Functionalized multi-walled carbon nanotubes for oil spill cleanup from water

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Abstract
The growing global economy resulted in an incessant increase in transportation and exploitation of oil. Hence, the oil spillage has been considered a serious threat to aquatic and terrestrial ecosystems. Therefore, water purification has been considered a major challenge around the world. There are numerous classical methods available for oil removal from water, but owing to multiple defects and disadvantages, research efforts have focused to find such adsorbents which can improve oil adsorption capability. Traditional adsorbent material typically applied in oil removal includes activated carbon, organoclays, wool, zeolites, etc. These materials suffer from several drawbacks such as low absorption capacity, non-selective absorption, and complicated reusability, whereas nano-adsorbents offer multiple advantages such as having multiple sorption sites, large surface area, short intra-particle diffusion distance, tuneable pore size, and ease of low-temperature modification. Multi-walled carbon nanotubes (MWCNTs) are extensively used adsorbent materials with a strong affinity for the removal of organic pollutants. The functionalization MWCNTs further increase the sorption capacity of adsorbents manifolds to remove organic materials. These nanocomposites are also compatible with green materials and considered environmentally friendly adsorbents. This review paper aims at providing an insight to understand the properties of the MWCNTs and their potential use to adsorb hydrocarbons from water. Moreover, the synthesis methods of those materials, their modification procedures including the functionalization with metal oxide nanoparticles, and applications are also discussed in detail.

Graphic abstract

Keywords Adsorbent · Oil spill · Metal oxide · Nanoparticles · Organic pollutants · Carbon nanotubes

Extended author information available on the last page of the article
Introduction

The global economy continues to expand rapidly through the exploitation and production of crude oil; however, the transportation of oil and its derivatives potentially remains a serious threat to the environment (Li et al. 2019a, b, c, d). Among many other challenges, the oil spills remain at the major ecological and environmental concern (Lin et al. 2019) as Dubansky et al. have reported that crude oil contamination of sensitive estuaries in Gulf coast is predictive of toxic impacts in exposed fish (Dubansky et al. 2013). The major oil spill incidents around the globe in recent years such as Rayong oil spill in the Gulf of Thailand 2013, the series of Tianjin explosion in China 2015, the sinking of Agia Zoni II tanker in the Saronic Gulf in Greece 2017, and the Sanchi tanker sinking in the East China Sea during 2018 have affected not only the marine life but also resulted in loss of valuable human lives and will continue to affect the ecosystem for decades (Li et al. 2019a, b, c, d). Oil spills release volatile organic compounds (VOCs) and heavier hydrocarbons into the aquatic environment causing severe damage to the ecosystem (Liang et al. 2014). The petroleum hydrocarbons, heavy metals, and other compounds also fall within the category of primary pollutants which have severe impacts on living organisms due to their neuro-toxic and carcinogenic effects (Zhao et al. 2018). Numerous research studies have extensively assessed these pollutants and have found that their toxicity levels have exceeded the limit values set by international standards (Anjum et al. 2019a, b). Water pollution is a threatening issue since it affects hundreds of millions of people within a short period. Due to the polar structure of the water molecule, it dissolves chemical and biological contaminants which affect the water supply system making it hazardous not only for aquatic life but also for public health (Gopakumar et al. 2019). The gravity of the situation made the treatment of oil spills an emerging contemporary problem and has sought the attention of researchers to work for the removal of organic contaminants and floating oils by developing novel cleanup methods (Al-Jammal and Juzsakova 2017).

Hence, it necessitated urgent and concerted efforts to develop modern methods for the remediation of organic matter- or hydrocarbon-polluted waters. There are several traditional depollution methods for cleaning oil spills including physical, chemical, and biological methods. Apart from that, another classification includes mechanical recovery of oil, if it is present in any certain area having natural or artificial barrier by the process of filtration, diffusion, stripping, skimming, in situ burning, gravity separation, emulsification, gelling agents or by using membrane bioreactors, dispersants, and solidifiers. These physical methods for cleaning oil spills suffer from many disadvantages such as being time-consuming, less efficient, and generate enough waste whenever used. In the case of non-mechanical recovery methods, numerous methods have been applied including chemical and some biological treatments such as adsorption, chemical coagulation, dispersing, burning, phyto-remediation, or bioremediation. From all these methods, adsorption is a top choice globally in industries as well as in research laboratories owing to its simplicity, safety, and remarkable efficiency for cleanup of oil spills as it does not involve any other potential risks (Valcárcel et al. 2008). There are three categories of adsorbents being employed in oil spillage cleanup such as natural organic, mineral, and synthetic organic adsorbents. Each category of adsorbents has a different capacity and functionality but has limitations in case of oil spillage cleanup (Al-Jammal and Juzsakova 2017). The first category of natural adsorbents consists of biodegradable materials, but those are to be avoided in case of fire. The second category of mineral adsorbents exhibits lower hydrophobicity and hence their capacity for oil adsorption is lower, while the third category of synthetic organic adsorbents has exhibited a high level of hydrophobicity, thus making them a suitable choice (Malakpour and Khadem 2016). Various commercial sorbent materials have been used for this purpose, including modified clay minerals, activated carbon, zeolites, exfoliated graphite, cellulose, propylene and other polymeric resins, and metal-oxide nanoparticles (Maleki 2016). However, most of these methods exhibit certain problems that limit their application as a wide-scale remediation technique. These issues include low absorption capacity, poor selectivity, and limited recycling (Maleki 2016).

