Carbon nanotube-based environmental technologies: The adopted properties, primary mechanisms, and challenges

Biao Song[a,b,1], Piao Xu[a,b,1], Guangming Zeng[a,b,*], Jilai Gong[a,b,*], Peng Zhang[a,b], Haopeng Feng[a,b], Yang Liu[a,b], Xiaoya Ren[a,b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China

[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China

* Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China.

E-mail addresses: zgming@hnu.edu.cn (G. Zeng), jilaigong@gmail.com (J. Gong).

[1] These authors contribute equally to this article.

Abstract

Carbon nanotubes (CNTs) show great potential and bright prospect in the field of environment. It is believed that this new kind of material will bring opportunities and benefits to the environmental protection and pollution control. In recent years, a lot of CNT-based environmental technologies have been developed and applied with successful results, but the adequate understanding and large-scale industrial applications of these technologies are lacking. This paper systematically reviews current environmental applications of CNTs, including pollution treatment and environmental remediation, environmental sample analysis, environmental monitoring and sensing, and design of environment-friendly products. The adopted properties of CNTs are introduced. The main roles of CNTs in these technologies are illustrated. Additionally, the main current challenges to realizing their practical applications are analyzed and discussed, involving toxicity and ecological risks, production costs, general applicability, long-term effect, and public acceptance. Further studies should give priority to the toxicity and environmental risk of CNTs when developing new CNT-based technologies. Research on standardizing toxicity testing and risk assessment of CNTs is highly recommended and a large number of toxicity data of CNTs are needed.

Keywords

Carbon nanotube; Environmental technology; Environmental application; Mechanism; Challenge

1. Introduction

Carbon nanotubes (CNTs) have shown great potential in many fields such as chemistry, materials, electronics, medicine, energy, and environment, since they were found by Iijima in 1991 (Iijima 1991). CNTs are hollow cylinders of carbon atoms in an arrangement of periodic hexagon. They are like graphite sheets rolled up on themselves to form tubes, which have a diameter size in the range of nanoscale. According to the number of graphite sheet, CNTs are divided into two main types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). CNTs exhibit many unique acoustical, optical, electronic, thermal, mechanical, and chemical properties, which enable their applications in various fields. For example, Wu et al. (2014) conjugated MWCNTs with prostate stem cell antigen antibody for ultrasound imaging and drug delivery due to the great echogenic property and biocompatibility of functionalized CNTs.

Environmental researchers have been exploring potential applications of CNTs based on the belief that this new kind of material will bring opportunities and benefits to the environmental protection and pollution control. Figure 1 shows the number of annual publications on CNTs and their environment-related part from 2007 to 2016, and the corresponding proportion of the latter in the former. Scientific activity on the research of CNTs is growing every single year during the past decade, bringing publications over 25,000 in 2016. In these publications, the proportion of the environment-related part is about 4.5%. The increase in number of the environment-related part and its proportion indicates that more and more people are committed to studying the relationship between CNTs and the environment. For potential environmental applications, numerous environmental technologies based on CNTs are researched and documented over the past decade. However, the adequate understanding and practical applications of CNTs in environmental engineering are lacking. What are the main roles of CNTs in these technologies? How will environment-related development of CNTs evolve? For solving these problems, it is important to review these technologies and identify the emerging trends.

In this review article, CNT-based environmental technologies are systematically summarized according to their environmental purposes. The adopted properties and main functions of CNTs in these technologies are introduced and analyzed. Selected papers are cited and discussed to give specific evidence on how CNTs function and what roles CNTs play in these environmental technologies. Additionally, the main current challenges to realizing their practical applications are discussed and the future research needs are proposed.

2. Environmental applications of CNTs

The development of new materials usually brings opportunities for the advance of other fields. CNTs with many attractive properties are showing great potential for environmental applications. According to different purposes, the current attempt and exploration in CNT-based environmental technologies are classified and illustrated in Fig. 2. The adopted CNT properties for their environmental applications and the main functions of CNTs are summarized in Table 1. The details are introduced as follows.

2.1. Pollution treatment and environmental remediation

The problem of environmental pollution is a global challenge (Chen et al. 2015; Cheng et al. 2016; Liang et al. 2017; Ren et al. 2018; Wan et al. 2018; Wu et al. 2017). With the involvement of CNTs, new ideas have been generated to solve this problem. Due to their unique physical and chemical properties, CNTs have been used in adsorption, membrane filtration, disinfection, and photocatalysis for pollution treatment and environmental remediation.

2.1.1. Adsorption

Adsorption is the accumulation process of adsorbate (a liquid or gas solute) onto the surface of an adsorbent (a solid or a liquid) (Özdes et al. 2009; Tan et al. 2015). It is simple and efficient to remove contaminants from environmental media by adsorption (Deng et al. 2013; Long et al. 2011; Tang et al. 2014). The high adsorption capacity of adsorbent is one of the basic conditions to achieve effective adsorption separation. CNTs exhibit high adsorption capacity due to their small size, unique hollow and layered structure, and large specific surface area. These properties enable them to be promising adsorbents for contaminant removal. However, CNTs show different adsorption capacity to different contaminants. For example, in a recent study by Song et al. (2017), the applied MWCNTs presented a maximum adsorption capacity of 162.1 mg/g to phenanthrene, but only 11.18 mg/g to Cd^{2+}. Different interaction mechanisms between them account for such a phenomenon. As illustrated in Fig. 3, the main adsorption mechanisms of organic compounds by CNTs include electrostatic interaction, π-π bonding interaction, hydrogen bonding interaction, and hydrophobic interaction (Pan and Xing 2008; Zhang et al. 2016). For the adsorption of heavy metals by CNTs, the mechanisms involve electrostatic attraction, physical adsorption, surface precipitation, and complexation that occurs between surface functional groups of CNTs and metal ions (Ihsanullah et al. 2016; Xu et al. 2012). In the example above, the strong hydrophobic interaction and π-π bonding interaction between the benzene ring of phenanthrene molecules and the graphene sheets of CNTs played a key role, thus showing a much higher adsorption capacity towards phenanthrene.

