

Chapter 2

Carbon Nanotube in Water Treatment

Thousands have lived without love, not one without water.

—Source: W.H. Auden: *Collected Poems: Auden*
by W.H. Auden, 1991.

Abstract The availability of safe and clean water is decreasing day by day, which is expected to increase in upcoming decades. To address this problem, various water purification technologies have been adopted. Among the various concepts proposed, CNTs based water treatment technologies have found to be promising because of its large surface area, high aspect ratio, greater chemical reactivity, lower cost, and energy, less chemical mass and impact on the environment. Therefore, research development and commercial interests in CNT are growing worldwide to treat water contaminants, which have huge impacts on the entire living systems including terrestrial, aquatic, and aerial flora and fauna. Here we reviewed most of the effective CNT based water purification technologies such as adsorption, hybrid catalysis, desalination, disinfection, sensing and monitoring of three major classes such as organic, inorganic and biological water pollutants. Since the Nanobiohybrid field yet remains to be matured, special importance has been paid on its mediated water purification technology. We have forayed into the deeper thoughts and compiled promises, facts and challenges of the important water purification technologies. Since water purification is a complex process; hydrologists, membrane technologists, environmentalists and industrialists can design “ONE POT” combination where effective water purification technologies would instate to tackle both the conventional and newly emerging toxic pollutants effectively.

2.1 Background

Earth water—a generous gift from the almighty God, and is the major constituent for all living organisms. Water has covered around 71% of the Earth’s surface area [1]. Figure 2.1 shows three pie charts of total water volume, and its distributions on

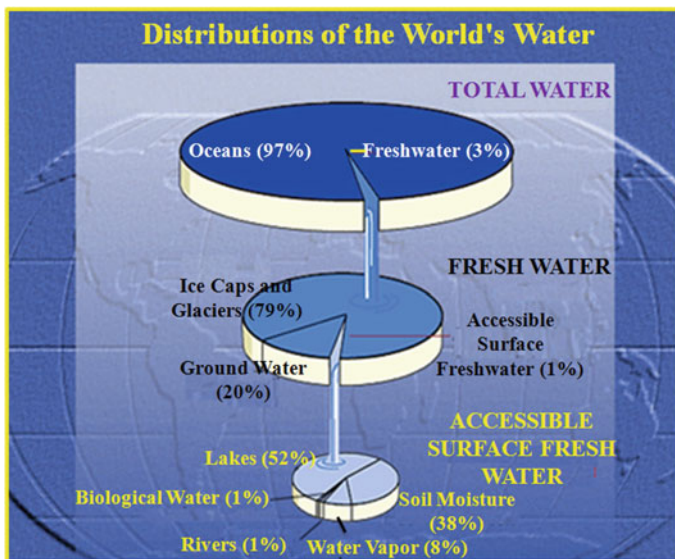


Fig. 2.1 Pie charts of total water volume on, in and above the Earth. The figure is adapted with permission from the Earth-Forum [25]

Earth's surfaces [25]. According to Fig. 2.1, water can exist in different forms such as gaseous (cloud vapors and atmospheres), liquids (seas and oceans, rivers, lakes), and solid waters (ice and glaciers). Although a higher percentage of water exists as saline water in the sea and oceans (97%) (Fig. 2.1 top chart), it cannot be used for drinking purpose due to its salinity and impurities.

Only (3%) freshwater exists as 79, 20 and 1% of the frozen, ground and accessible fresh surface waters, respectively (Fig. 2.1 middle chart). This accessible fresh water (1%) covers 53% in the rivers and streams; and the remaining percentages are in the forms of vapor, moisture, and biological (Fig. 2.1 down chart). These clearly indicate the unavailability of pure fresh water facilities for drinking which are necessary for sustaining and growing of all living organisms on Earth.

While limited fresh water availability is so obvious, many persistent pollutants have been simultaneously added into the world water bodies through both point and nonpoint origins. This leads to a global decrease in the availability of clean and safe water forms of water resources. Three major classes of water pollutants such as organic, inorganic, and biological contaminants have been dwindled the finite fresh water resources. Moreover, climate change due to persistent global warming could bring variation in natural systems, leading to ice-melting, sea level rise, soil, and fresh water submergence, increase evaporation and so on, which have collectively been contaminated the oceans [21]. While it is difficult to control or significantly reduce water pollution, the lack of cost-effective water purification technology has accelerated the problems. At some places, polluted water is not treatable for recycling especially in developing countries because of lacking cost effective, but

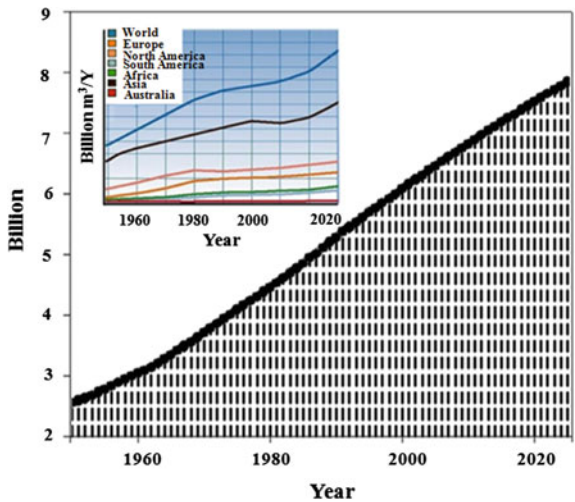
sensitive water purification technology. Therefore, a novel, sensitive and cost-effective water purification technology is an urgent need, and the failure to develop such a system might further endanger the life processes and eco-friendly human existence.

2.2 Water Scarcity and Its Consequences

Increasing world population with water demands is highly interlinked and inter-dependent with each other. World population has been increasing day by day (80 million/year) [135, 136], which could directly increase water demand in the near future. Figure 2.2 represents the trends of population growths and their water demands from 1950 to 2025. This alarms the looming crisis of water can be seen, if corrective steps are not taken at right time.

Figure 2.3 represents the water scarcity of different areas on Earth. It shows many countries have encountered with little, physical and economical water scarcities, while some are waiting to reach. In the last century, water usages have been more than twice the rate of population growth [129], resulting in global water shortages. Such fresh water crisis brings problems not only to human, but also to the eco-systems. It has already been affected many continents, mainly developing countries, which accommodate almost 40% populace of our planet [129]. People in the developing countries depend mainly on the ground water facility due to the lack of expensive water purification techniques. Approximately 30% of the fresh and clean water accumulated in aquifers have commonly been utilized for irrigation to cultivate food grains, vegetables and fruits, leading to a water depletion of about 12 billion m³/year [58], endangering biodiversities, flora and fauna.

Fig. 2.2 Schematic representation of population growth (*outer plot*) and their corresponding water demand (*inner plot*) from 1950 to 2025. The plot was generated using the data from [58, 132]



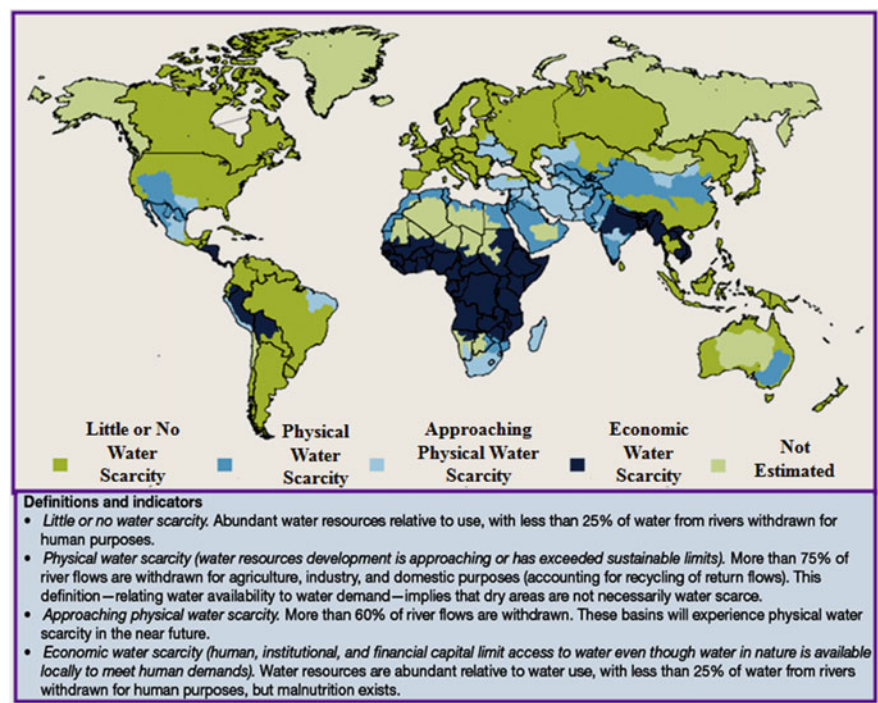
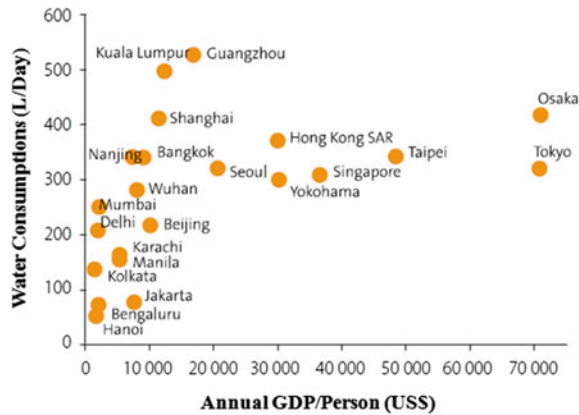


