (Rocha et al., 2017). The lack of electron density around the
745 semiconducting SWCNTs would have favored high pesticide adsorption (Rocha et al., 2017).
746 By contrast, the adsorption of pesticides by CNTs is mostly restricted in batch systems, and
747 only a few studies have tested these materials in continuous flow experiments (Dichiara et al.,
748 2015a). The uptake of diquat dibromide in a fixed bed system by SWCNTs and MWCNTs was
749 not as high as in a batch system, but the former allowed the complete removal of the
750 contaminant over time (Dichiara et al., 2015a). Multiple mechanisms (i.e., hydrophobic
751 interaction, π - π binding, and micropore filling) were identified for the adsorption of diquat
752 dibromide by CNTs (Dichiara et al., 2015a). Thus far, information on pesticide removal with
753 the application of CNTs is not as extensive as the data on other organic contaminants.

754

755 **6. CNT-based water treatment technologies**

756 *6.1. Drinking water purification*

757 Compared with many conventional adsorbents commonly used in advanced water treatment
758 processes, CNTs have larger specific surface area. Generally SWCNTs hold a larger surface
759 area than MWCNTs. Surface oxygen content, which is another parameter that influences the
760 contaminant removal performance of CNTs, may be increased through oxidation process. The
761 adsorption capacity can also be increased up to 70% at an appropriate pH value. Enhanced
762 performance is also achieved with neutral PPCP molecules (e.g., triclosan and ibuprofen) than
763 their ionized forms (Wang et al., 2015). The presence of NOM and inorganic salts in the
764 influent may affect the adsorption process (Upadhyayula et al., 2009; Jung et al., 2015). In-
765 depth studies about detailed adsorption mechanisms of multi-pollutants, pilot or full-scale

766 operation of CNT processes, and commercial application of CNTs for drinking water
767 purification processes are still rare. Information on endocrine-disrupting compounds (EDCs)
768 and PPCPs adsorption using CNTs are inadequate as well (Ren et al., 2011). **Table 4**
769 summarizes the treatment performance of selected EDCs and PPCPs in either synthetic water
770 or water treatment plant effluent using different types of CNTs from recent studies. CNT
771 properties (e.g., surface area, charge, and functional groups) and operating parameters (e.g.,
772 pH, contact time, initial concentration, and temperature) play a vital role in determining the
773 treatment capacity of EDCs and PPCPs in CNT-based adsorption systems (Agnihotri et al.,
774 2006; Shi et al., 2010; Ahmed et al., 2012; Wang et al., 2015). Adsorption rate and capacity
775 were related to the physicochemical properties of organic pollutants (e.g., molecular size,
776 shape, hydrophobicity, and charge properties) (Cho et al., 2011; Joseph et al., 2011a; Ncibi and
777 Sillanpää, 2015). Wang et al. (2015) reported that SWCNTs and MWCNTs can effectively
778 remove triclosan, acetaminophen, and ibuprofen. However, in their study, the performance
779 ranged from approximately 10% to 95% owing to various factors. The removal efficiency
780 increased with increasing aromatic ring numbers in the compounds (e.g., ibuprofen < triclosan).

781 **Table 4**

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

EDC and PPCP contaminants	Adsorbent	Surface area (m ² g ⁻¹) 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 115^c (Zaib et al.,
water 2012)

17 α -ethinyl estradiol SWCNTs 407 Synthetic 35.6-35.7^c (Joseph et al.,
water 2011b)

Bisphenol A (BPA) and 17 β -estradiol (E2) SWCNTs NA Synthetic BPA: 122^c; E2: 162^c (Heo et al.,
water 2012)

Bisphenol A (BPA) SWCNTs and 338-467 Synthetic SWCNT: 55.5^c (Renshaw et
MWCNTs wastewater MWCNT: 19.4^c al., 2011)