The unique structure of CNTs provides three kinds of adsorption sites: external surface, interstitial space, and internal cavity (Ji et al. 2010). Nevertheless, CNTs with few defects display low adsorption capacity for heavy metals. Substantial effort has been put on improving adsorption performance of CNTs towards heavy metals by surface modifications, such as acid treatment, grafting specific functional groups, and loading metals or microorganisms. For example, Li et al. (2003) applied different oxidants (HNO_3, $KMnO_4$, and H_2O_2) for the oxidation of CNT surface, which increased the adsorption capacity for Cd^{2+} from 1.1 mg/g to 5.1, 11, and 2.6 mg/g, respectively. The oxidation treatment generated many oxygen-containing functional groups such as carboxyl, carbonyl, and hydroxy, which increased the electrostatic attraction between CNTs and metal cations. The authors measured the amount of oxygen-containing functional groups on the CNT surface by Boehm's method, and the results (total amount) were 4.04, 3.36, and 2.52 mmol/g, respectively. This could partly explain the increase of the adsorption capacity. Shao et al. (2010) used plasma technique for grafting chitosan onto MWCNTs and applied the modified MWCNTs for removal of UO_2^{2+}, Cu^{2+}, and Pb^{2+} from aqueous solutions. The abundant amino and hydroxy of chitosan can react with reactive carbon sites generated by reactive nitrogen species in plasma discharge process. In the adsorption process, the unreacted amino and hydroxy can form chelate compound with metal ions, which increased the adsorption capacity of the modified MWCNTs. Zhao et al. (2010) loaded titanium dioxide nanoparticles onto MWCNTs for adsorption of Cd^{2+} from aqueous solutions, showing a significantly higher adsorption capacity (137 mg/g) compared with that of unloaded MWCNTs (33 mg/g). In this example, CNTs were used as a support for other adsorbent due to the large specific area of CNTs. It can not only reduce the aggregation of metal nanoparticles in preparation process but also combine the adsorption capacity of metal nanoparticles and CNTs. Additionally, considering the practical use, magnetic nanoparticles were intentionally incorporated into MWCNTs for magnetic separation of the adsorbents after treatment (Gong et al. 2009). Now, the characteristic of magnetic separation has been requisite for powder adsorbent material to function in aqueous solutions.

2.1.2. Membrane filtration

Membrane filtration is a common way for water purification. Unlike adsorption treatment, the membrane is usually immovable in the filtration process and the contaminants are intercepted when the wastewater flows past the membrane. In the field of membrane technologies, CNTs have been explored as functional materials of fabricating membranes. The utilization is mainly based on the following two considerations. On the one hand, high adsorption affinity of CNTs can intercept various contaminants in the water. On the other hand, smooth and hydrophobic walls of the hollow CNTs have little resistance to water molecules, allowing their quick transport through the membrane (Das et al. 2014). Figure 4a showed a water purification process using a general CNT membrane. CNTs are loaded onto a support membrane material to form an active adsorption layer. When contaminated water flows through the CNT membrane, the contaminants can be intercepted and adsorbed onto the CNTs, but no CNTs will be released into the effluent with the assistance of support material. Wang et al. (2015) prepared a CNT composite membrane by loading MWCNTs onto a polyvinylidene fluoride membrane, and applied it for the removal of pharmaceuticals and personal care products in water. Their results showed that the membrane exhibited a high removal efficiency towards triclosan and the equilibrium surface concentration of triclosan on MWCNTs was up to 1918.9 mg/g (with the pseudo-second-order kinetic equation). The support of polyvinylidene fluoride membrane prevented the CNTs from releasing into the filtrate, reducing the risk of CNT ingestion by human body. Moreover, the transmembrane pressure of CNT membrane filtration was much lower (< 100 kPa) compared with reverse osmosis (> 1000 kPa).

Apart from intercepting contaminants, CNT membranes are also designed as electrochemical filters for degradation of organic pollutants and inactivation of viruses and bacteria (Fig. 4b). This further takes advantage of the excellent electrical conductivity of CNTs. The primary removal mechanism is electrochemical oxidative degradation (Liu and Vecitis 2012; Vecitis et al. 2011). As illustrated in Fig. 4b, when organic pollutant is intercepted by the CNTs, the pollutant can be directly oxidized due to the contact with CNT anode and electron loss. On the other hand, indirect oxidation may occur through generating reactive species, such as reactive oxygen species (ROS). Latest research by Bakr and Rahaman (2017) evaluated the performance of an electrochemical CNT filter for removal of bisphenol-A. The results of their experiments showed that the contaminant can be almost completely eliminated by the CNT filter with an applied direct voltage of 3 V. The electrochemical CNT filters combined electrochemical degradation (or inactivation) and conventional filtration, which greatly reduced the operation time from hours to minutes. The authors studied the effect of residence time (2.0 and 14.9 s) on the degradation of bisphenol-A and analyzed the degradation products by liquid chromatography combined with mass spectrometry, and they concluded that direct electron transfer would show more obvious effect on the degradation of bisphenol-A with longer residence time based on the experimental results. In a case reported by Liu et al. (2015), tetracycline was degraded by an electrochemical CNT filter at a total cell voltage of 2.5 V, and the calculated energy consumption was 0.084 kWh/m^3 which is much lower than that caused by conventional treatment of municipal wastewater (0.80 kWh/m^3). The authors stated that the removal mechanism of electrochemical CNT filtration involved mass transfer of tetracycline to the CNT surface, adsorption of tetracycline by CNTs, electron transfer (oxidative degradation of tetracycline), and desorption of the oxidation products. For confirming the proposed mechanism and studying the degree of tetracycline electrooxidation, the authors further compared the electron flux and tetracycline molecular flux, and drew a conclusion that indirect oxidation by ROS generated from the cathode might also contribute to a fraction of the oxidative degradation. Similar electrochemical oxidative mechanism is also applicable for the capture and inactivation of viruses and bacteria by electrochemical CNT filters (Vecitis et al. 2011).