Fig. 2.3 Areas encountered with water scarcities on Earth. The figure is adapted with permission from the International Water Management Institute (IWMI) [49]

Water crisis has directly linked to the global food, and health security, economic growth, social progress and ultimately political stability [59]. Figure 2.4 demonstrates a relationship between gross domestic product (GDP) and the rate of water consumptions in some Asian cities [130]. Although per capita GDP of Singapore,

Fig. 2.4 Water consumption and per capita income in selected Asian cities. The figure is adapted with permission from the United Nations Development Programme [130]



Taipei and Tokyo have found more than Kuala Lumpur, Guangzhou, Shanghai and Hong Kong SAR; its per capita water consumptions are considerably lower. It hypothesizes a proportional relationship between water demands and per capita growth. The cities that are rapidly developing total water demands, which simultaneously create an inhibitory effect to the growth of per capita also.

Accumulating wastewaters from surroundings has been increased the transmission of various illnesses especially mosquito, water, and food-borne diseases such as dengue, malaria and hepatitis. Different water pollutants have shown different detrimental human health effects. For instances, persistent organic pollutants (POPs) [145] cause hormonal imbalance, alter reproductive behavior and birth defects, cancer, heart diseases and so on [110]. These have shown harmful effects because of their desensitized behaviors to chemical, biological, and photocatalytic degradation processes [110]. Consequently, they could have long-range transport, high cellular uptake followed by bioaccumulation into the human body that leads to cellular toxicity [110].

First, the most notorious organic wastewater pollutants are phenols and its derivatives which have been persisted more commonly in nature and are toxic for biological bodies [34]. Most of them have been leached and mixed into the water environment from both natural and anthropogenic sources. For instance, they often come up with the pyrolysis of forest trees and volcanic eruptions. Aquatic flora and fauna such as sweet flag and algae have known to synthesize many phenolic compounds as secondary metabolites [37, 83]. In addition, plant's and animal's decompositions have acted as natural sources for phenol-type water pollutants [34]. However, anthropogenic sources and industrial wastes (oil refinery, coal, pharmaceutical, agro-chemical, explosive, Masonite, plastic, etc.), have been accumulated into the environment, resulting fresh and clean water crises [34, 40, 143].

The effects of phenolic wastewater pollutants are huge and unavoidable. They often have accumulated into the body, break salutary food chains resulting in vulnerable environmental consequences. For example, it has been shown that the phenolic water contaminants of >50 ppb are injurious for aquatic species, whereas drinking of 1.0 g phenol could be fatal for human [4]. Moreover, phenolic contaminants have shown to decrease the overall efficiency of wastewater treatment plants [14]. For instance, high concentrations of phenolic water pollutants have inhibited the growth of beneficiary microorganisms, which has been used for treating municipal wastewater in water treatment plants [14].

Figure 2.5 shows some common phenolic water pollutants with their interconversion fates. Herein the catechol, pyrogallol, 3,4-dihydroxyphthalic acid, vanillic acid, 4,5-dihydroxyphthalic acid, cis-4,5-dihydroxy-cyclohexa-1(6), 2-diene-1,4-dicarboxylic acid, 3-hydroxybenzoic acid, 3-dehydroshikimic acid and 4-hydroxybenzoic acid could be converted into the 3,4-DHBA by simple decarboxylation, oxidation, or dehydration reactions.

In addition, 3,4-DHBA and its other phenol-type derivatives which have bactericidal effects could increase their availability in nature [66]. The 3,4-DHBA is commonly found in fruits and vegetables such as olives, grape wines, plant-derived beverages, and so on [71, 84, 142]. Therefore, food processing industrial

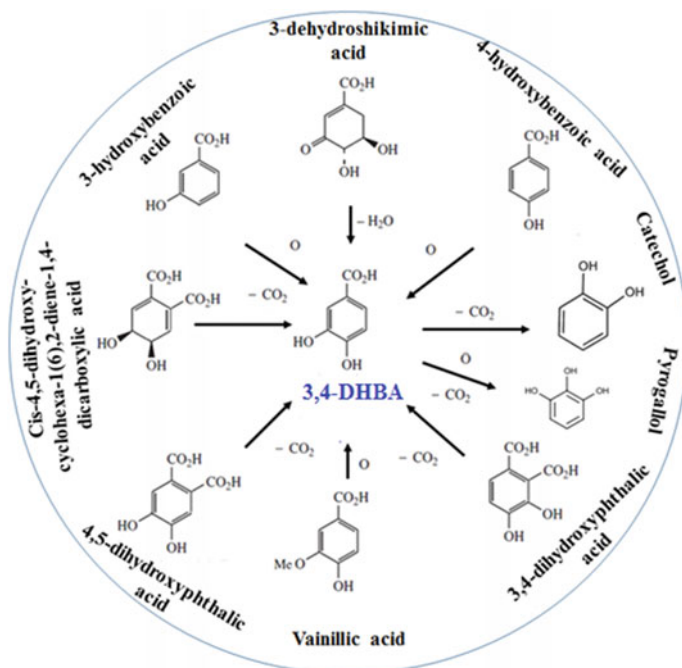


Fig. 2.5 Schematic diagram of the interconversions of some major phenolic water pollutants into the 3,4-DHBA

wastewater effluents have contaminated with a higher concentrations of 3,4-DHBA that continuously dwindling our limited fresh water resources day by day [112]. These have attracted scientists to test the toxicity effects of 3,4-DHBA on both animal, and human tissues and observed contradictory biological effects [10]. Some studies have claimed that 3,4-DHBA acts as an antioxidant at lower concentrations for the liver, stomach, pancreas, colon, urinary bladder, skin and oral malignant cells [43, 92, 96, 125–128]. But other studies have assured that it induces oxidative stress, hepatotoxicity, and neurotoxicity and promoted tumor formation [10, 93]. However, Babich et al. [10] examined detailed effects of 3,4-DHBA concentrations from 0.5 to 25 mM on normal human cells (S-G and GN61), malignant (HSG1), non-malignant (HSC-2) and carcinoma (CAL27) cells derived from the human oral tissues as shown in Fig. 2.6 [10]. This shows 5, 7.5, and 10 mM of 3,4-DHBA could induce significant initial cytotoxicity ($p < 0.01$) toward S-G, CAL27; and HSG1, HSC-2, GN61 cells, respectively. By observing the similar trends of sensitivities of normal and malignant cells, the group hypothesized that the effects of 3,4-DHBA on malignant cells were dormant. Moreover, it induced toxicity towards the normal human cells, which could be increased with increasing the concentrations of 3,4-DHBA. However, nontoxic level of 3,4-DHBA was observed between 0.5 and 2.5 mM for all cell lines.

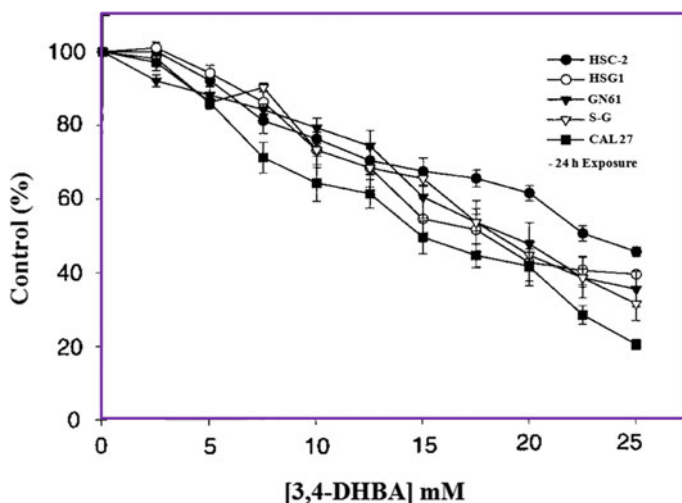


Fig. 2.6 Cytotoxic effects of 3,4-DHBA towards the different human cell lines as determined by neutral red assay. The figure is adapted with permission from Wiley [10]

Although a few studies such as Fenton [33, 112], adsorption [115], O_3 /UV or H_2O_2 /UV [13] and microbial degradation [17] have been adopted to eradicate 3,4-DHBA from water; they are less sensitive, time consuming, and generating chemical masses to the environment [60]. Therefore, implementation of those methods to tackle 3,4-DHBA is unthinkable, and the paradigm calls to develop novel water purification technology to mitigate 3,4-DHBA from water.