Since the last decade, the field of nanotechnology has greatly revolutionized the methods for environmental remediation because nanoparticles hold manifold merits such as large surface area, more active adsorption sites, high reactivity, and small size (Ibrahim et al. 2019). The carbon nanotubes (CNTs) can simply be defined as a group of carbon nanomaterials that have a tubular structure and have an arrangement of hexagonal carbon atoms bonded covalently. The CNTs, in comparison with other nanoparticles, show relatively higher adsorption affinity toward volatile organic compounds removal as reported by Maleki (2016); water treatment for including oil and toxic organic compounds reported by Parmar et al. (2019); and heavy metal ions removal by Wu et al. (2019). Likewise, in the most recent times, CNTs are considered as potential adsorbents finding a variety of remediation applications in almost all environmental fields including removal of organic pollutants and heavy metals from aqueous media (Lin et al. 2019; Li et al. 2019a, b, c, d). This attention is attributed to several characteristic features these possess as narrated by Hu et al.
Functionalized multi-walled carbon nanotubes for oil spill cleanup from water

Functionalyzed multi-walled carbon nanotubes for oil spill cleanup from water published up to 2020. Another interesting review article authored by Arora and Attri presented more generalized information about CNTs. It briefly discussed types of CNTs including single-walled, double-walled, and multi-walled followed by their applications in water treatment, desalination, antimicrobial activity, sensing, and monitoring. This review article does not present any single method regarding oil removal.

The ever-increasing transportation and exploitation of oil we have resulted in oil spillage polluting the surface waters. The increased oil contamination of water demands brilliant and efficient depollution methods. To date, there exists no generalized method for complete remediation of oil from contaminated waters. The classical methods are not so efficient as to decontaminate emulsified oil from water and require high operational costs. Hence, the combination of methods is a preferred choice of the researchers. The critical analysis of the relevant literature indicated that adsorption is a promising method being highly efficient, cost-effective, and environmentally friendly. This review aims at exploring the potential of functionalized MWCNTs for the remediation of oil components from water. The modification of MWCNTs results in increasing the hydrophobic properties of the oil adsorbents and subsequent removal of hydrocarbon from oil spill sites. This review paper aims at providing an insight to understand the properties of the MWCNTs and their potential use to adsorb hydrocarbons from water. The synthesis methods involved, the ways of their modification including the functionalization or modification with metal oxide nanoparticles followed by their applications, are also discussed in detail.

Classification of carbon nanotubes

Carbon nanotubes have been mainly categorized based on several graphene sheets. As reported by Sun et al. (2017), there exist three categories of CNTs according to the literature available to date such as single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and multi-walled CNTs (MWCNTs) as illustrated in Fig. 1. Each class has specific characteristics, hence showing promising applications in several fields ranging from microelectronics to energy storage, from drug delivery to sensors, and from catalysis to adsorption methods for removal of organic pollutants (Liang et al. 2014). SWCNTs attracted the massive attention of scientists after their discovery in 1991 because of their superior properties including thermal and mechanical stabilities and electrical aspects. Later, it was reported that the SWCNTs provided a lower shielding effect as compared with MWCNTs (Apul and Karanfil 2015; Zhang et al. 2019).
The surface properties of the CNTs can be modified via surface functionalization, and in this way, the hydrophobic or oleo-phobic surfaces can be generated by simple modifications. In this way, their surfaces become highly selective (Ren et al. 2011). Hence, for applications like the removal of organic pollutants and heavy metals (Pourzamani et al. 2015), the MWCNTs are preferred. The MWCNTs are stiff materials, are relatively cheap, are easy to produce, have a large surface area, and exhibit good thermal stability and strong affinity for organic materials and other ionic pollutants (Sengupta and Gupta 2017).

**Synthesis of carbon nanotubes**

Numerous techniques and methods have been devised and used for the synthesis of MWCNTs for a variety of applications in a wide range of fields. There are two approaches for the synthesis of CNTs such as bottom-up approach and the top-down approach. The methods involved in these approaches are shown in Fig. 2. The most common of these methods include laser ablation, arc discharge, and chemical vapor deposition (CVD) (Mubarak et al. 2014).

The most popular and economically feasible method for the synthesis of MWCNTs is CVD method. This method works in a way to cleave a carbon atom-containing gas that flows continuously through nanoparticles catalyst to produce carbon atoms followed by generating CNTs deposited on the catalyst surface or the substrate. CVD involves the decomposition of a carbon source such as hydrocarbon gas by catalyst at a relatively higher temperature. The sol–gel method for the synthesis of CNTs involves mainly two processes, i.e., hydrolysis of precursor either in acidic or in basic medium and poly-condensation of hydrolyzed products. This method is particularly efficient where the experimental conditions require surface modification (Halbos et al. 2016). Chemical precipitation is employed for the removal of heavy metals from wastewater. This method offers the advantage of being facile as well as high yield. Chemical decomposition and vapor–liquid reaction methods are also used for preparing nanomaterials for purpose of adsorption. Photolithography is used in micro-fabrication in which geometric shapes are transferred on the substrate surface. In this process,

![Classification of Carbon Nanotubes based on Structure](image1)

**Fig. 1** Classification of CNTs based on the structure

![Various methods used for the synthesis of CNTs](image2)

**Fig. 2** Various methods used for the synthesis of CNTs (Murshed and Castro 2014)
photosensitive polymers are used. Ion-beam lithography as it is evident from its name uses light ions such as proton or helium ions focused toward the surface to produce nanostructures or smaller integrated circuits. This method is still in the improvement phase as there are several limitations for higher resolution. However, it results in highly pure MWCNTs along with strong control over various parameters including the length, diameter, and morphology (Mursheed and Castro 2014). For large-scale production, the most recognized approach is the decomposition of hydrocarbons, i.e., methane or acetylene as carbon precursors assisted by catalysts. The catalysts used in the preparation of MWCNTs are Co-Mo/MgO, Ni/glass substrate, bimetallic salts of iron(II), iron(III), and cobalt(II) on calcium carbonate or stainless steel (Sharma et al. 2015; Korayem et al. 2017). The further purification of the synthesized MWCNTs is carried out by chemical oxidation by sonicking the MWCNTs (Chen et al. 2014) with concentrated nitric acid to remove the metal catalyst particles and the carbonaceous impurities (Liew et al. 2016). It is pertinent to mention that insufficient dispersion usually limits the properties of CNTs composites. Hence, during synthesis, the mechanical dispersion or chemical dispersion methods are a good choice to achieve complete dispersion. These methods include ultrasonic treatment, magnetic stirring, functionalization, or the use of surfactant (Modugno et al. 2015).