2.1.3. Disinfection

Another important reason for the use of CNT membrane filter in inactivation of viruses and bacteria is the antibacterial property of CNTs. In addition to antibacterial use in membrane technology, CNTs can also be applied as antibacterial agents directly (Mocan et al. 2017). Chi et al. (2016) used MWCNT suspensions for inactivation of *Escherichia coli*, and the antibacterial effect was proved to be dependent on both the functionalization of MWCNTs and medium nutrition. In such an antibacterial process, cell membrane damage caused by direct contact with CNTs was considered the main antibacterial mechanism (Chi et al. 2016; Kang et al. 2008). Research results of Aslan et al. (2010) indicated that shorter CNTs are more toxic. They explained it with a higher density of the open tube ends, which suggested that the antibacterial effect of CNTs is mainly due to their shape and size. As presented in Fig. 5, CNTs with different length exhibit different antibacterial behaviors. Short CNTs can directly pierce the wall and membrane of bacterial cell, leading to the membrane damage and leakage of intracellular components. Long CNTs may wrap the whole cell body, causing membrane damage through chemical interactions between the functional groups on CNT surface and the cell wall (Chen et al. 2013). Additionally, CNTs that enter the bacterial cell can induce oxidative stress and generate a lot of ROS, resulting in oxidative damage and even death of the bacterial cell (Mocan et al. 2017).

Though CNTs alone showed perceivable antibacterial effects on many pathogenic microorganisms, these effects are usually not to a substantial level (Dong and Yang 2015). Therefore, in order to enhance the antibacterial performance in applications, some other antibacterial substances are incorporated. Mohan et al. (2011) used MWCNTs decorated with silver and copper nanoparticles for killing *Escherichia coli*. In their experiments, the incorporation of silver and copper nanoparticles increased the antibacterial efficiency from 20% (acid-treated MWCNTs) to 97% and 75%, respectively. The silver and copper nanoparticles themselves have strong bactericidal capacity, but they tend to aggregate to minimize the surface energy during the preparation process. Using CNTs to load these bactericidal nanoparticles can stabilize and disperse the nanoparticles. Moreover, the combination of CNTs and bactericidal nanoparticles exhibited a synergistic bactericidal effect. Merli et al. (2011) increased the antibacterial effect of lysozyme by immobilizing it on MWCNTs through covalent cross-linking with 1-ethyl-3-(3-dimethylamino-propyl)carbodiimide (EDC) and N-hydroxysuccinimide (NHS). In their experiments, the modified nanocomposites showed a more significant effect on inactivation of *Staphylococcus aureus* (16% survival) compared with free lysozyme (55% survival) and acid-treated MWCNTs (80% survival). This could be attributed to the synergistic bactericidal effect of MWCNTs and lysozyme, and the authors considered that the immobilization of lysozyme on MWCNTs enhanced the biological activity of lysozyme. Zardini et al. (2012) functionalized MWCNTs with arginine and used them for inactivation of *Escherichia coli*, *Staphylococcos aureus*, and *Salmonella typhimurium*. Their results showed that the antibacterial activity was 3.04, 1.84, and 2.33 times greater than pristine MWCNTs, respectively. It was reported that the enhanced antibacterial activity was related to the increased interaction between the functionalized MWCNTs and the cell membrane of bacteria. After the functionalization with arginine, positive charges on the surface of MWCNTs were increased due to the increase of cationic functional groups. The cell membrane was negatively charged, which made the bacteria easy to be captured through electrostatic adsorption, thus enhancing the antibacterial activity. Taking into consideration the formation of harmful disinfection by-products (e.g., chlorite, trihalomethanes, and haloacetic acids) in traditional disinfection process of water (e.g., chlorination), these CNT-based antibacterial agents display a promising prospect for their antibacterial application in water purification (Song et al. 2016).

2.1.4. Photocatalysis

In the field of photocatalysis, the main current challenges are to increase the catalyst ability of responding to visible light, and to decrease the recombination of photo-induced electron-hole pairs during the photocatalytic process (Zhou et al. 2018). It has been reported that CNTs are capable of solving these problems (Natarajan et al. 2017; Seyed Dorraji et al. 2017; Wang et al. 2017). The roles of CNTs in the photocatalyst composite may involve two aspects (Fig. 6). On the one hand, CNTs can generate electron-hole pairs on the CNTs by direct irradiation due to their semiconductor characteristic and narrow band gap energy (Robel et al. 2005). On the other hand, CNTs can transfer electrons from the photocatalytic nanoparticles along their network, slowing down the recombination rate of electron-hole pairs (Seyed Dorraji et al. 2017). The uncombined electron and hole are the key of degrading contaminants. They can induce the generation of ROS. Figure 6 shows the generation of two main ROS, hydroxyl free radical and superoxide anion free radical. Both the free radicals are strong oxidants, which can cause the oxidative degradation of organic pollutants.

Numerous studies focus on the enhancement of photocatalytic efficiency by loading photocatalytic nanoparticles onto CNTs. Roozban et al. (2017) decorated MWCNTs with ZnO nanoparticles and applied them for degradation of methyl orange. When only ZnO nanoparticles were used, the maximum removal efficiency was 79.14%. With the help of the MWCNTs, the maximum removal efficiency was increased to 94.15%, which was mainly attributed to the faster electron transfer and separation of electron-hole pairs by MWCNTs. Natarajan et al. (2017) synthesized MWCNTs/TiO_2 nanotube composites and explored their application in photocatalytic degradation of rhodamine 6G dye. According to their results, 89% rhodamine 6G can be degraded by 50 mg catalyst within 60 min. The authors studied the photocatalytic mechanism with photoluminescence analysis, in which a low (high) photoluminescence intensity suggested a low (high) recombination rate of electron-hole pairs. Their results showed that the incorporation of MWCNTs could obviously decrease the photoluminescence intensity. For verifying the photocatalytic degradation of rhodamine 6G dye, the authors analyzed the total organic carbon (TOC) and chemical oxygen demand (COD) in the solutions, and the synthesized photocatalyst was effective in removing TOC and COD, with maximum removal percentages of 64% and 83%, respectively. Apart from the effective separation of electron-hole pairs, the tubular structure, enhanced adsorption, and synergic effect of MWCNTs and TiO_2 were considered to interpret the enhanced photocatalytic performance. Yang et al. (2016) studied the photocatalytic degradation of phenol by chrysanthemum-like CNT/Cu_2O nanocomposites, and a removal efficiency of 85.8% was achieved within 60 min under the experimental conditions. For understanding the formation mechanism of the synthesized photocatalyst, the authors captured samples at different stages (5, 30, 60, 240 min) during the synthetic process, and observed the morphology through scanning electron microscope. It was revealed that the whole synthetic process involved the reduction of copper ions to Cu_2O nanoparticles, the aggregation of Cu_2O nanoparticles to nanospheres, and the reconstruction of Cu_2O

nanospheres to chrysanthemum-like nanostructure. The CNTs were interwoven with Cu_2O nanoparticles and embedded into Cu_2O nanospheres during the synthetic process. The closely connection of Cu_2O nanoparticles with CNTs and unique hierarchical nanostructures mainly accounted for the excellent photocatalytic activity. Based on more practical consideration, Li et al. (2012) prepared a recyclable CNT-CdS hybrid sponge for removing organic contaminants from water. This unique sponge was multifunctional and could simultaneously adsorb and degrade organic pollutants. During a photocatalytic process, only the CdS nanoparticles on the outside surface were reactive. Other CdS nanoparticles inside the sponge were used for recycling after directly stripping off the surface part. The CNT sponge was used as support for grafting CdS nanoparticles. On the other hand, CNTs showed high adsorption affinity to many organic contaminants and could transfer electrons from CdS nanoparticles, which significantly increased the photocatalytic activity.