Second, the inorganic pollutant such as arsenic which has been widely recognized as a deadly poison and causative agent of various lethal diseases [5]. This pollutant has been affected 140.0 million people in more than 70 countries [135]. Additionally, other metals such as mercury, lead, and chromium have also shown harmful effects on the living systems [5]. Radioactive metals, e.g., uranium, radium, thorium, etc., have been commonly found in industrial wastewater effluents. These substances are more toxic and lethal even if consumed at lowest level. Other metals such as cadmium, copper, zinc, and cobalt have shown multiple pathological effects such as diarrhea, anemia, nausea, cancer, renal failure, ulcers, gastro-intestinal tract infections, poor growth, fever, lung irritation, and so on [5, 97, 149].

Finally, biological water pollutants mainly bacteria, viruses, fungi, and algal blooms have shown to occur many water born diseases [29, 35]. These pollutants could contaminate beaches that lead to decrease recreational value of water resources with social disturbances. Therefore, effective handling of both the conventional priority and newly emerging pollutants is prerequisite to maintain a healthy ecosystem and disease-free society and nation. Thus water pollution is a chain of reactions, and even a single substrate can affect entire system, hindering social progress and economic growth in daily life processes.

2.3 Threats to Conventional Water Treatment Technologies

Changing of human lifestyles over the years has consistently added different notorious anthropogenic pollutants into aquatic matrices. Eradicating these toxic pollutants is either impossible or difficult using the traditional water purification methods. Here we summarize the most common threats of current water purification technologies as shown in Fig. 2.7. It clearly reflects that a single method is insufficient to remove multiple water pollutants. Most of the methods typically depend on influent water qualities such as turbidity, pH, and temperature that could decrease pollutant sensing ability. In addition, low concentration and small dimensions of some water pollutants are difficult to sense and mitigate by existing water purification technologies. Finally, high operating costs shrink the availability of effective technologies especially in developing countries [131].

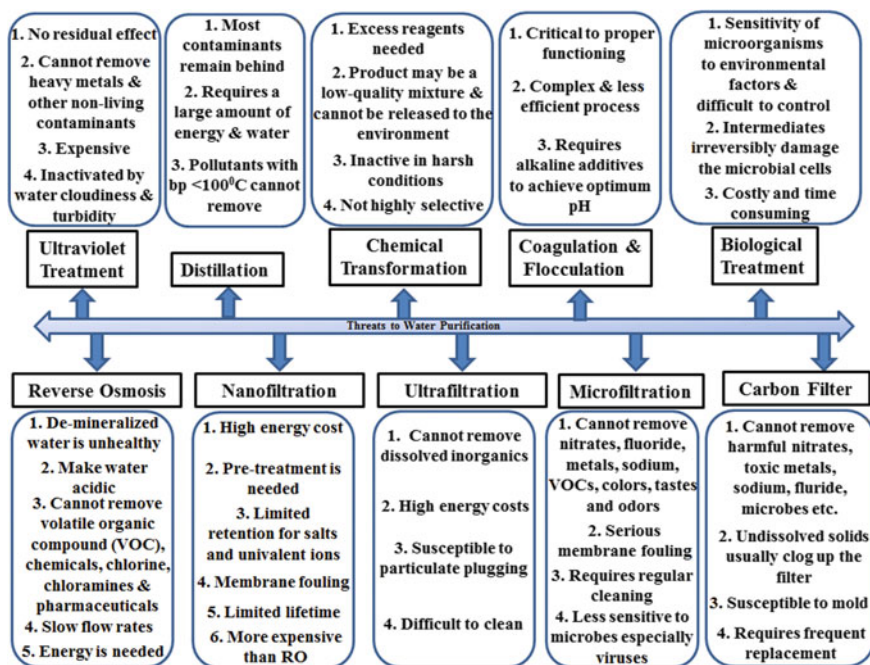
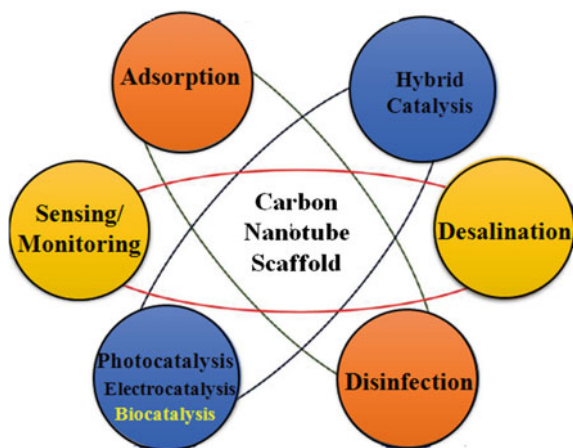


Fig. 2.7 Some major threats of conventional water purification technologies

Fig. 2.8 Scaffold functions of CNTs in water treatment technologies



2.4 Carbon Nanotube Scaffold Functions in Water Purifications

Figure 2.8 illustrates the scaffold functions of CNT in water purifications. According to Fig. 2.8, CNT has been widely used as excellent adsorbent media at first for multiple organic, inorganic, and biological water pollutants [6, 107, 131]. Second, CNTs could be used as hybrid catalysts where they may participate in photocatalysis, electrocatalysis, and as nanocarrier for enzyme immobilization or Nanobiohybrid catalysis. These have added new dimension in catalytic degradation of water pollutants. Herein CNTs have made a suitable platform for accelerating the catalytic rates [106]. Third, doped CNTs in various membrane engineering technologies have been used for both the sea and brackish water desalinations [21]. They can be used as pores in engineered membranes or membranes themselves by aligning them together. Finally, high electrical conductivities have made CNT suitable for electrochemical sensor technology to trace and mitigate contaminants, pathogens and high complexity of wastewater matrices [87, 106].

2.4.1 Adsorption

Adsorption is a process where substance (pollutant) concentrations are increased and adsorbed into the layers/sheets of a solid material owing to the operation of surface forces. Basically, it is a surface phenomenon where the substance is adsorbed that is called adsorbate and creates a film on the adsorbent (where adsorbate are adsorbed) surface. Adsorption present in CNTs has been frequently used for capturing wide variety of water pollutants [44, 89, 108, 131, 144]. Some CNT properties have made them versatile for adsorptive processes. For

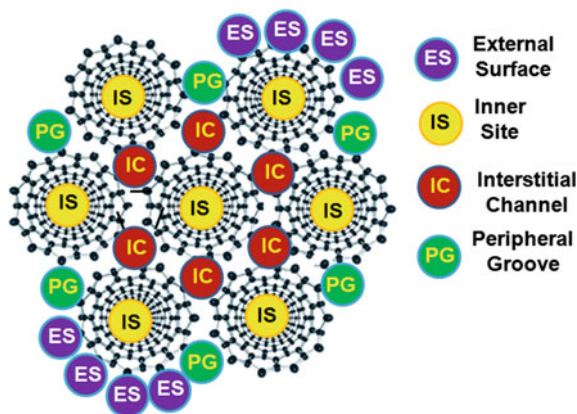


Fig. 2.9 Structural representation of four predicted major adsorption sites of CNTs in a bundle. Close-ended CNTs: adsorption takes place $PG > ES > IC$, whereas open-ended CNTs: adsorption proceeds IS of open-ended CNT walls $>$ forms 1D chains in the $PG >$ filling of the remaining axial sites of $IC >$ completion of a quasi-hexagonal monolayer on the ES

example, (a) the total CNT surface area is high (SSA 100–300 m^2/g) for high sorption capacity, (b) high pore volume of fibrous material increases surface accessibility and (c) malleable surface charge provides control to select for a specific water pollutant. The effect of CNT morphology and topology on transport and diffusion of water pollutants is displayed in Fig. 2.9.