In nanocomposites applications, the successful utilization of CNTs depends upon their homogenous dispersion within a polymer matrix or solvent for maximizing their contact surface area with polymer matrix. As CNTs have diameters on nanoscale, the entanglement during growth and the substantial van der Waals interaction between them forces them to agglomerate into bundles. This agglomeration suppresses the mechanical, electrical, and thermal properties of composites. Ultrasound energy can be used to agitate particles in a solution in sonicator resulting in the separation of individualized nanoparticles from the bundles. This method has been suitable to disperse CNTs in liquids with low viscosity, such as water, ethanol, and acetone (Sengupta and Gupta 2017). The physical method or the non-covalent treatment and chemical method or covalent treatments are two other available approaches.

Chemical methods use surface functionalization of CNT to improve their chemical compatibility with the target medium, i.e., polymer matrix or solvent by enhancing wetting or adhesion characteristics, thus resulting in a reduction in their tendency to agglomerate (Fatemi and Foroutan 2016). This approach is, however, not a risk-free as aggressive chemical functionalization such as the use of strong acids at higher temperatures may result in structural defects in tubes. However, the non-covalent treatment seems to be attractive because of the possibility of adsorbing various groups on the CNT surface without disturbing the system and achieving individually dispersed nanotubes. Among the reagents used for dispersion, the surfactant has been more common. Non-covalent functionalization is attractive because the π-electron cloud of the graphene sheet of the CNT is not disturbed and the characteristic properties of the CNT are preserved at lower cost and in less time. To exfoliate the CNTs bundles, the tube surface can be modified, via van der Waals forces and π–π interactions, by adsorption or wrapping of surfactants, polymers, or biomolecules (Saifuddin et al. 2013).

Adsorption of organic compounds over multi-walled carbon nanotubes

Adsorption technology over MWCNTs is one of the promising treatment options for pollutant removal due to their efficiency, simplicity, inexpensive feature, and non-sensitivity to toxicity. To date, numerous models have been tried to describe the adsorption of organic molecules over CNTs in the aqueous phase, such as Freundlich, Langmuir isotherms, and others. Organic chemical adsorption over MWCNTs is equivalent to or even higher than that on activated carbon. Thus, the surface area may not be a direct factor to forecast organic chemical–MWCNTs interactions. Su and Lu related the higher organic material adsorption over CNTs to larger average pore diameter and volume, morphology, and functional groups (Su et al. 2010).

It is worthy to mention that the adsorption over CNTs is of paramount importance (Pan and Xing 2008) due to the existence of high-energy adsorption sites, such as CNT and functional groups and interstitial and groove regions between the CNTs bundles (Ma et al. 2017a, b). These adsorption sites mainly exist overgrown CNTs. Thus, adsorption seems to be a general feature. The second is the condensation phenomena, in which the pores and capillaries of CNTs become filled with liquid condensed from the vapor. While the organic chemicals adsorb on the CNTs surfaces, multilayer adsorption might happen. In this process, the first couple of layers collaborate with the surface, while the molecules further to the first two layers interact with each other. This process is known as surface condensation (Pan and Xing 2008).

The outer surface of separate CNTs supports evenly distributed hydrophobic sites for organic chemicals. If hydrophobic interaction is the only mechanism between organic chemicals and CNTs, the adsorption may be anticipated to occur via chemical bonds. However, hydrophobic interactions cannot entirely describe the interaction between organic chemicals and CNTs (Yang et al. 2016). Other mechanisms comprise π–π interactions (between bulk π systems on CNTs surfaces and organic molecules with carbon–carbon double bonds or benzene rings), hydrogen...
bonds (because of the functional groups on CNT surfaces),
and electrostatic interactions (because of the charged CNTs
surface).

**Functionalization of multi-walled carbon nanotubes**

The chemical co-precipitation method was adopted to prepare magnetic MWCNTs loaded with poly-aluminum chloride (PAC) under microwave irradiation. The characterization confirmed that MWCNTs were magnetized and modified by PAC to remove humic acid from aqueous media with enhanced adsorption capacity (Li et al. 2019a, b, c, d). MWCNTs were loaded with mono-dispersed magnetite nanoparticles (like a sponge) and further treated via amino group functionalization. It was used for the removal of tetrabromo-bisphenol-A (TBBPA) from aqueous solutions. The sponge comes with a simple regeneration procedure and exhibits reasonably good adsorption capacity making it an effective adsorbent for water treatment (Wu et al. 2019).

Similarly, MWCNTs modified with magnetic hybrid material and chitosan through the CVD method were also reported for removal of TBBPA. It was proved to be eco-friendly, efficient, and reusable adsorbent (Zhou et al. 2014). The fluorination of MWCNTs through the solid-phase reaction method enhanced the adsorption performance of organic compounds (Li et al. 2016). Fluorination also enhanced the electro conductivity, surface polarity, and capacitive character of MWCNTs (Maiti et al. 2012; Lu et al. 2016). MWCNTs modified with pristine, hydroxyl, and carboxyl functional groups have also been reported for investigating the adsorption behavior of commercial humic acid (Yang et al. 2018). Another effort was made to coat MWCNTs with titanium oxide through the sol–gel process to investigate the effect of TiO₂ in the protection of the MWCNTs (Ardila-Rodríguez et al. 2019). Three nanometals (nano-crystalline zinc, copper, and iron) were grafted by various approaches on the surface of MWCNTs to understand the adsorption behavior of perfluorooctanoic acid in aqueous solutions (Liu et al. 2018).