2.2. Environmental sample analysis

Accurate determination of contaminants in environmental samples is an important research part of analytical chemistry. When contaminant concentrations in samples are lower than the detection limit of instrument, preconcentration of the contaminants is necessary for accurate and reliable analysis results. Solid phase extraction (SPE) and solid phase microextraction (SPME) are widely used for this purpose.

SPE is a method for analyte collection/isolation from a solution. Its general procedure is to allow a solution to pass through a solid phase adsorbent, and then to wash off the adsorbed analyte into a collection bottle by another solvent (Hennion 1999). The solid phase adsorbent is a core part that determines the SPE performance. Use of CNTs as SPE adsorbent has been proposed due to the high adsorption affinity of CNTs for various organic and inorganic substances. Figure 7a presents a schematic diagram of the SPE process. After the extraction, the original sample can be purified and concentrated. Compared with traditional SPE adsorbents (e.g., silica gel, alumina, and kieselguhr), CNTs have a larger specific surface area and a shorter diffusion route. These characteristics contribute to high extraction capacity, short extraction time, and great extraction efficiency (Zolfonoun and Yousefi 2016). Tuzen et al. (2008) conducted a solid phase extraction of six heavy metals (Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}) at trace levels by using MWCNTs as extractor, and then determined their concentrations by flame atomic absorption spectrometry. The authors investigated the effects of pH, amount of MWCNTs, sample volume, eluent type, amount of chelating agent on the recovery of the heavy metals. Their results indicated that the experimental data were repeatable and reliable with a lower value of relative standard deviation (< 5%). Lalović et al. (2017) employed MWCNTs as SPE adsorbents for pharmaceutical extraction from surface water and ground water before the quantitative measurement by a high performance liquid chromatograph coupled to a mass spectrometer. According to their results, the analytical method showed good linearity and low detection limit (0.2–103 ng/L) for multiple pharmaceuticals. It was reported by the authors that the unique structure and characteristics of CNTs enable them to strongly interact with organic molecules through non-covalent bonding (e.g., electrostatic force, hydrogen bonding, hydrophobic interactions, π-π stacking, and Van der Waals force), thus CNTs exhibit high adsorption capacity towards organic analytes and these analytes are not difficult to be eluted from CNTs in the subsequent step. The authors further studied the effect of chemical treatment of CNTs on the extraction efficiency, and the results showed that the treatment with HCl could decrease surface oxygen groups of CNTs and favour the extraction of pharmaceuticals.

SPME is a solvent-free extraction method based on the equilibrium partitioning of analyte between the sample solution and the solid phase adsorbent which is coated on the SPME fiber (Tamayo et al. 2007). After equilibrium, the analyte can be thermally desorbed at the vaporizing chamber of a gas chromatograph (GC) directly or eluted with a solvent for further analysis (Fig. 7b). Compared with SPE, SPME can be more simple, faster, and cheaper. The material for coating SPME fiber is vital to a satisfactory extraction performance. CNTs have been considered as coating materials due to their attractive adsorption properties. For a good coating effect, researchers have developed many coating techniques, such as physical deposition, chemical bonding, sol-gel technique, and electrochemical/electrophoretic deposition (Ghaemi et al. 2014). Jiang et al. (2009) applied a sol-gel technique to coat CNTs onto a stainless steel fiber for SPME. In their experiments, carboxyl and hydroxy functionalized CNTs were used for preparing stable and homogeneous sol solution, as the dispersity and solubility of the functionalized CNTs were better. In the gelification process, polysiloxane chains were immobilized on the CNTs and contributed to the formation of the matrix structure. The involvement of CNTs can solve some problems of polymers in the applications, such as limited applicable range of temperature, aging, and degradation under intense light irradiation. The prepared SPME fiber in this example exhibited excellent thermal stability, low carry-over, and no competition effect, and the extraction efficiency of five tested solutes is higher than a commercial polydimethylsiloxane fiber of 7 μm. Asadollahzadeh et al. (2010) coated SPME fiber with CNT/polypyrrole composite by electrochemical deposition and the device was used for analysis of phthalate esters in aqueous solution. The authors stated that the electrochemical deposition was superior to using adhesives (e.g., dibutyl phthalate, epoxy resin, ethylcellulose, and terpineol mixture) for coating SPME fiber with CNTs, because these adhesives may lower the conductivity, thermal stability, resistance to organic solvents, and even adsorption capacity. The coated fiber exhibited a high adsorption capacity, a porous structure, and an excellent extraction efficiency for phthalate esters. Their experimental results suggested that the detection limit of this kind of analytical method for phthalate esters varied between 0.05–0.1 mg/L under optimized conditions. Moreover, such a fiber can be used over 60 times for the analysis through direct immersion of the SPME fiber in water.

2.3. Environmental monitoring and sensing

The fascinating properties of CNTs have also drawn great attention of many researchers in the field of environmental monitoring and sensing. It is promising to incorporate CNTs into conventional monitoring and sensing techniques.