The external surface, inner site, interstitial channel, and peripheral groove constitute the four possible sites for adsorption (Fig. 2.9). Most of the organic pollutants sorb at external surface and inner site of open-ended CNTs. The external surface of CNTs can be functionalized for attaching both organic and inorganic pollutants. MWCNT usually contributes more pore volumes of inner sites than the SWCNTs. SWCNTs are prone to form bundles because of their strong van der Waals forces along the tube length axis that results in formation of interstitial channels and peripheral grooves (a positive influence for adsorption kinetics). But as grown SSA of SWCNT (400–900 m^2/g) and MWCNT (200–400 m^2/g) which is substantially decreased upon aggregation (a negative influence for adsorption kinetics). SWCNTs of same diameter packed into a bundle (homoaggregation) which results in uniform diameter of interstitial channel. Mismatch diameter in SWCNT bundle (heteroaggregation) poses larger diameter of interstitial channel than homoaggregation. Similar observations have been found in aggregated MWCNTs. Interstitial channels have found important for sorbing PAHs (e.g., naphthalene and tetracene) water pollutants displaying diameter <1 nm. It has been shown that the diameter of intertubular spacing of the bundle structure of 1.43 nm, which increased from 1.43 to 2.20 nm upon tetracene adsorption into SWCNT. Sorbate configuration determines their interactions with peripheral grooves area of aggregated CNTs. Inorganic molecules adsorb at peripheral groove sites, and the

rate might be faster in close-ended CNTs. The site is generally reached to equilibrium faster than the inner sites because of its external face to the solvent.

Functionalizing CNT can mediate specific pollutant adsorption, increases CNT colloidal stability and chemical reactivity. Three different methods have been explored for CNT functionalizations such as (a) physical non-covalent wrapping, (b) covalent wet chemical agent treatments, and (c) endohedral filling of CNT hollow cavity. Major interaction forces between CNT functionalities and water pollutants are covalent bonding, hydrogen bonding, electrostatic interactions, ion exchange, hydrophobic interactions, π - π electron coupling, and mesopore filling. Some important evidences of the roles of CNT functionalities for pollutant adsorptions are illustrated in Fig. 2.10. It ensures both the organic and inorganic wastewater pollutants can effectively bind with the functionalized CNT. Although CNT functionalization could substantially increase sorption of various water pollutants, it will decrease CNT ability for binding of hydrophobic organic water pollutants, e.g., naphthalene, phenanthrene, pyrene, and polychlorinated biphenyls that interact strongly with virgin CNT through π - π and hydrophobic interactions. Chemical functionalizations disrupts π - π carbon networks and increase wettability of surface. Therefore, great care needs to be taken to functionalize a material in a controlled fashion, so that one can preserve hydrophobic CNT skeleton and immobilize hydrophilic groups for multi-pollutants wastewater treatment.

After absorbing the pollutants for a certain concentration into the adsorbent, equilibrium is reached and the relationship between the amounts of pollutant adsorbed and in water, is called an adsorption isotherm. The kinetics of this mechanism have been evaluated mathematically using different models such as Langmuir, Freundlich, Halsey, Henderson, Smith, Elovich liquid film diffusion, intraparticle diffusion, and Lagergren [5]. Wang et al. [133] observed the adsorption of Pb(II), Ag(I), Cu(II), and Co(II) ions on MWCNT, and the adsorption data were fitted well to the Langmuir model as shown in Fig. 2.11 [133].

Figure 2.12 shows some observed evidences of pollutants adsorption onto CNT surfaces. As we can see, TEM image of MWCNTs after Pb (II) adsorption which is not uniform and mainly adsorb at the tips and defective sites of the MWCNTs (Fig. 2.12b) [133]. SEM image of *Eschericia coli* (*E.coli*) bacteria exposed to SWCNTs clearly suggests loss of their morphology (Fig. 2.12c) [53]. Sponge-like CNT adsorbent floated on oil polluted water and simultaneously can remove oil with a large adsorption capacity (from 80 to 180 times their own weight for a wide range of solvents and oils) (Fig. 2.12d) [38], and finally salt adsorption by CNT membranes (Fig. 2.12e) [141].

2.4.2 Hybrid Catalysis

CNT has been popular in photocatalysis of multiple water pollutants because of their high electrical conductivity and charge transferring ability [26]. Good electrical conductivity of CNT might be resulted from the presence of reactive surface

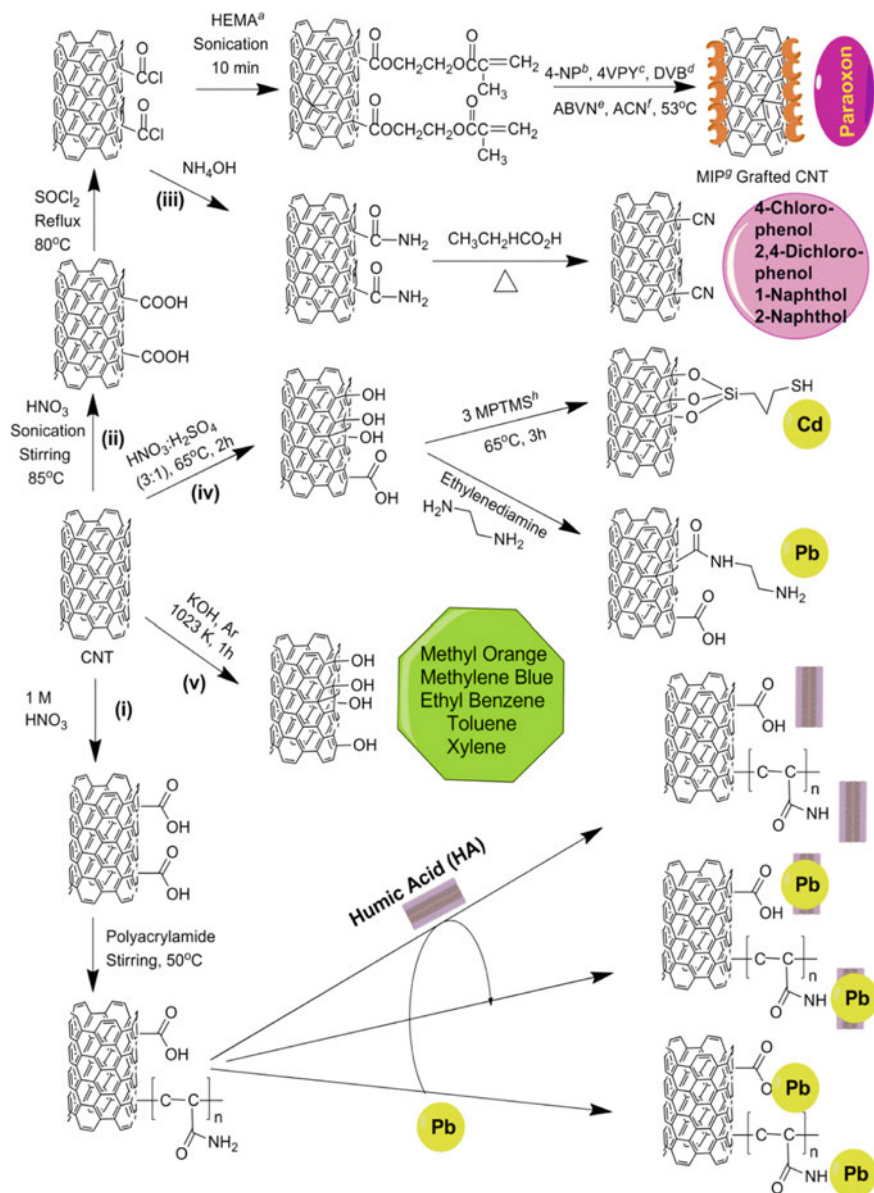


Fig. 2.10 Functionalization of CNT as adsorbent for organic and inorganic water pollutants. Here ^a2-hydroxyethyl methacrylate, ^b4-nitrophenol, ^c4-vinyl pyridine, ^ddivinylbenzen, ^e2,2-azobis (2,4-dimethyl)valeronitrile, ^facetonitrile, ^gmolecularly imprinted polymers and ^h3-mercaptopropyltrimethoxysilane

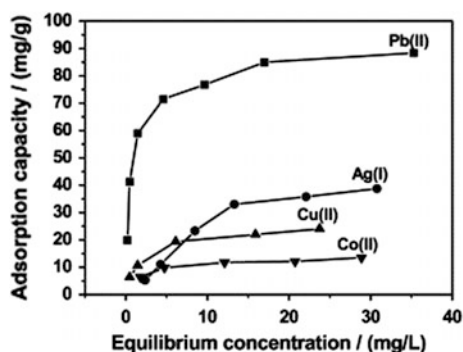


Fig. 2.11 Adsorption isotherms of acidified MWCNTs to Pb (II), Ag (I), Cu (II), and Co (II) at 25 °C. Figure is adapted with permission from Elsevier [133]