NSAIDs^f

Diclofenac	MWCNTs	162	WTP	22.3 °	(Sotelo et al., 2012)
			effluent		
Ibuprofen	SWCNTs and MWCNTs	1020,283	WTP	10-95% removal	(Wang et al., 2015)
			effluent		
Bactericide/disinfectant					
Triclosan (TCS)	SWCNTs and MWCNTs	1020,283	WTP	10-95% removal	(Wang et al., 2015)
			effluent		
Triclosan	MWCNTs	281	NA	157.7 °	(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 °	(Sotelo et al., 2012)
Atrazine	SWCNTs	407	Synthetic water	4.97 °	(Jung et al., 2015)
Diuron	MWCNTs	258.6 to 427.5	Aqueous solution	As prepared: 42.6 ° Oxidized: 49.2 °	(Deng et al., 2012a)
Dicholbenil	MWCNTs	83-558	Synthetic solution	17.5 °	(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	

783

784 ^a Adsorption capacity from Brouers–Sotolongo model

785 ^b Distribution coefficient (L kg⁻¹) calculated from Freundlich model

786 ^c q_m = maximum adsorption capacity calculated from Langmuir model (mg g⁻¹)

787 ^d K_F = Capacity factor (mg g⁻¹)/(m³ mg⁻¹) for Freundlich model

788 ^e NA = not available

789 ^f NSAIDs = Nonsteroidal anti-inflammatory drugs

790 ^g Utilization efficiency of the adsorbent in a fixed bed process

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

798

799 **Table 5**

800 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)	SWCNTs 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

<i>E. coli</i>	SWCNTs	407	3.18×10^{12} CFU mL ⁻¹	(Brady-Estévez et al., 2008)
<i>E. coli</i> and <i>B. subtilis</i>	PVK-SWCNTs	NA	>90% inactivation	(Ahmed et al., 2012)
<i>E. coli</i> DH5 α	MWCNTs-Ag	NA	96% inactivation	(Su et al., 2013)
<i>E. coli</i> K12	SWCNTs	407	(79 \pm 9)% inactivation	(Brady-Estévez et al., 2008)

<i>Streptococcus mutants</i>	MWCNTs (surface modified)	250	Viable cells reduced by 7.5 log (Bai et al., 2011)
<i>Agrobacterium</i>	MECNTs	88	Biodegradation efficiencies is 54.2% (Xia et al., 2010)
<i>Escherichia coli (E.coli) K12</i> and <i>Staphylococcus aureus (S.aureus)</i> SH 1000	SWCNTs	NA	CNT aggregation: 6.54×10^{-9} (Upadhyayula et al., 2008) and 8.98×10^{-9} (<i>E. Coli</i>); 1.00×10^{-7} and $1.66 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$
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 <i>E. Coli</i>	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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801

802 ^a q_m = Maximum adsorption capacity (mg g⁻¹)

803 ^b NA = Not available

804 *6.2. Water desalination*

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

811 **Table 6**

812 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,	28.05 L m ² h water flux and N 90% salt rejection	(Zhao et al., 2014)
			transmembrane pressure 16 bar	
Polyethersulfone/0.045% MWCNT	200 mg L ⁻¹ each of Na ₂ SO ₄ , MgSO ₄ , and NaCl	4 bar, pH (7.0 ± 0.1), 25 ± 1 °C	Rejection of Na ₂ SO 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)	76% salt rejection	(Shawky et al., 2011)
		3.9 MPa		

MWCNT/carbonized membranes	nanofibrous	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 CNT/polyamide membrane	functionalized nanocomposite	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 ₂ SO 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 ₂ SO 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)

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

824 Modification of the CNT pores to selectively sense and reject contaminants can be achieved
825 without even causing a significant damage to the inner surface characteristics of the nanotubes
826 (Cohen-Tanugi and Grossman, 2012). A membrane developed by supporting oxidized CNTs
827 on macroporous α -alumina was able to retain salinity-causing ions even at high temperatures
828 (Tofighy et al., 2011). This could be achieved through the combined effects of ion retention
829 and unimpeded water permeation across the CNT-membrane. The concentration of ions in the
830 feed water may significantly influence the desalination efficiency of the membrane (Corry,
831 2011; Bhadra et al., 2013). However, owing to the easy water permeation property of the CNT-
832 membrane, the effect of ion concentration may be largely overcome (Daer et al., 2015). In
833 addition, specially-aligned CNTs may generate desirable channels in the membrane enabling a
834 highly efficient desalination performance, and can act as “gatekeepers” for a size controlled
835 separation process (Das et al., 2014). In terms of energy consumption, CNT membranes are a
836 more cost-effective desalination technology than RO and forward osmosis (FO) (Fritzmann et
837 al., 2007; Jia et al., 2010; Elimelech and Phillip, 2011; Goh et al., 2013). Despite its relatively

838 short research history, CNT-based desalination technologies are developing at a fast pace, and
839 have seen many pilot to full-scale deployments in water treatment plants worldwide.