During the last few years, a concerted effort has been undertaken to make MWCNTs highly selective while minimizing the hydrophobicity feature. It lowers the interference in sorption processes. Numerous MWCNTs-based composites having higher sorption capacity have been reported (Zhang et al. 2019). Among these modifications, the surface modification of MWCNTs with organic functionalities remained a distinguished technique including the use of a variety of functional groups such as hydroxyls, amides, carboxylate, phosphates, and sulfates onto MWCNTs surfaces as shown in Fig. 3 (Su et al. 2010; Omachi et al. 2013).

The process of modification with organic functionality is quite simple as the action of strong oxidizing agents such as hydrogen peroxide, nitric acid, sulfuric acid, and potassium permanganate increases the hydrophilicity and can introduce carboxylate groups onto the MWCNTs surface (Anjum et al. 2019a, b). Similarly, the further addition of any functionality on the surface of nanotubes can be carried out after the first step. The MWCNTs-based adsorbents have greatly exhibited remarkable sorption performance as compared to others. Additionally, the sorption performance can also be enhanced through functionalization of MWCNTs surface or by producing MWCNTs-based composites that show high selectivity for adsorption too. Functionalization of CNTs can be classified into covalent and non-covalent categories as shown in Fig. 4 (Jun et al. 2018).

It is worth mentioning that the non-covalent tuning of CNTs is preferable for the enhancement of interfacial properties of the CNTs as it avoids the destruction of CNTs’ structure (Fig. 5) (Kotagiri and Kim 2014).
Fig. 4 Classification of CNTs functionalization methods (Jun et al. 2018)

Fig. 5 Interfacial structures of CNTs after functionalization (Kotagiri and Kim 2014)
Figure 6 illustrates some of the main covalent functionalizations of CNTs (Yrgiannis et al. 2021). Functionalization of CNTs surfaces is carried out using a wide range of functional groups as given in Fig. 6. Functionality imparts useful properties which are lacking in the original MWCNTs. The surface modification of the CNTs with non-covalent modifications such as van der Waals force and π–π interactions is preferable as it enhances the interfacial properties of the CNTs by avoiding the destruction of CNTs structure (In-Yup et al. 2011). The important interactions are between aliphatic C–H donors and aromatic π-acceptors and interactions between aromatic C–H donors and aromatic π-acceptors.

MWCNTs modified by using nitric acid and KOH had been reported to affect the surface area. This was investigated by the absorption of bisphenol-A in an aquatic environment (Shih et al. 2017). Likewise, MWCNTs functionalization was performed using acidic treatment in the presence of sulfuric acid and nitric acid solution (Sousa et al. 2017). Figure 7 illustrates some of the main covalent surface chemistry techniques for the CNT functionalization (Ribeiro et al. 2016).

On the other hand, functionalized MWCNTs with cobalt phthalocyanine were used to modify the glassy carbon electrode to quantify pesticide residue in grape and mango fruit samples (Ribeiro et al. 2016). Most of the research studies were carried out to study the efficient removal of pollutants from the aqueous media containing dyes, metal ions, and other pollutants. It is very important that the potential of adsorbents or composites should be demonstrated in the case of real wastewater samples or oil-contaminated water samples since other components including salts, silicates, phosphates, and carbonates in wastewater can compete with target species for the sorption sites present on the surface of MWCNTs (Sadegh et al. 2016). Likewise, the remaining natural organic constituents of water such as humic and fulvic acids will also occupy sorption sites which may affect the actual adsorption results. In another research study, the catalytic oxidation of volatile organic compounds was carried out over MWCNTs doped with platinum nanoparticles by utilizing their porous structure, hydrophobic nature, and thermal stability (Joung et al. 2014). Silver nanoparticles-decorated MWCNTs were prepared for the electrochemical degradation of benzene in a natural aqueous solution (Cesarino...
et al. 2013). Zhang et al. have used MWCNTs to study the effect of the amount of MWCNTs as filler on the cementitious composites through electromagnetic wave adsorption and shielding properties. The experimental results indicated the improvement in these properties of the cement with successive addition of the MWCNTs resulted in changes in size and diameter of MWCNTs (Zhang et al. 2019). Magnetic MWCNTs were synthesized using the co-precipitation method loaded with poly-aluminum chloride followed by microwave irradiation. The magnetized MWCNTs showed enhanced adsorption capacity after surface modification for the removal of humic acid from aqueous media (Li et al. 2019a, b, c, d).

During the last decade, the modification of MWCNTs with metal oxides proved to be more efficient and attracted significant attention in several fields because of the high modulus of elasticity and stability in a wide temperature range as compared with other materials (Sengupta and Gupta 2017). The metal oxide modifications included iron oxide, titanium dioxide, nickel oxide, cerium oxide, aluminum oxide, tin oxide, zinc oxide, etc. (Mallakpour and Khadem 2016). The combination of MWCNTs with metal oxides opened new avenues of functionalities with improvement in electronic, optical, and mechanical properties (Yamamoto et al. 2008; Tang et al. 2013).