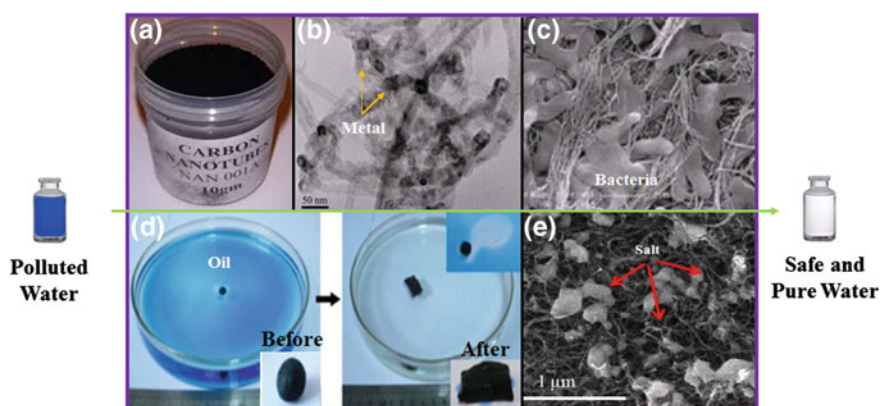


Fig. 2.12 Adsorption of water pollutants on CNT surfaces. **a** Pristine CNTs, **b** metal, **c** bacteria, **d** oil and **e** salt adsorptions onto CNT surfaces. The figures are adapted with permissions from Elsevier, ACS, Wiley and Sons and Nature [38, 53, 133, 141]

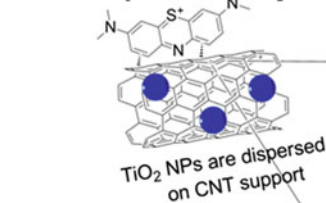
groups, sp^2 carbons, curvature pattern, topological defects, and edge-plane sites [111]. Another potential hybrid catalyst has been used to degrade water pollutants in a process called catalytic wet air oxidation (CWAO). This can be defined as the dissolved and suspended water pollutant's oxidation using an oxidizing agent such as O_2 from air in the presence of catalyst. In addition, recently CNTs have also been used for immobilizing enzymes [28]. Immobilized enzymes have shown good thermostability, broad pH ranges, and higher reusability in the fields of water purification [6, 90, 137], pharmaceuticals, chemical synthesis, biosensors, and so on [62]. The suitability of CNTs for enzyme attachment is because of their known atomic structure, big surface area, mass transfer, and good enzyme loading capacities which help to develop an effective Nanobiohybrid catalyst for water purifications [137].

2.4.2.1 Photocatalysis

CNTs have been used as reinforced photocatalytic composite materials along with other semiconductors such as TiO_2 , ZnO , and so on [23]. Photocatalysis means a photoreaction that is accelerated by light/photon in the presence of single or multiple catalyst(s). Functionalities on CNTs have shown important interactions for doping CNTs with different photocatalytic agents [113]. These have increased CNT total surface area, defects, electrical conductivity and so on, which enhance the overall photocatalytic rate. Two methods have been applied for synthesizing CNTs based photocatalytic composites. First, covalent and non-covalent attachment of desired nanoparticles on CNT surface [102]. Second, in situ synthesis of nanoparticles of interest followed by electrochemical deposition [140]. The main advantage of this method is to get a uniform composite nanomaterial produced by selective deposition of nanoparticles in the CNT active sites. Therefore, CNT can be considered as suitable support for multiple catalysts doping in photocatalytic reactions.

Figure 2.13 shows the possible mechanism of actions following CNTs for enhancing photocatalytic activity. Band gap or energy gap is a common phenomenon in solid state physics, and can be defined as energy intervals (ΔE_g) (no electrons exist) between the valence and conduction bands (V/CBs). VB is the highest energy state with electrons, whereas CB is the lowest energy band in the

1. MB molecules transfer from the solution to the catalysts' surface and be adsorbed via π - π conjugation between MB and CNT aromatic regions and so, the adsorptivity of dyes increases compared to bare TiO_2



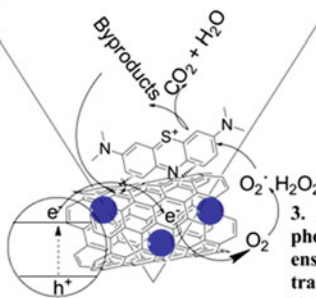
Light Energy (λ, ν)

e^-

h^+

2. The chemical bonds of Ti-O-C and good transparency of CNT render a red shift in the photoresponding range and facilitate a more efficient utilization of light for the catalyst

4. Byproducts (if any) are trapped by the porous CNT surface, so that the redox reaction can take place effectively without any interference that enhances overall photocatalytic rate



3. CNT is an acceptor of the photogenerated electrons and ensure fast charge transportation in view of its high conductivity, and therefore, an effective charge separation can be achieved

Fig. 2.13 Mechanism of photodegradation of methylene blue (MB) over CNT/nanoparticle composite

absence of electrons. Photons from different light sources are exposed to a catalyst nanoparticle, the VB electrons getting excited then and rapidly move to the CB. This creates a vacancy or hole (h^+) in VB. These holes (h^+) then react with H_2O or OH^- ions followed by hydroxyl radical ($\cdot OH$) formation that directly oxidizes the adsorbed water pollutants on CNT surfaces. On the other hand, the excited electrons from VB to CB form $\cdot OH$ which reacts with O_2 followed by the formation of superoxide radical ion ($O_2^{\cdot -}$). This highly reactive radical attacks and oxidizes the target pollutant rapidly. However, the major drawback in photocatalysis is to have a chance of recombination of charges avoiding photodegradation. This electron–hole recombination can be prevented by making a composite CNT material with other semiconductor nanoparticles. CNTs in metal composites act as insulating nanomaterial or barrier junction, which inhibits the recombination and increases photocatalysis rate. CNT can capture electrons due to its high charge conducting ability that ultimately gives less chance to electrons for recombining with holes. Consequently, CNTs could be sponsored as photo-generated electron acceptor that enhances interfacial electron transfer process, whereas the semiconductors are good electron donors under irradiation [32, 109, 114, 122]. But, the overall process has also been regulated by some factors such as the nature and type of semiconductors, light radiation, pH, temperature, and target pollutant concentrations [64, 65].

2.4.2.2 Catalytic Wet Air Oxidation

CWAO has considered one of the most effective water treatment methods, and has commercially been used for last 60 years [78]. CNTs have been used along with other catalysts such as Pt, Pd, Ru, and so on [31, 139] to increase catalytic efficiency and decrease costs [78]. Yang et al. [139] reported MWCNTs for CWAO of phenol in a batch reactor as shown in Fig. 2.14 [139]. Carboxylic groups ($-COOH$) on CNTs showed good catalytic activity in phenol oxidation (1000 mg/L) at 160 °C and 2.0 MPa (Fig. 2.14b). Liquid O_2 adsorbed, and dissociated on MWCNTs graphite sheets produced dissociated oxygen atom (DOA) [88]. Functionalities mainly $-COOH$ groups generated by treating MWCNTs with H_2SO_4/HNO_3 and the DOA could form HO_2 . Then the radical could mineralize phenol to CO_2 , H_2O and low organic compounds [111]. Kim and ihm [61] summarized the degradation of major industrial organic water pollutants by CNTs based CWAO process [61].

2.4.2.3 Nanobiohybrid Catalysis

Figure 2.15 illustrates a Nanobiohybrid catalyst prototype for sensing, monitoring, and degrading of multiple pollutants in water. The Nanobiohybrid could be made by attaching enzymes on CNTs via one of the three major routes such as binding to a support (physical adsorption and covalent bonding), cross-linking (carrier free) and encapsulation or entrapment [48]. In physical adsorption, spontaneous