840

841 **7. Interaction of CNTs with environmental colloids**

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

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

863 MWCNTs and more efficiently agglomerated them as compared to kaolinite (Zhang et al.,
864 2012). By contrast, shale attracted CNTs through hydrophobic interactions due to the higher
865 concentration of organic matter (Zhang et al., 2012). Environmental conditions (e.g., ionic
866 strength) would significantly influence the above interactions. For example, a higher
867 concentration of electrolytes or electrolytes with a higher valent cation would promote the rapid
868 agglomeration of CNTs in the presence of any clay minerals (Saleh et al., 2008; Zhang et al.,
869 2012; Schwyzer et al., 2013).

870 The interaction of CNTs with environmental macro or nanoparticles might also influence
871 the former's adsorption capacity towards contaminant species. For example, Chen et al. (2017)
872 recently reported that SiO₂ or Al₂O₃ nanoparticles inhibited the adsorption of sulfamethoxazole
873 by MWCNTs. The increasing particle size of SiO₂ nanoparticles significantly affected
874 sulfamethoxazole adsorption capacity, whereas Al₂O₃ provided a reverse effect in terms of
875 their particle sizes (Chen et al., 2017). These results were probably due to the variable hetero-
876 aggregation behavior of the nanoparticles with CNTs depending on their dissimilar surface
877 change properties. Further research is needed to investigate the aggregation behavior of CNTs
878 in the presence of different macro and nanoparticles in the environment so as to optimize their
879 contaminant remediation ability.

880

881 **8. Economic assessment**

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

888 SWCNTs (Apul and Karanfil, 2015; Jia and Wei, 2017). The price of commercial CNTs falls
889 in the ranges of \$0.6 to \$25 per g of MWCNTs and \$25 to \$300 per g of SWCNTs depending
890 on the purity level and tube diameter of the products, as well as on the type of functionalization
891 undertaken in their preparation (www.cheaptubes.com; accessed on 07 May 2017). Thus,
892 MWCNTs are more frequently used than SWCNTs in environmental applications. However,
893 SWCNTs show better performance than MWCNTs in some environmental sensing
894 applications. MWCNTs might offer additional indirect benefits because they are usually less
895 toxic to non-target microorganisms in the environment than SWCNTs (Shrestha et al., 2013;
896 2015). Nonetheless, the development of technologies for large-scale production of high quality
897 CNTs (possibly from renewable carbon and catalyst precursors) (Gournis et al., 2002;
898 Bakandritsos et al., 2005; Su, 2009) requires further research to make CNT-based
899 environmental remediation technologies accessible. The cost of CNT-based water/wastewater
900 treatment technologies also depends on (i) the cost/complexity of CNT functionalization, (ii)
901 the type of water treatment (i.e., batch vs. continuous flow process), (iii) the need for
902 solid/liquid separation (e.g., magnetic CNTs can be easily recovered), and (iv) the recycling
903 cost and efficiency (i.e., CNTs typically exhibit higher regeneration capability). Contaminant
904 concentration in effluents can be one of the most critical factors in determining whether to
905 employ a batch or fixed bed treatment process to achieve an efficient and cost effective
906 treatment (Dichiara et al., 2015c). Empirical models can be used to choose the most appropriate
907 treatment process (either batch or fixed bed) that would minimize the adsorbent loading and
908 ultimately achieve the targeted removal of contaminants (Dichiara et al., 2015c). Further
909 research is needed to optimize the process parameters for cutting costs in CNT-based water
910 treatment technologies.

911

912 **9. Conclusions and future research direction**

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

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

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

940

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947

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