Fig. 7 Surface chemistry techniques for functionalization of MWCNTs (Wu et al. 2010)
Applications of multi-walled carbon nanotubes in oil spills and organic hydrocarbons removal

MWCNTs as adsorption media have significantly achieved great attention because of their excellent hydrocarbon removal capacities following the surface functionalization as detailed by Kim et al. (2012) similarly for the reduction of dyes as studied by Duan et al. (2016). MWCNTs-based adsorbents have been widely explored for the removal of heavy metals from industrial effluents and have shown high sorption performance among all known adsorbents. In oily sludge, various classes of organic compounds exist such as aliphatic, aromatics, hetero-atom-containing compounds and asphaltenes (Padaki et al. 2015). The contribution of the hydrophobic effect was investigated for the sorption of organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) (Peng et al. 2017). Similarly, MWCNTs exhibited enhanced surface area, high binding affinity, higher capacity, and excellent thermal stability for PAHs (Bunkoed and Kanatharana 2015). Due to the large-scale transportation of crude oil, a large quantity of liquid oily waste generates mostly in waterways. Hence, many serious environmental problems have emerged due to leakages and spills. Currently, several techniques are being employed for the separation of the spilled oil and water or the emulsified oily wastewater (Xu et al. 2018). These methods include membrane filtration, electrochemical methods, air flotation, gravity separation, and biochemical methods. However, certain disadvantages are associated with these methods, including high operational cost, low efficiency, low flux rates, etc. (Sengupta and Gupta 2017). In addition to that, the functionalized MWCNTs and graphene oxide have also been found effective in the acidic medium as well as under neutral conditions for the separation of the emulsified oil from water due to the presence of different functional groups on MWCNTs and graphene oxide. However, because of electrostatic repulsion between oil droplets and the demulsifiers under alkaline conditions, the above-mentioned combination was found to be inappropriate. The functionalization of MWCNTs was inappropriate for the separation of oil from water under basic/alkaline conditions because of electrostatic repulsion. MWCNTs were synthesized through the CVD method with precursor gases and subsequently tested for the adsorption of lead(II) from aqueous media (Mubarak et al. 2016). Unleaded gasoline adsorbed with high rate from polluted aqueous media using MWCNTs (Lico et al. 2019). Another method was also reported for the removal of phenol and other aromatic compounds using adsorption over MWCNTs (Carvalho et al. 2012).

MWCNTs were prepared by using composite catalyst Co-Mo/MgO as a growth nanocatalyst. The prepared adsorbents were used on an industrial scale for adsorption and removal of asphaltenes/heavy hydrocarbons from water. These composites were the best choice since they showed high adsorption capacity to remove asphaltenes (Hosseini-Dastgerdi and Meshkat 2019). The extraction and removal of PAHs from wastewater are one of the most promising applications of MWCNTs because the hydrophobic sites adsorb the aromatic pollutants (Akinpelu et al. 2019). MWCNTs doped with ferric oxide nanoparticles were utilized for the de-oiling process from wastewater (Fard et al. 2016). The direct removal of tiny oil droplets from oily water was carried out over MWCNTs prepared using the CVD method (Zhu et al. 2019). Fresh MWCNTs were synthesized in a fluidized-bed reactor by catalytic pyrolysis of propylene over Fe/Mo/Al₂O₃ catalysts in a nano-agglomerate fluidized-bed reactor. These composites possess outstandingly good adsorption capability, and this feature was investigated for recycling different metal ions and surfactants (Liu et al. 2015a, b). Fresh MWCNTs possess higher specific surface area as well as unsaturated surface atom coordination, hence exhibit higher chemical reactivity and adsorption properties, and have become an attractive option as sensors (Nudrat et al. 2018).

Therefore, the functionalized MWCNTs are widely used for adsorbing different pollutants including methylene blue by Wang et al. (2019) and Cheng et al. (2014) used β-MnO₂ nano-pincers as an efficient catalyst for degradation of inorganic materials. Similarly, Arasteh et al. (2010) reported adsorption of 2-nitrophenol over MWCNTs having the functionality of carboxylic acid, and Ibrahim et al. (2019) used functionalized CNTs for adsorption of methyl orange dye. Hu et al. (2019) used polymer-functionalized CNTs for selective adsorption of organic pollutants, and Ali (2012) used functionalized MWCNTs for water treatment of wastewater and regarded these materials as new-generation adsorbents. Due to the presence of electrostatic force and hydrophobic interactions, the MWCNTs exhibit solid interaction with organic molecules and are easy to aggregate (Apul and Karkanil 2015; Ma et al. 2017a, b). MWCNTs were used as adsorbents to investigate the adsorption of ciprofloxacin from aqueous solutions (Li et al. 2018). MWCNTs activated with persulfate were modified with nitric acid and then used for the degradation of phenol (Yang et al. 2019). Following the carboxylation of the MWCNTs, another application was the removal of toxic industrial waste surfactant, i.e., linear alkyl-benzene-sulfonate from industrial and household wastewater (Heibati et al. 2016). The removal of hydrophobic contaminants such as toluene, benzene, and p-xylene in aqueous media was studied as well after modification of MWCNTs by using a combination of maleic acid, tartaric acid, salicylic acid, and citric acid (Liu et al. 2018).
Applications of alumina-doped multi-walled carbon nanotubes

As compared with all other metal oxides, alumina has shown great potential for a large number of applications in multiple scientific disciplines as it possesses excellent properties of thermal and chemical stability, wear resistance, and high strength (Mansoor). However, the challenges associated with alumina such as low fracture toughness and its brittleness have, to some extent, limited its applications (Mallakpour and Khadem 2016). Hence, by combining the MWCNTs with alumina, these defects in the alumina matrix can be minimized. Most of the reported studies have investigated the effects of MWCNTs on chemical, mechanical, and electrical properties of alumina, and because of these specific characteristic properties of alumina, the composite preparations are widely used (Singla et al. 2015). Yamamoto et al. reported the modification of MWCNTs with alumina matrix followed by acidic treatment. The resultant MWCNTs–ceramic composites exhibited high-temperature stability and high toughness. Another property, the hardness, was studied by using CVD method by Yamamoto et al. where the crack bridging behavior of alumina matrix combined with MWCNTs with a single-nanotube pull-out technique. They also prepared hybrid alumina composites through the mechanical mixing method. For the superfast growth of MWCNTs, anodic aluminum oxide was used (Dadras and Faraji 2018). Similarly, another application was found in the improvement in the combustion characteristics and performances of diesel engines after blending diesel fuel with nanoparticles of aluminum oxide, silicon oxide, and carbon nanotubes (Chen et al. 2018). Asmaly et al. also studied the modification of MWCNTs with aluminum oxide in order to produce composites with higher adsorption capacity for phenol and 4-chlorophenol in aquatic media (Asmaly et al. 2015a, b). Alumina decorated onto functionalized MWCNTs was successfully applied for the effective removal of Cd (II) and trichloro-ethylene simultaneously from contaminated groundwater (Liang et al. 2015).