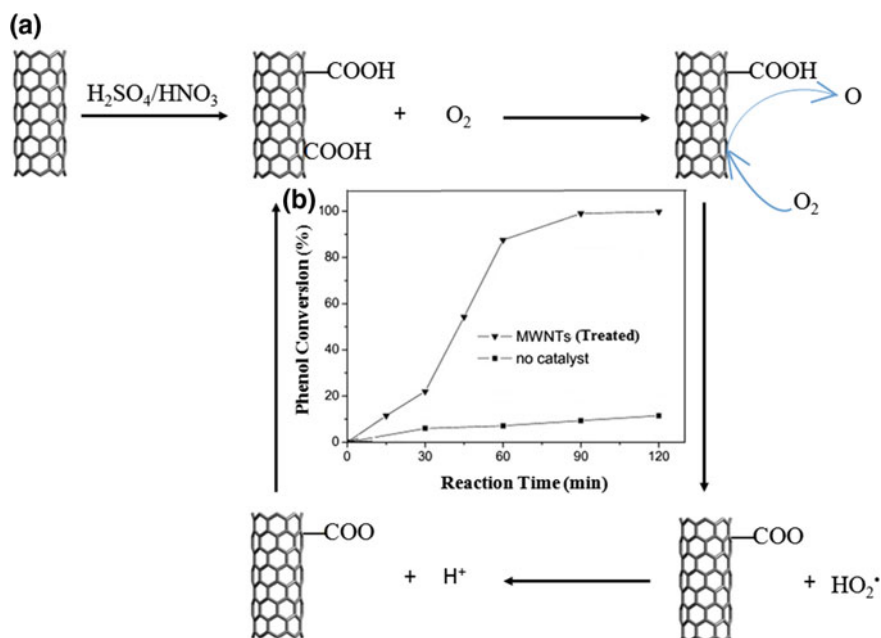


Fig. 2.14 **a** Mechanism of producing the radical (HO_2^\bullet) in CWAO for phenol degradation by $\text{H}_2\text{SO}_4/\text{HNO}_3$ treated MWCNTs and **b** efficiency of phenol removal. The figure is adapted with permission from Elsevier [139]

adsorption of enzymes into CNTs has occurred due to the inheritance hydrophobic and electrostatic interactions between CNTs and enzyme catalyst (Fig. 2.15I) [30, 95].

Covalent bonding of enzymes with CNT has been popular by inducing the reaction of the free amine groups on the surface of enzymes with COOH groups that could be generated by sidewall oxidation of CNTs and subsequent activation using carbodiimide chemistry (Fig. 2.15II) [9, 47, 51]. Cross-linking polymers such as chitosan, poly(diallyldimethylammonium chloride), and so on can also be used to immobilize enzymes on CNTs [69, 123]. In addition, LBL approach has been adopted for immobilizing enzymes using enzymes encapsulation process. It permits the coating of various enzymes, producing multilayer enzyme films on CNTs [28] as shown in Fig. 2.15III. The covalently bonded enzymes would be better for the Nanobiohybrid applications in water purifications.

This is due to least chances of enzyme leaching from the supports compared with non-covalent approach [28]. Non-covalent enzyme immobilization is typically popular for fabricating the biosensor devices. This is because of maintaining intact CNT skeletal integrity and enzyme configurations that yield higher electrical conductivity [28]. However, encapsulation or entrapment methods have been popular for attaching more than one enzyme molecule. This method can be used to develop

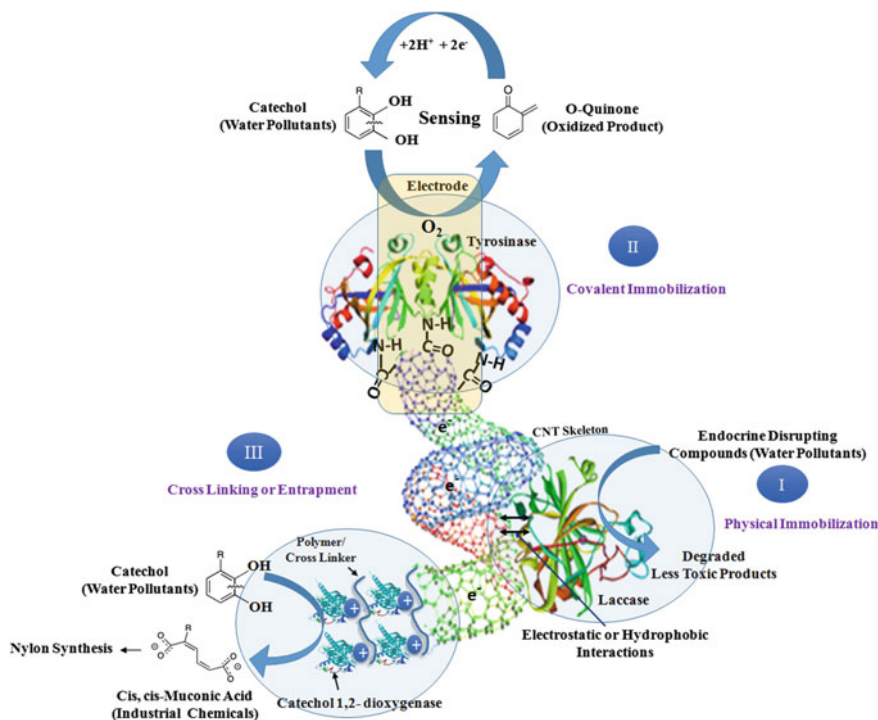


Fig. 2.15 Mechanisms of a potential Nanobiohybrid catalyst for water purification

a single biohybrid catalyst which can degrade a range of different water pollutants by multiple immobilized enzyme complexes.

Here we summarized some major observations of Nanobiohybrid-mediated water purifications in Table 2.1. However, besides CNTs, there are many other supports such as glass beads [85], agar [101], hydrophobic, and ionic supports [103], membranes [80], nanofibers [137], nanoparticles [82] and the combination of different supports [91] have been well documented for the various enzymes immobilizations which have also shown higher thermostability, shelf life, and reusability and successfully used for multiple applications.

Nanobiohybrid has some advantages over conventional chemical oxidation of water pollutants [8, 15, 28]. It can be applied for water purifications where other chemical transformations of water pollutants are not possible. In addition, the catalyst has greatest efficiency for disintegrating the electron resonance of benzene ring containing aromatic water pollutants in contrast to photocatalysis. Furthermore, recovered Nanobiohybrid catalyst could be used for multiple times [123], so the method is economically viable. Consequently, the hybrid can play three major functions with high selectivity and sensitivity in water purifications (Fig. 2.15):

Table 2.1 Some major evidences of the actions of Nanobiohybrid catalysts in water purifications

Material type	Water pollutant	Major observation	Refs.
MWCNTs-Laccase	ABTS ^a , Bisphenol and Catechol	<ul style="list-style-type: none"> • Enzyme loading capacity was highest for O-MWCNTs and lowest for C₆₀ • No obvious structural change of enzyme observed after immobilization 	[100]
MWCNTs-Tyrosinase	Phenol derivatives	<ul style="list-style-type: none"> • Selectively oxidized phenol and its derivatives with high stability of the catalyst 	[123]
SWCNTs-HRP ^b SWCNT-DM ^c -Con A ^d -HRP	Dibenzothiophene (DBT)	<ul style="list-style-type: none"> • Increased enzyme loading with high specific activity triggered efficient DBT degradation • DBT removal rate: 66.46 and 94.65% for SWCNT-HRP and SWCNT-DM-Con A-HRP catalysts, respectively 	[73]
SWCNTs-1,2 HQD ^e	Catechol	<ul style="list-style-type: none"> • Removed catechol with wide pH and temperature ranges 	[124]
MWCNTs-SBP ^f	p-Cresol	<ul style="list-style-type: none"> • Nanobiohybrid retained 40–60% activity after multiple time uses • Highly stable and reusable than free enzyme in removing p-Cresol 	[9]
SWCNT, MWCNT, SWCNTs-Crude enzyme, MWCNTs-Crude enzyme	Aniline	<ul style="list-style-type: none"> • Enzymes adsorption increased in MWCNTs than SWCNTs • Effective aniline removal observed in SWCNTs-enzyme compared with MWCNTs-enzyme indicated efficient reaction between aniline and enzymes on the surface of SWCNTs. This played a key role in the rapid enzymatic biodegradation of aniline 	[138]

^a2,2'-azino-bis-(3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt, ^bhorseradish peroxidase, ^cn-dodecylβ-D-maltoside, ^dConcanavalin A, ^ehydroxyquinol 1,2 dioxygenase and ^fSoybean peroxidase

(i) binding and pre-concentrating the pollutants; (ii) removal and/or degradation of pollutants; and (iii) sensing and monitoring the pollutants in water. Moreover, it can be used in industry for yielding commercially important compounds or value-added chemicals which have been produced by mitigating of organic wastewater pollutants (Fig. 2.15III). In short, the technique would have double benefits—it reduces total water contaminants, and simultaneously this increases commercial value.