Due to the excellent electrical conductivity, large specific surface area, and superior mechanical strength, CNTs have been used for electrochemical sensing as individual CNT devices, modifiers of electrode surfaces, and CNT paste/composite electrodes (Merkoçi et al. 2005; Zhang et al. 2015c). Kumar et al. (2016) fabricated an aligned network of SWCNTs by dielectrophoresis and applied it as a gas sensor for monitoring NO_2 concentrations. The gas sensor is based on the mechanism that the conductance of the sensor increases with the increasing adsorption amount of NO_2 on SWCNTs. The unique properties of SWCNTs enable the sensor to exhibit a faster response, a high sensitivity, and a great selectivity. According to their experimental results, the sensor response to NO_2 increases with the increasing concentration of the gas. The authors also developed a model which involves reversible and irreversible adsorption of NO_2 on the surface of SWCNTs to explain the response of the gas sensor, and this model was validated to be effective in fitting the experimental data. For 4-methoxyphenol detection, a glassy carbon electrode was modified with Cr_2O_3-CNT composite by Rahman et al. (2017). Their results showed that, at a signal-to-noise ratio of 3, the sensitivity was 1.4768 μA/(cm^2·μM) and the detection limit was 0.06428 ± 0.0002 nM. The incorporation of semiconducting metal oxides and CNTs significantly enhanced the sensor signal. The Cr_2O_3-CNT composite could sensitively detect 4-methoxyphenol through chemical interactions. Due to the high defect density and oxygen deficiency, the Cr_2O_3-CNT composite was able to adsorb a large amount of oxygen, thus accelerating the oxidation of 4-methoxyphenol and releasing more free electrons. As a result, the conductance of the electrode and the current response increased rapidly when exposed to 4-methoxyphenol solutions. Recently, Baciu et al. (2017) used a silver-decorated CNTs-epoxy composite as electrode for voltammetric detection of nitrite and ammonium from groundwater. Due to the surface passivation effect and slow rate of electron transfer, determining nitrite and ammonium with a bare solid electrode is usually difficult. Using silver-decorated CNTs-epoxy composite can overcome these problems, and direct oxidation of ammonium and nitrite catalyzed by the nanoparticles were responsible for the sensitive detection. Moreover, the electrode presented high electrocatalytic activity to the oxidation of ammonium and nitrite at separated response voltage values (+0.15 V for ammonium and +0.7 V for nitrite) with a saturated calomel electrode as reference electrode, thus the fabricated electrode can be applied for simultaneous determination of ammonium and nitrite in aqueous solution. Under the optimized operating conditions, the detection limits were calculated to be 0.7 μM and 1 μM for nitrite and ammonium, respectively. In the above studies, the high sensitivity and low detection limit may be attributed to signal amplification of the sensor in the presence of CNTs (Fig. 8). On the one hand, large specific surface area of CNTs provides a large load capacity for signal molecules. On the other hand, excellent electrical conductivity of

CNTs enables a faster electron transfer. These are helpful for amplifying sensing signal.

CNTs also play roles in signal amplification of biosensors. In order to realize ultrasensitive detection of biomolecules, a lot of signal amplification strategies based on functional nanomaterials have been proposed. After functionalization, nanomaterials can be widely used as tracers, carriers, catalysts, optical emitters, and electric conductors for amplifying sensing signal (Lei and Ju 2012). Tang et al. (2010) prepared horseradish peroxidase-nanosilica-doped MWCNTs and used them for signal amplification in ultrasensitive immunoassay detection of staphylococcal enterotoxin-B. The electrochemical immunosensor used an enzyme-linked immunoassay. The combination of enzyme and antibody may change the enzyme structure or occupy the active center of enzyme, which decreases the catalysis of substrate, while the combination of antibody and antigen (analyte) can release the enzyme and increase the catalysis of substrate. Therefore, the concentration of antigen (analyte) can be indirectly determined via the change of enzyme activity. In this example, the MWCNTs functioned as enzyme carriers and biocatalysts for noise reduction and signal amplification of the immunosensor. With the assistance of CNTs, better results were obtained, which was showed by a greater variation extent of signal current. In a case of immunosensing detection of tau protein through surface plasmon resonance, MWCNTs were used as carriers for secondary antibody of tau protein to amplify sensing signal, and an amplification effect of 10^2 folds was observed (Lisi et al. 2017). In immunoassay, two kinds of antibody (primary and secondary antibody) are commonly used. The primary antibody can identify antigen (analyte) through specific binding, while the secondary antibody is used for binding primary antibody to detect the signal of primary antibody. In the example above, MWCNTs were conjugated with the secondary antibody and amplified the sensing signal, which can be attributed to the increased availability of the secondary antibody due to the mass of MWCNTs and their large specific surface area. For the purpose of observing an evident signal change, Deng et al. (2011) carried out a signal amplification strategy by catalytic reduction of dissolved oxygen on CNTs in an electrochemiluminescence immunoassay of quantum dots (CdS). Their results indicated that the nitrogen-doped CNTs facilitated catalytic reduction of O_2 at the sidewall of CNTs, resulting in an amplified electrochemiluminescence. The nitrogen-doped CNTs showed a higher adsorption capacity for dissolved O_2 and accelerated the formation of superoxide radical, which improved the electrochemiluminescence emission of the immunosensor. In addition to the signal amplification, CNTs also play roles in improving operational stability and expanding application scope of sensors for environmental monitoring and sensing (García-Aljaro et al. 2010; Hsu et al. 2017; Ma et al. 2017; Zhu et al. 2017).

2.4. Design of environment-friendly products

Environmental-friendly products are becoming increasingly welcome due to the deterioration of living environment quality and the enhancement of public environmental consciousness. Environmental-friendly products, sometimes called green products, are something that harms the environment as little as possible during the processes of their production, sale, use, and recycle. CNTs add new inspiration and ideas to the design of environmental-friendly products. Using MWCNTs as anode composites of an environment-friendly lithium ion battery was explored by Bongu et al. (2016). The MWCNTs promoted charge transport, increased diffusion kinetics, and mitigated mechanical stress, resulting in an increase of steady-state reversible capacity from 200 mAh/g to 840 mAh/g. Keshri and Agarwal (2011) reinforced Al_2O_3 coatings with CNTs for the marine environment. Through the reinforcement of CNTs, a higher wear resistance and a lower friction coefficient of the coatings were achieved. These improved characteristics are helpful for the reduction of fouling, seaweed, and shellfish attaching to the surface of ship hull, which finally leads to a decrease in use of toxic chemicals to remove them (Beigbeder et al. 2010; Chambers et al. 2006; Keshri and Agarwal 2011). Chen and Huang (2017) evaluated heat transfer in CNT wick of heat pipes. Owing to the excellent thermal and interfacial properties of CNTs, a higher heat transfer capability and a more compact size of the heat pipe were realized. Using CNTs to replace harmful materials and conserve energy in products makes the products environmental-friendly. It is worthy of belief that more environmental-friendly products based on CNTs would be produced in the near future.