Applications of titania-doped multi-walled carbon nanotubes

The preparation of TiO$_2$ nanostructures is usually done through the hydrothermal method, where TiCl$_4$ is used as a precursor, along with mixing deionized water and ethanol as starting materials in the ratio of 3:7 in an ice bath. Another method for the preparation of titania-doped MWCNTs is the wet impregnation process. The photo-catalytic performance of these composites was tested for the degradation of methyl orange (MO). The results indicated that modified nanocomposites exhibited higher MO degradation efficiency than the pure nano-TiO$_2$ (Duan et al. 2016).

It is well understood that, after UV light irradiation, electrons were excited from the valence band (VB) to the conduction band (CB) of TiO$_2$, which resulted in leaving behind defect electrons (h+) at original sites. Due to rapid recombination of charge carriers, photo-catalytic reaction results in a fraction of these electrons and defect electrons/holes showing low reactivity. As shown in Fig. 8, the improved catalytic activity of titania-modified MWCNTs can be due to the dominant contribution of nanotubes in MWCNTs/TiO$_2$ composites. It mainly increased the recombination time for photo-generated electron–hole pairs. It is also evident from the delocalized π-structure nature of MWCNTs that it promotes the electron transfer causing hole–electron separation (Duan et al. 2016).

Titanium dioxide–MWCNTs composites exhibit much better stability and non-toxicity with enhanced capability for the photo-oxidative destruction of hydrocarbons (Mallakpour and Khadem 2016). Titanium dioxide nanoparticles can be prepared using titanium chloride as a precursor (Halbos et al. 2016). The steps can be explained by Eqs. (1–4) (Rasheed et al. 2019):

\[
\text{TiCl}_4 + 3\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \xrightarrow{\text{Ice bath/mixing}} \text{Ti(OCH}_2\text{CH}_3)_3\text{(OH)} + 4\text{HCl}
\]

(1)

\[
\text{Ti(OCH}_2\text{CH}_3)_3\text{(OH)} \xrightarrow{\text{Autoclave}} \text{Ti(OH)}_4 + 3\text{CH}_2\text{CH}_2
\]

(2)

\[
\text{Ti(OH)}_4 \xrightarrow{\text{Annealing}} \text{TiO}_2 + 2\text{H}_2\text{O}.
\]

(3)
The overall reaction can be given as follows:

\[
\text{TiCl}_4 + 3\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow 4\text{HCl} + 3\text{CH}_2\text{CH}_2 + \text{TiO}_2 + 2\text{H}_2\text{O}.
\]

(4)

One of the advantages of titanium oxide in combination with MWCNTs is the formation of active sites to enhance the contaminant adsorption on the catalysts (Tang et al. 2018). For the preparation of titanium oxide–MWCNTs composites, numerous methods have been reported. These methods include CVD for preparing MWCNTs and treated with TiO\(_2\), electro-spinning, sol–gel synthesis, electrophoretic deposition, and mechanical mixing (Zhou et al. 2010). TiO\(_2\) was prepared in our laboratory and modified with MWCNTs using the hydrothermal method. The process is illustrated in Fig. 9.

Figure 9 explains the work which has been carried out in the laboratory of the Institute of Environmental Engineering, University of Pannonia (Abdullah et al. 2021). Nanometal oxide nanoparticles-modified MWCNTs have been used for the removal of kerosene from water. Figure 10 illustrates the mechanism of kerosene removal from water using fresh, acid-treated MWCNTs and metal oxides nanoparticles-modified MWCNTs.

In other studies, the photodegradation of various organic pollutants in aqueous media has been efficiently carried out over titania-doped MWCNTs, e.g., the photodegradation of benzene derivatives, methylene blue, and carbamazepine, malachite green (Tarigh et al. 2015). Because of the carbon–oxygen–titanium bonds, the photo-catalytic activity of the preparations markedly increased (Mallakpour and Khadem 2016). This has been confirmed by Zhou et al. while working on the destruction of organic pollutants (Mao et al. 2015). Titanium dioxide–MWCTNs composites have also been applied for the modification of glassy carbon electrodes for heavy metal detection in aqueous samples. Liu et al. prepared this composite as a precursor for the degradation of methylene blue via the hydrothermal method (Liu et al. 2015a, b). Similarly, photo-catalytic activities of the titanium dioxide–MWCTNs composites have been studied by Tarigh et al. for degradation of malachite green, for degradation of methyl orange by Duan et al. (2016) and in several other applications including applications such as hydrogen production to wastewater treatment (Budimirović et al. 2017).