2.4.3 Desalination

On the basis of current fabrication systems, there are two types of CNT membranes such as (i) vertically aligned (VA) and (ii) mixed matrix (MM) CNT membranes [3] as shown in Fig. 2.16. The VACNT membranes can be synthesized by aligning perpendicular CNTs with supportive filler contents (epoxy, silicon nitride, etc.) between the tubes (Fig. 2.16a) [42]. On the other hand, a MMCNTs membrane consists of several layers of polymers or other composite materials (Fig. 2.16b). These membranes work with low energy consumption because of CNT's frictionless water transport capability through nanotubes hydrophobic hollow cavity. The membrane is highly sensitive toward the multiple water pollutants and salts. In addition, due to the CNT cytotoxicity, the CNT membrane has antifouling and self-cleaning abilities with high recrudescence and reusability facilities. For instance, Dumée et al. [24] observed the highest water permeability of SWCNTs (5,5), and (8,8); and sodium ion retention was reached (99%) in (5,5) and (6,6) SWCNTs at flux rates of $12 \text{ kg m}^{-2} \text{ h}^{-1}$ [24]. Moreover, functionalities such as positive ($-\text{NH}_3^+$), negative ($-\text{COO}^-$, sulfonic acids) and hydrophobic (aromatic) groups could be implanted by using different wet oxidizing agent treatments of

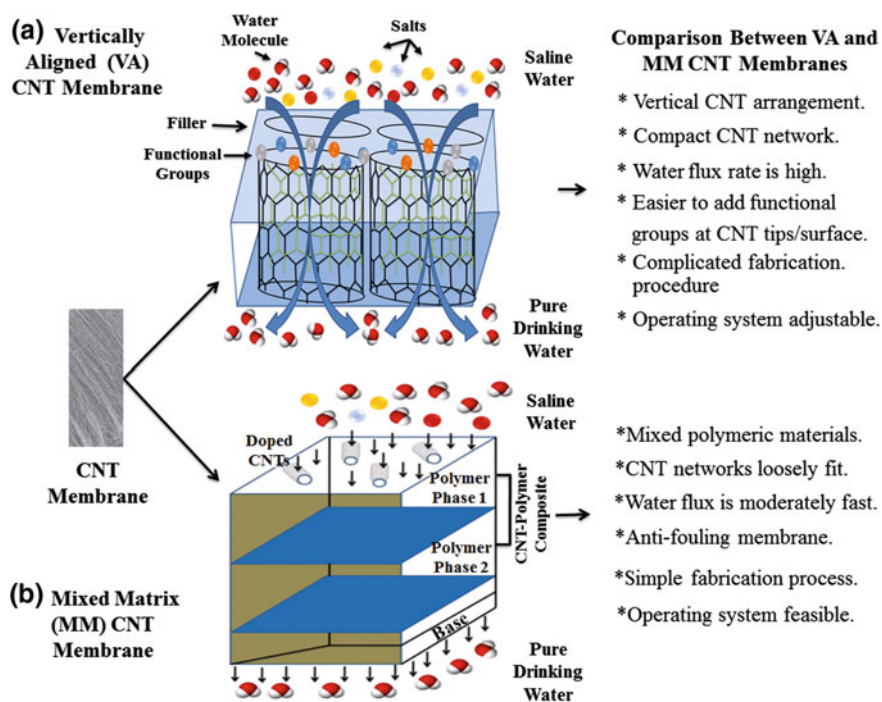


Fig. 2.16 Schematic illustration of two types of CNT membranes. **a** VA and **b** MM-CNT membranes

CNT [36, 56]. The groups can reject a selective water pollutant and also attract water molecules through nanotube hole. Chan et al. [19] simulated and fabricated CNT membrane (diameter 1.5 nm) with two zwitterions at tip ends. The group was achieved 100% ion rejection, which was 0.0% in nonfunctionalized membrane [19].

2.4.4 Disinfection

Aggregated mesoporous CNTs [41] have been utilized to remove biological contaminants such as bacteria and viruses from water. Figure 2.17 shows some possible mechanisms for disinfecting microbes adsorbed onto CNT sheets.

Cytotoxic CNTs have shown higher pathogens decontamination rate [54] compared with AC [18, 119]. Therefore, pathogen contaminated effluents could be found in AC treated water. Liu et al. [76] studied the toxic effects of pristine SWCNTs on both Gram-positive bacteria such as *Staphylococcus aureus* (*S. aureus*), and *Bacillus subtilis* (*B. subtilis*) and Gram-negative bacteria such as *E. coli* and *Pseudomonas aeruginosa* (*P. aeruginosa*) [76]. The group observed that the dispersed individual CNT could puncture cell membrane integrity rapidly and strongly than aggregated CNTs. Soft and smooth cells such as Gram-positive bacteria could be more vulnerable to attack by CNTs than Gram-negative bacteria. This effect can be vice versa depending on the cell membrane compositions. This piercing effect can be increased using dispersed CNT solution, increasing their concentrations and shaker speed augmentation during incubation. Although few other possible toxicity mechanisms have proposed by some groups such as inhibition of electron transports, leakage, and penetration of cell membrane and generation of reactive oxygen surface (ROS) (Fig. 2.17b) [39, 52, 63, 72, 94, 104]; most of these mechanisms are not yet experimentally proofed. Kang et al. [54]

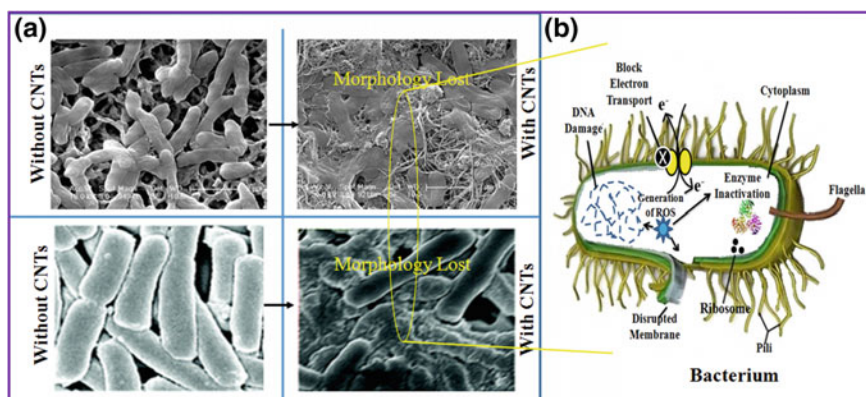


Fig. 2.17 **a** SEM images of bacteria before and after CNT exposures, and **b** some possible mechanisms of CNTs mediated bacterial cell death. Figure **a** is adapted with permission from ACS [52, 77]

observed the dominant toxicity resulted from using SWCNTs than MWCNTs [54]. The group oxidized 4.1 μm of MWCNTs by $\text{H}_2\text{SO}_4/\text{HNO}_3$ that yielded higher toxicity than 77 μm of MWCNTs bundles in diameters. It clarifies size-dependent toxicity mechanisms and can be a key parameter to ascertain antibacterial activity. Kang et al. [54] hypothesized higher toxicity induced by short, unzipped, and dispersed MWCNTs toward bacteria [54]. Other factors such as incubation time, buffer types, concentration, and functionalities have shown regulatory effects on CNT antibacterial activity [7, 55]. As an initial foray into the CNT microbial cytotoxicity, we confirmed that the scientists, who have been active in the field, only focused on bacteria physiological changes upon CNT treatments using SEM, AFM, and TEM. However, only these characterization methods cannot accurately explain the effects of CNT toxicity on bacterial cell proliferation. More biological experiments such as pattern of gene expressions, transcriptomics, proteomics, and genomics data comparisons along with other system biology approaches of CNTs treated bacteria could be effective for settling the mechanisms of cellular deaths. In addition, misinterpretation could be resulted from the use of pristine CNTs contaminated with amorphous carbons, metal catalysts, nanofibers, etc. Liu et al. [77] hypothesized the CNT toxicity can be dependent on its geometrical compositions and surface functionalities [77]. Therefore, more study is necessary to acquire the nature of bacterial cell death when CNT is an adsorbent media and should be treated with cautions.

2.4.5 Sensing and Monitoring

Rapid sensing of trace water pollutants has remained a critical job by using conventional sensor technologies. Moreover, complex wastewater matrices have increased this difficulty level. The paradigm has called to develop highly sensitive and fast responsive CNT-based devices or sensors. This is because of some CNT specialties such as fast electron conductivity, high adsorbing power (so that water pollutants can concentrate on CNT surfaces before sensing), hydrophobicity, high recovery rate, and increased reaction rate. As shown in Fig. 2.15II, enzymes immobilized on CNTs oxidize the water pollutants followed by electrons transformation for high signal detection. In addition, charged or ionic pollutants adsorbed into CNTs have given electrical conductance by measuring the ratio between analyte concentrations and current fluctuations [86]. López and Merkoçi [79] designed enzyme (tyrosinase)-integrated-CNT-epoxy composite electrode (CNTECE-Tyr) and compared with tyrosinase biosensor based on a graphite epoxy composite (GECE-Tyr) for quantifying phenolic water pollutants such as catechol [79]. Herein CNTECE-Tyr electrode showed higher signals reflecting the good electrocatalytic properties of CNTs over graphite sheet. It was of 46 and 294 mA/mM cm^2 for GECE-Tyr and CNTECE-Tyr, respectively with a current intensity 90% higher in CNTECE-Tyr compared with GECE-Tyr.