3. Challenges for environmental applications of CNTs

Although mass production of CNTs can be achieved by the modern chemical industry and great progress has been made in CNT-based environmental technologies, there is still a distance to their large-scale applications in real environmental engineering (Zhang et al. 2011). Several main challenges on the road to realizing the practical applications are presented in Fig. 9.

3.1. Toxicity and ecological risks

Analysis of the life cycle of CNT products suggested that CNTs can be released into the environment during the whole life cycle (including production, use phase, recycling, and disposal) (Köhler et al. 2008). In this respect, the main challenge lies in the uncertainties of CNT toxicity and their ecological risks. The toxicity mechanism of CNTs is complicated and it is difficult to expound the specific toxicity with a universal mechanism. CNT characteristics (e.g., impurities, length, shape), exposure routes (e.g., intravenous injection, dermal exposure, inhalation), and action mechanisms (e.g., oxidative stress, DNA damage, interstitial fibrosis) all affect the toxicity of CNTs (Liu et al. 2013). Though much effort has been made on investigating CNT toxicity, currently no direct evidence of human exposure or definitive study in vivo is available for illustrating the real danger of CNTs towards humans (Ong et al. 2016). Ecological risks of CNTs show greater uncertainty due to more complex and variable environmental conditions. For example, accumulated CNTs in riverine sediment not only show toxicity to the benthos, but also influence the transport of coexisting contaminants (Song et al. 2018). Edgington et al. (2010) reported that natural organic matter could increase aqueous stability of MWCNTs after being adsorbed onto their hydrophobic surface. The increased stability thus leaded to a longer detention time of MWCNTs in water, as well as a longer exposure time for aquatic organisms. As a result of this, the toxicity of MWCNTs towards two pelagic organisms, *Daphnia magna* and *Ceriodaphnia dubia*, was increased in their experiments. Besides, artificial modifications of CNTs may also result in the change of toxicity. Pasquini et al. (2012) investigated the cytotoxicity of nine surface functionalized SWCNTs and drew a conclusion that surface functionalization indirectly affected the cytotoxicity through the alteration of SWCNT aggregation state (including morphology and dispersity). A large number of experimental data are needed for verifying the toxicity and ecological risks. Additionally, many standardization activities on the reference materials of CNTs and their characterization for industrial applications have been carried out and received positive results (De Volder et al. 2013; Oh 2009; Tian et al. 2015). However, standards for the toxicity testing and ecological risk assessment are lacking.

3.2. Production costs

Over the past decade, global CNT production increased rapidly. It was reported that the annual manufacturing capacity worldwide was over 10,000 tonnes in 2012 and global CNT market was expected to grow at a compound annual growth rate of 15.5% from 2013 to 2018 (Paiva and Covas 2016). The mass production and consumption of CNTs bring about continuous decrease in CNT price from over 1,000 USD/kg in the nineties to less than 50 USD/kg by 2016 (Paiva and Covas 2016). However, such a price is still too high for industrial applications of CNTs. Lam et al. (2006) reported that the target goal of CNT price by the US Department of Energy is only 8 USD/kg in 2010. Moreover, highly purified CNTs remain expensive. For example, the prices of high purity MWCNTs (> 98%) and SWCNTs (> 95%) in September 2017 are 5 and 200 USD/g, respectively (from Timesnano, Chengdu Organic Chemicals Co. Ltd., Chengdu, China). To achieve a lower price of CNTs, the improvement of manufacturing/purification technology and the expansion of market demand are needed.

3.3. General applicability

Having general applicability is also a key step towards large-scale industrial applications. However, the use of some CNT-based environmental technologies is limited in both application ranges and conditions. Taking CNT adsorbents for example, most of the studies focused on the specific pollutant under specific conditions, but in practical engineering, many kinds of pollutants are usually involved and the environmental conditions are much more complicated. The synergistic effect, inhibitory effect, or no effect of coexisting substances needs to be considered in practical applications. In a case of investigating the adsorption of nickel and phenol onto MWCNTs by Abdel-Ghani et al. (2015), it was found that both the two pollutants showed an inhibitory effect on the adsorption of each other. When they applied the adsorbent into the treatment of real industrial wastewater, the removal efficiency did not reach the level obtained in treating synthetic water. Therefore, the CNT adsorbents do not have the superiority in certain aspects of practical engineering compared with traditional ones. This is mostly because these studies are laboratory scale and many engineering issues are not considered.

3.4. Long-term effect

Many CNT-based technologies show excellent effects in the short term, but their long-term effects remain uncertain. On the one hand, the uncertainty comes from the changes of CNT-based materials over time. Because CNTs may undergo chemical, physical, and biological transformation in natural environment, the environmental durability cannot be ensured (Lowry et al. 2012). On the other hand, long-term application effect may not be satisfactory. Chouhan et al. (2016) reported that biotransformation of MWCNTs could be caused by resistant bacteria through surface oxidation process. Thus, it is difficult to predict the long-term remediation effect if applying CNT-based stabilizing agent for remediation of contaminated soil or sediment. Song et al. (2017) studied the phytotoxicity of sediments contaminated with cadmium and phenanthrene after in situ remediation by using MWCNTs as adsorbents, and their results indicated that the phytotoxicity might increase after a long-time remediation (60 days). Currently, a large number of the long-term experiments are needed for further examining these CNT-based technologies. Additionally, many CNT-based adsorbents and photocatalysts showed excellent effects in their applications for the first several times, but the effects would still decrease after more recycling (Hu et al. 2010; Jiang et al. 2013; Mamba et al. 2015; Tang et al. 2012; Wang et al. 2014; Zhang et al. 2015b). When these CNT-based materials are no longer able to be used, the disposal of these CNT-contained waste is also a problem. Therefore, further improvement and optimization of these CNT-based technologies are required.

3.5. Public acceptance

Public acceptance towards CNT-based environmental technologies is one of the major issues that affect the development of them. It is difficult to effectively implement an environmental technology without public acceptance. Just like the nuclear power and genetically modified food, current public attitude to benefits and risks of the technologies is vague owing to the limited public knowledge (Currall et al. 2006; Siegrist et al. 2007). As public attitude is evolved by psychological dynamics related to cultural cognition, efforts should be made to improve the cognition by spreading information scientifically (Gupta et al. 2012; Kahan et al. 2008). In addition, guide and management measures need to be developed for industrial applications of CNT-based environmental technologies, because a failing application will undoubtedly reduce the public acceptance. Thus, supervision of CNT production and use activities requires reinforcement.