Applications zinc-oxide-doped multi-walled carbon nanotubes

ZnO is among the earliest discovered metal oxides and is an integral part of gas-sensing materials due to the high mobility of conductive electrons, and has good thermal and chemical stability. Similarly, MWCNTs show better performance even at a lower temperature because of excellent electrical properties and high surface area (Potirak et al. 2014). The ZnO-doped MWCNTs are being synthesized using various
approaches with remarkable functional properties suitable for a variety of chemical and industrial processes. Zhu et al. preferred a handy sol–gel technique for coating MWCNTs with ZnO nanoparticles, which resulted in better photocatalytic performance (Zhu et al. 2009). Similarly, Park et al. synthesized one-dimensional ZnO nanostructures on screen-printed MWCNT films via thermal chemical vapor deposition using gold nanoparticles as a catalyst (Park et al. 2008). Zinc oxide is known as a semiconductor oxide having some exclusive properties such as low cost, large excitation binding energy, wide band gap, and eco-friendliness (Chen et al. 2013). The combination of MWCNTs and zinc oxide after deposition of zinc oxide over MWCNTs enhances the adsorption capacity to give better efficacy for a wide range of applications. But it results in low photo-catalytic activity because the recombination rate of the photo-induced electron–hole pairs is much faster as compared with surface redox reactions (Chanaewa et al. 2012; Shao et al. 2013). The combination of MWCNTs and zinc oxide after deposition of zinc oxide over MWCNTs enhances the adsorption capacity to give better efficacy for a wide range of applications. But it results in low photo-catalytic activity because the recombination rate of the photo-induced electron–hole pairs is much faster as compared with surface redox reactions (Chanaewa et al. 2012; Shao et al. 2013). This composite was also used for the quantification of hydrogen peroxide in swimming pool environment (Wayu et al. 2015). The photo-catalytic removal of methylene blue was also studied over zinc oxide–MWCNTs composites (Dai et al. 2012). Chang et al. investigated MWCNTs tethered with zinc oxide, and it was deduced that the presence of MWCNTs improved its catalytic activity for the degradation of cyanide in aqueous solutions as well as for the removal of acetaldehyde (Chang et al. 2011). Another application was reported in the pharmaceutical field using MWCNTs in which an electrochemical sensor was developed by modification of glassy carbon electrodes with zinc oxide and gold nanoparticles. It was then applied for the determination of acetaminophen (Kenarkob and Pourghobadi 2019; Ali et al., 2015). ZnO has been prepared in our laboratory by the sol–gel method, which can be followed based on Eqs. (5–7) (Zhou et al. 2013):

\[
\text{ZnCl}_2 + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2 + 2\text{NaCl} \tag{5}
\]

\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}. \tag{6}
\]

The overall reaction can be given as follows:

\[
\text{ZnCl}_2 + 2\text{NaOH} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{NaCl}. \tag{7}
\]

**Applications of iron-oxide-doped Multi-walled Carbon Nanotubes**

Iron oxide usually magnetite (Fe₃O₄) being ferromagnetic (hematite has low iron content and is part of rust and is paramagnetic) is also known as magnetic metal oxide. It is combined with MWCNTs through both physical and chemical methods. One of the most prominent features is the combination of magnetite with MWCNTs to produce super-paramagnetism preparations (Li et al. 2010). It is considered as one of the most attractive magnetic metal oxides and has received widespread attention due to its unique physical and chemical properties and various advantages such as high reversible capacity, rich abundance, low cost, and eco-friendliness (Pang et al. 2015). The composite material is made of a combination of MWCNTs with magnetite. It bears a large specific surface area, has hollow structure, is highly porous, and exhibits strong interaction to adsorb pollutants.
Another application for the removal of pollutants from wastewater was also reported using this combination of MWCNTs and the iron oxide (Ji et al. 2012). Asmaly et al. reported the use of this composite material for the removal of phenol from water (Asmaly et al. 2015a, b).

Mechanisms of organic hydrocarbons removal over nanomaterials and multi-walled carbon nanotubes

For the cleaning of hydrocarbons-polluted water bodies, MWCNTs have been extensively used in recent times because of multiple advantages such as better separation performance, ease of surface modification, and regeneration. Jiaqi et al. have reported the carboxylated ethylenediamine functionalization of Fe_3O_4, SiO_2 nanoparticles for the removal of methylene blue dye from water (Jiaqi et al. 2019). As it is a cationic dye having a positive charge, the adsorbent surface contains a huge negatively charged carboxylate anion available in solution. Resultantly, the strong electrostatic attraction causes rapid adsorption as shown in Fig. 10.

Similarly, another approach using nano-sized metal oxides for removal of water pollutants including hydrocarbons is reported by Zafar et al. A nano-structured zinc oxide adsorbent was developed, characterized, and efficiently used to get rid of methyl orange, azo dyes (Hu et al. 2015), and amaranth from water (Zafar et al. 2019). The mechanism for the separation is given in Fig. 11.

The study of the recent literature indicates another similar application of MWCNTs with surface functionalization for the removal of hydrocarbon from surface water with enhanced hydrophobicity (Al-Jammal et al. 2020). Al-Jammal et al. used hydrocarbon model molecules to study the hydrocarbon removal from water including aromatic, aliphatic, and alicyclic compounds. The micro-emulsion functionalization produced hydrophobic adsorbents and proved to be excellent hydrocarbon adsorbents as shown in Fig. 12.

The mechanism of kerosene removal in the case of fresh MWCNTs can be explained as follows (Abdullah et al. 2020). In the case of fresh MWCNTs, the adsorption of kerosene takes place by van der Walls bonding between carbon atom of MWCNTs and the carbon atom in kerosene. In the case of MWCNTs functionalized with acid, hydrogen bond forms between the hydrogen atom of MWCNTs and oxygen atom of the carboxyl group (primarily electrostatic force of attraction). Finally, in the case of MWCNTs modified with metal oxides nanoparticles, hydrogen bonding forms between the oxygen atom of the metal oxides nanoparticles over MWCNTs and hydrogen atom of kerosene as illustrated in Fig. 13.

Similarly, if the mechanism of adsorption of methylene blue is considered over fresh MWCNTs (Abdullah et al. 2020), initially \( n-\pi^* \) bond is formed between electron pair on the nitrogen atom of methylene blue and \( \pi^* \) bond on the carbon nano-tube. The bond could be a hydrogen bond between the electron pair of nitrogen and the hydrogen at the ends of tubes or defect sites. Then, by oxidizing the MWCNTs, carboxyl or hydroxyl groups can bond with methylene blue via an ionic bond. However, it prevents methylene blue from bonding with the MWCNTs by hydrogen bond or \( n-\pi^* \) bonds, because of spatial interruption.