2.4.6 Research Gaps and Challenges

Pristine CNTs are often contaminated with various metal catalysts, ash and carbonaceous agents. These act as additional adsorbent sites of CNTs towards the water pollutants. The impurities have determined nanotube's pore diameters, morphology and could influence or inhibit adsorption behaviors [2]. In catalysis, metal and amorphous carbon impurities have contributed towards the observed catalytic behaviors and mislead total electrocatalytic activity [12]. Furthermore, CNT impurities could have several detrimental effects on enzyme immobilizations. First, non-nanotube carbon materials could inhibit maximum immobilization efficiency. Second, metals in pristine CNTs could thwart immobilized enzyme's reaction rates. Moreover, different CNT geometries and impurities might complicate the procedures and compromise CNT performances in sensor devices. Separating metallic from semiconducting CNTs has remained a challenging job because of their complex carbon networks. Synthesis of homogenous CNTs with perfect geometry for high power density is also appreciable for upgrading this technology. One pot combination of CNTs with classical electrochemical techniques could be a nice electrical device for water pollution control. It would increase the overall catalysis rate, fast mass transport, good control over the classical current flow in small geometry.

Although several approaches such as gas and liquid phase reactions [74], direct oxidation [70, 147], electrochemical oxidation [27], and wet chemical purifications [22, 98, 134] have been adopted to remove CNT impurities and manipulate solubilities, they often degrade CNT, shortening, and burning under extreme heat and excessive chemicals. Removing impurities with intact nanotube integrity is one of the toughest tasks in CNT-based water purification applications. For instance, HNO_3 mediated CNT purification could produce defected and curled CNT fragments [22, 75]. Moreover, the method could not remove 100% impurities from CNTs even at elevated temperatures [105]. In order to get intact CNT, several physical methods have been designed such as filtration [117], high temperature annealing [68], and repetitive centrifugations [46]. But the methods could not purify CNTs completely and also have less dispersed CNT samples. Therefore, more studies are necessary to develop novel CNT purification technology which would not only remove CNT generic impurities, but maintain an intact CNT skeleton. The treatment procedure should also anchor appropriate functionalities that might give appropriate overhead to attach other molecules or compounds, needed for upgrading the current water purification technologies.

Defects in CNTs may help in adsorption processes [148], but cannot be suitable in sensor and photocatalytic water purification technologies. Lower electrical conductivity has observed in defected MWCNTs [99] because it scatters the electron transportation of CNTs [81]. However, localized edge-plane defects at CNT tip ends and around the tube walls where one of the concentric tubes terminates could generate high peak current [11]. This observation is also similar with another study [16]. The group observed high charge density at pentagonal defects of nanotube

mouths than those observed in the regions of hexagonal graphite. It indicates a relationship between topological defects and CNTs electroactivity [16], which are necessary for developing an effective and highly conductive CNTs based sensor and photo-electronic water purification devices.

Besides CNT purifications, another major hurdle is to manipulate their solubility in water. If anyone wants to remove pollutants out of water, it should be considered to bring wastewater into the reactive surfaces of CNTs. Pristine CNTs are not soluble in water because of hydrophobic graphite sheet [118]. As a result, various covalent and non-covalent functionalization strategies have been adopted [45, 146]. But most of the covalent wet oxidation techniques have failed to give durable CNT solubility in water. Two methods such $\text{H}_2\text{SO}_4/\text{HNO}_3$ and KMnO_4 have been effective for adding $-\text{COOH}$ groups and ultimately increased CNT solubility [121]. But higher CNTs solubility might come from $\text{H}_2\text{SO}_4/\text{HNO}_3$ treated CNTs. Although the method has frequently been used for immobilizing enzymes on CNTs [30], this might not be suitable for sensor and photocatalytic CNT applications. This is because of yielding defected CNTs that might hamper electron transportations. Based on CNT solubility profiles, Upadhyayula et al. [131] hypothesized less soluble CNTs should be used in adsorbing media because of their handling and practical difficulties [131], whereas highly soluble CNTs could be used in composite membrane technology. Furthermore, bacteria have shown highest affinity toward semi-soluble CNTs [131]. Therefore, selection of appropriate wet oxidizing agents for purifying and solubilizing CNTs depends on desired water purification technology where CNT solubility and defect manipulations are required.

In desalination technology, the major challenges are to obtain an effective CNT membrane, controlled CNT growth method, processing and applications. Kar et al. [57] observed difficulties to install a dense membrane having CNTs of 12–13 order of magnitudes/ cm^2 [57]. Any irregularities in membrane shape could compromise with water passage and pollutant retention. Other hurdles in desalination are CNT tip functionalization and CNT selectivity to specific pollutant. Highly reactive carbon atoms at CNT mouth could be oxidized with different agent treatments which have been used for CNT purification and functionalization. But such treatments are often corrosive enough that cut CNTs into short fragments leading to membrane leakage. In addition, hydrophilic functionalities generated at CNT tips stimulate fast water transport through the hollow tubes, but have created steric blockage by the ions that are attracted and saturated at CNT mouths [20]. The affinity between functional groups and water molecules may cause a temporary pause of water molecules transportation around the CNT functionalized tip ends. Thus the functionalization is a rate limiting step which must be carefully optimized to tune the CNT membrane permeability to water molecules and solutes. Finally, doping of CNTs into RO, UF, NF, or MF membranes is still a challenging task for upscaling existing water purification technologies. Probably it can be a judicious choice to use costly SWCNTs in small amounts for doping rather than using alone as aligned membrane. However, standard experimental procedure with pilot projects is necessary to integrate CNTs into the existing membranes, which would upgrade overall water purification technologies efficiency with reduced efforts and time [116].

Special attention to CNT toxicity is important because of its various environmental fates and toxicity phenomena. Pristine CNTs have shown toxicity to living organisms [50, 67]. Smart et al. [120] hypothesized three potential properties of CNTs in determining their toxicity levels in the environment [120]. First, high aspect ratio of CNTs helped them to react with cellular membranes followed by their adsorption and transportation of toxic substances into the living organisms. Second, CNT longer retention time made its smooth contact with cell wall that increases the chance for damaging surrounding tissues. Finally, pristine CNT toxic impurities could have greater reactivity and toxicity within the particle. For instance, CNTs with metal ions such as Fe(II), Ni, and so on have shown toxicity to living cells [67].

Although CNT-based water purification technologies have faced some challenges, most of them are temporary. But the feasibility of most of the water purification technologies, such as adsorption, hybrid catalysis, disinfection, sensing and monitoring and so on at large scale yet appeared to be low. The commercial availability of these technologies should be encouraged because these meet most of the commercial features such as high water permeability, desalination capacity, pollutants selectivity, robustness, antifouling, energy savings, material costs, scalability and compatibility with industrial settings.

2.5 Conclusions

Global challenges particularly industrialization, urbanization, and anthropogenic activities have been continuously polluted water, raising the issues of various diseases, food safety and biodiversity of terrestrial, aquatic, and aerial, flora and fauna. In order to overcome the fresh water availability, CNT-based water purifications sowed the seeds of novel and innovative wastewater purification technologies because of its large surface area, high aspect ratio, greater chemical reactivity, lower cost, and energy, less chemical mass, and impact on the environment. Here we reviewed CNT-mediated effective decontamination processes such as adsorption, hybrid catalysis, desalination, disinfection, sensing and monitoring of three major classes such as organic, inorganic, and biological water pollutants. Nanobiohybrid catalysis has recently been grown as a novel technology with high selectivity, sensitivity, stability, and reusability. But a few studies have been adopted and/or published on Nanobiohybrid decontaminations, and most of them have dealt only to determine permissive and non-permissive levels of water pollutant concentrations. It appeals more study to mature the field from various angles not only to sense the novel toxic water pollutants, but to mitigate them from complex wastewater matrices. As a corollary, we emphasized the importance of Nanobiohybrid-mediated water purification technology. We believe that upgrading the Nanobiohybrid technology by controlling its steering speeds and improving its performances would be a robust solution to face current threats, and challenges of water purifications through both incremental and revolutionary ways. Finally, we

forayed into the deeper thoughts and compiled promises, facts and challenges of the important water purification technologies. Since water purification is a complex process, hydrologists, membrane technologists, environmentalists and industrialists can design “ONE POT” combination where effective water purification technologies would instate to tackle both the conventional and newly emerging toxic pollutants effectively. With the hope of this, let us think a best future of improved and efficacious decontamination platform, and thereby ensure plethora of fresh water for all.

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