4. Conclusions and future research needs

CNTs have been attracting extensive attention of scientists and numerous CNT-based environmental technologies have been developed in recent years. The adopted properties and main roles of CNTs in these technologies are summarized and illustrated in this review article. These technologies are very valuable to solving environmental problems. Considering their development and current status, it is significant to turn “potential” into “practical” in applications. Based on a comprehensive understanding of the challenges, in our view, the research priorities should be focused on toxicity and environmental risk assessment of CNTs in the near future. For one thing, solving these problems is required before large-scale industrial applications. For another, many new environmental problems have occurred about CNTs as emerging contaminants (Calisi et al. 2016; Sun et al. 2015; Velzeboer et al. 2013; Zhang et al. 2015a; Zhou et al. 2013). The urgent needs are meeting the challenges to obscure toxicity mechanisms and unclear ecological risks of CNTs. Research on standardizing toxicity testing and risk assessment of CNTs is highly recommended, and a large number of toxicity data are needed. Furthermore, other challenges mentioned above should also be gradually dealt with, and more practical factors should be considered when developing new CNT-based environmental technologies in the future.

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References

Abdel-Ghani NT, El-Chaghaby GA, Helal FS (2015) Individual and competitive adsorption of phenol and nickel onto multiwalled carbon nanotubes. J. Adv. Res. 6:405-415. https://doi.org/10.1016/j.jare.2014.06.001

Asadollahzadeh H, Noroozian E, Maghsoudi S (2010) Solid-phase microextraction of phthalate esters from aqueous media by electrochemically deposited carbon nanotube/polypyrrole composite on a stainless steel fiber. Anal. Chim. Acta. 669:32-38. https://doi.org/10.1016/j.aca.2010.04.029

Aslan S, Loebick CZ, Kang S, Elimelech M, Pfefferle LD, Tassel PR (2010) Antimicrobial biomaterials based on carbon nanotubes dispersed in poly(lactic-co-glycolic acid). Nanoscale 2:1789-1794. http://dx.doi.org/10.1039/c0nr00329h

Baciu A, Manea F, Pop A, Pode R, Schoonman J (2017) Simultaneous voltammetric detection of ammonium and nitrite from groundwater at silver-electrodecorated carbon nanotube electrode. Process. Saf. Environ. 108:18-25. https://doi.org/10.1016/j.psep.2016.05.006

Bakr AR, Rahaman MS (2017) Removal of bisphenol A by electrochemical carbon-nanotube filter: Influential factors and degradation pathway. Chemosphere. 185:879-887. https://doi.org/10.1016/j.chemosphere.2017.07.082

Beigbeder A, Mincheva R, Pettitt ME, Callow ME, Callow JA, Claes M, Dubois P (2010) Marine fouling release silicone/carbon nanotube nanocomposite coatings: on the importance of the nanotube dispersion state. J. Nanosci. Nanotechno. 10:2972-2978. http://dx.doi.org/10.1166/jnn.2010.2185

Bongu CS, Ragupathi J, Nallathamby K (2016) Exploration of $MnFeO_3$/Multiwalled Carbon Nanotubes Composite as Potential Anode for Lithium Ion Batteries. Inorg. Chem. 55:11644-11651. http://dx.doi.org/10.1021/acs.inorgchem.6b00953

Calisi A, Grimaldi A, Leomanni A, Lionetto MG, Dondero F, Schettino T (2016) Multibiomarker response in the earthworm *Eisenia fetida* as tool for assessing multi-walled carbon nanotube ecotoxicity. Ecotoxicology. 25:677-687. http://dx.doi.org/10.1007/s10646-016-1626-x

Chambers LD, Stokes KR, Walsh FC, Wood RJK (2006) Modern approaches to marine antifouling coatings. Surf. Coat. Tech. 201:3642-3652. https://doi.org/10.1016/j.surfcoat.2006.08.129

Chen H, Wang B, Gao D, Guan M, Zheng L, Ouyang H, Chai Z, Zhao Y, Feng W (2013) Broad-Spectrum Antibacterial Activity of Carbon Nanotubes to Human Gut Bacteria. Small 9:2735-2746. http://dx.doi.org/10.1002/smll.201202792

Chen M, Xu P, Zeng G, Yang C, Huang D, Zhang J (2015) Bioremediation of soils contaminated with polycyclic aromatic hydrocarbons, petroleum, pesticides, chlorophenols and heavy metals by composting: Applications, microbes and future research needs. Biotechnol. Adv. 33:745-755. https://doi.org/10.1016/j.biotechadv.2015.05.003

Chen Q, Huang Y (2017) Scale effects on evaporative heat transfer in carbon nanotube wick in heat pipes. Int. J. Heat. Mass. Tran. 111:852-859. https://doi.org/10.1016/j.ijheatmasstransfer.2017.04.027

Cheng M, Zeng G, Huang D, Lai C, Xu P, Zhang C, Liu Y (2016) Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review. Chem. Eng. J. 284:582-598. https://doi.org/10.1016/j.cej.2015.09.001

Chi MF, Wu WL, Du Y, Chin CJM, Lin CC (2016) Inactivation of *Escherichia coli* planktonic cells by multi-walled carbon nanotubes in suspensions: Effect of surface functionalization coupled with medium nutrition level. J. Hazard. Mater. 318:507-514. https://doi.org/10.1016/j.jhazmat.2016.07.013

Chouhan RS, Qureshi A, Yagci B, Gülgün MA, Ozguz V, Niazi JH (2016) Biotransformation of multi-walled carbon nanotubes mediated by nanomaterial resistant soil bacteria. Chem. Eng. J. 298:1-9. https://doi.org/10.1016/j.cej.2016.04.019

Currall SC, King EB, Lane N, Madera J, Turner S (2006) What drives public acceptance of nanotechnology? Nat. Nanotechnol. 1:153-155. http://dx.doi.org/10.1038/nnano.2006.155

Das R, Ali ME, Hamid SBA, Ramakrishna S, Chowdhury ZZ (2014) Carbon nanotube membranes for water purification: A bright future in water desalination. Desalination. 336:97-109. https://doi.org/10.1016/j.desal.2013.12.026