After modification of MWCNTs with nanoparticles, the chain will lengthen and the interruption will decrease, so methylene blue can bond freely with the MWCNTs. In addition to that, it can bond with the oxidized MWCNTs, which bonds the metal oxide nanoparticles by ionic bonds formed between negatively charged oxygen atom on the metal oxide and the positively charged sulfur in methylene blue. Mechanisms of methylene blue adsorption over metal oxides-modified MWCNTs are explained in Fig. 14.

**Fig. 11** The interaction of dye/hydrocarbons with zinc oxide nanoparticles

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Multi-walled carbon nanotubes: first-hand choice nano-adsorbents for oil spill cleanup

The most important thing after the oil spill has taken place in the ocean because of either leakage or shipping accidents is to remove the oil rapidly; otherwise, it will be dispersed vast area throughout the water body. Recently, several researchers have worked to develop nano-adsorbents with high capacity and efficiency to remove oil from water (Kohli and Bhatt 2020). Professors Anyuan Cao and Dehai Wu (Gui et al. 2010a, b) discovered unique, robust, and very light MWCNTs/sponges. It can selectively and speedily absorb the oil spill from the water surface that provides an important answer to the oil spill issue. The modified carbon nanotube can absorb oil up to 180 times its weight, which is more highly efficient as compared with the commercially available absorbers for oil spill cleanup (Gui et al. 2010a, b). Another group of researchers, Chen et al. (2020) were introduced long-chain hexadecyl siloxane groups into hydroxylated multi-walled carbon nanotubes (MWCNTs-OH) to obtain modified carbon nanotubes (CNTs) with super-hydrophobic characteristics. They showed that super-hydrophobic/super-oleophilic polyurethane sponge exhibited excellent super-hydrophobic properties, with a water contact angle of $157.4 \pm 1.1^\circ$, and water droplets roll-off angle of only $6.7^\circ$. Also, its mechanical strength was greatly improved by the introduction of CNTs (Chen et al. 2020).

Since improving the adsorption performance and simplifying the oil recovery process, the various modification methods have been reported recently and Table 1 provides deep insight. Peng et al. (2019), Kukkar et al. (2020), and Singh et al. (2020) all have discussed the fabrication of hydrophobic/oleophilic sponges and summarize the recently reported modify materials onto sponges. Furthermore, some additional material properties are also presented, which make sponges superior capacity for addressing oil spills under extreme conditions (Gao et al. 2017). Hence, Qiao et al. (2019) reported a review to obtain a better understanding of the materials that could be used to obtain efficient oil adsorbents with magnetic iron oxide nanoparticles. Along with it made efforts to find out suitable synthesis strategies by encapsulating iron oxides with organic or inorganic coatings or embedding them in a matrix/support. Another purpose was to identify the desirable characteristics of CNTs materials such as high oil removal efficiency as rightly achieved by Kukkar et al. (2020) and Zeng et al. (2020).

Conclusions

Since the transportation of oil results in several oil spillage, this problem has been regarded as a serious threat to the environment; among many other challenges, the oil spillages still remain a major ecological and environmental concern. This review of MWCNTs’ functionalization methods for the removal of oil and organic pollutants suggested that the sorption capacity of modified MWCNTs can be enhanced. MWCNTs’ composites have shown high potential for application in oil removal, in particular, and in several other fields of pollutant removal making them the first-hand choice for the researchers. The ease of modification and variety of composite materials prepared has greatly enhanced the confidence.
of the scientists to use MWCNTs in a variety of applications. The most suitable and feasible method for functionalization is physical treatment or non-covalent functionalization as it does not disturb the π-system. The properties of the composite materials have shown the next level of use of MWCNTs. These are compatible with green materials as well; hence, these composites can be labeled as environmentally friendly adsorbents, thereby allowing the use of small amounts, generating less waste, and minimizing energy consumption. These materials will surely have an excellent and bright future for efficient oil/water separation, oil absorption, removal of organic contaminants and dyes, emerging contaminants from industrial wastewaters, and photo-catalysis to keep surface waters free from contamination and pollution.

Fig. 13 Proposed mechanism for removal of kerosene from water using fresh, acid-treated, and metal oxides nanoparticles-modified MWCNTs (Abdullah et al. 2020)
Fig. 14 Proposed mechanisms of bonding between MB and fresh MWCNTs (a), proposed mechanisms of bonding between MB and oxidized MWCNTs (b), and proposed mechanisms of bonding between MB and metal oxides nanoparticles-modified MWCNTs (c, d) (Abdullah et al. 2020)

Table 1 Adsorption capacities of different adsorbents for hydrocarbons

| Used adsorbent                        | Oil pollutant      | Adsorption capacity (g/g) | Removal efficiency (%) | References                        |
|---------------------------------------|--------------------|----------------------------|-------------------------|-----------------------------------|
| Raw Posidonia oceanica fiber          | Crude oil          | 5.3                        | 99.98                   | (Ben Jmaa and Kallel 2019)         |
| Sisal (Agave sisalana)                | Heavy crude oil    | 6.3                        | 92                      | (Annunciado et al. 2005)          |
| Sawdust                               | Heavy crude oil    | 6.4                        | 95.5                    | (Annunciado et al. 2005)          |
| Microemulsion/MWCNTs                  | Kerosene           | 4.70                       | 94                      | (Al-Jamal et al. 2020)            |
| Hydrophobic alumina                   | Crude oil          | 0.200                      | 95                      | (Franco et al. 2014)              |
| Coconut coir activated carbon         | Crude oil          | 4.86                       | –                       | (Anwana Abel et al. 2020)         |
| Banana peel                           | Gas oil            | 5.31                       | –                       | (Alaa El-Din et al. 2018)         |
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Declarations

Conflict of interest The authors declare that there is no any actual or potential conflict of interest including any financial, personal, or other relationships with other people or organizations that could inappropriately influence or be perceived to influence the work or its outcome in this article.

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