De Volder MFL, Tawfick SH, Baughman RH, Hart AJ (2013) Carbon nanotubes:

Present and future commercial applications. Science 339:535-539. http://dx.doi.org/10.1126/science.1222453

Deng JH, Zhang XR, Zeng GM, Gong JL, Niu QY, Liang J (2013) Simultaneous removal of Cd(II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent. Chem. Eng. J. 226:189-200. https://doi.org/10.1016/j.cej.2013.04.045

Deng S, Hou Z, Lei J, Lin D, Hu Z, Yan F, Ju H (2011) Signal amplification by adsorption-induced catalytic reduction of dissolved oxygen on nitrogen-doped carbon nanotubes for electrochemiluminescent immunoassay. Chem. Commun. 47:12107-12109. http://dx.doi.org/10.1039/c1cc15766c

Dong X, Yang L (2015) Dual functional nisin-multi-walled carbon nanotubes coated filters for bacterial capture and inactivation. J. Biol. Eng. 9:20. http://dx.doi.org/10.1186/s13036-015-0018-8

Edgington AJ, Roberts AP, Taylor LM, Alloy MM, Reppert J, Rao AM, Mao J, Klaine SJ (2010) The influence of natural organic matter on the toxicity of multiwalled carbon nanotubes. Environ. Toxicol. Chem. 29:2511–2518. http://dx.doi.org/10.1002/etc.309

García-Aljaro C, Cella LN, Shirale DJ, Park M, Muñoz FJ, Yates MV, Mulchandani A (2010) Carbon nanotubes-based chemiresistive biosensors for detection of microorganisms. Biosens. Bioelectron. 26:1437-1441. https://doi.org/10.1016/j.bios.2010.07.077

Ghaemi F, Amiri A, Yunus R (2014) Methods for coating solid-phase microextraction fibers with carbon nanotubes. TrAC Trend. Anal. Chem. 59:133-143. https://doi.org/10.1016/j.trac.2014.04.011

Gong JL, Wang B, Zeng GM, Yang CP, Niu CG, Niu QY, Zhou WJ, Liang Y (2009) Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. J. Hazard. Mater. 164:1517-1522. http://dx.doi.org/10.1016/j.jhazmat.2008.09.072

Gupta N, Fischer ARH, Frewer LJ (2012) Socio-psychological determinants of public acceptance of technologies: A review. Public. Underst. Sci. 21:782-795. http://dx.doi.org/10.1177/0963662510392485

Hennion MC (1999) Solid-phase extraction: method development, sorbents, and coupling with liquid chromatography. J. Chromatogr. A. 856:3-54. https://doi.org/10.1016/S0021-9673(99)00832-8

Hsu CW, Lin ZY, Chan TY, Chiu TC, Hu CC (2017) Oxidized multiwalled carbon nanotubes decorated with silver nanoparticles for fluorometric detection of dimethoate. Food. Chem. 224:353-358. https://doi.org/10.1016/j.foodchem.2016.12.095

Hu J, Shao D, Chen C, Sheng G, Li J, Wang X, Nagatsu M (2010) Plasma-Induced Grafting of Cyclodextrin onto Multiwall Carbon Nanotube/Iron Oxides for Adsorbent Application. J. Phys. Chem. B 114:6779-6785. http://dx.doi.org/10.1021/jp911424k

Ihsanullah, Abbas A, Al-Amer AM, Laoui T, Al-Marri MJ, Nasser MS, Khraisheh M, Atieh MA (2016) Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. Sep. Purif. Technol. 157:141-161. https://doi.org/10.1016/j.seppur.2015.11.039

Iijima S (1991) Helical microtubules of graphitic carbon. Nature 354:56-58. http://dx.doi.org/10.1038/354056a0

Ji L, Chen W, Bi J, Zheng S, Xu Z, Zhu D, Alvarez PJ (2010) Adsorption of tetracycline on single‐walled and multi‐walled carbon nanotubes as affected by aqueous solution chemistry. Environ. Toxicol. Chem. 29:2713-2719. https://doi.org/10.1002/etc.350

Jiang R, Zhu F, Luan T, Tong Y, Liu H, Ouyang G, Pawliszyn J (2009) Carbon nanotube-coated solid-phase microextraction metal fiber based on sol–gel technique. J. Chromatogr. A. 1216:4641-4647. https://doi.org/10.1016/j.chroma.2009.03.076

Jiang T, Zhang L, Ji M, Wang Q, Zhao Q, Fu X, Yin H (2013) Carbon nanotubes/TiO_2 nanotubes composite photocatalysts for efficient degradation of methyl orange dye. Particuology 11:737-742. https://doi.org/10.1016/j.partic.2012.07.008

Köhler AR, Som C, Helland A, Gottschalk F (2008) Studying the potential release of carbon nanotubes throughout the application life cycle. J. Clean. Prod. 16:927-937. https://doi.org/10.1016/j.jclepro.2007.04.007

Kahan DM, Braman D, Slovic P, Gastil J, Cohen G (2008) Cultural cognition of the risks and benefits of nanotechnology. Nat. Nanotechnol. 4:87. http://dx.doi.org/10.1038/nnano.2008.341

Kang S, Herzberg M, Rodrigues DF, Elimelech M (2008) Antibacterial Effects of

Carbon Nanotubes: Size Does Matter! Langmuir. 24:6409-6413. http://dx.doi.org/10.1021/la800951v

Keshri AK, Agarwal A (2011) Wear Behavior of Plasma-Sprayed Carbon Nanotube-Reinforced Aluminum Oxide Coating in Marine and High-Temperature Environments. J. Therm. Spray. Techn. 20:1217-1230. http://dx.doi.org/10.1007/s11666-011-9669-2

Kumar D, Kumar I, Chaturvedi P, Chouksey A, Tandon RP, Chaudhury PK (2016) Study of simultaneous reversible and irreversible adsorption on single-walled carbon nanotube gas sensor. Mater. Chem. Phys. 177:276-282. https://doi.org/10.1016/j.matchemphys.2016.04.028

Lalović B, Đurkić T, Vukčević M, Janković-Častvan I, Kalijadis A, Laušević Z, Laušević M (2017) Solid-phase extraction of multi-class pharmaceuticals from environmental water samples onto modified multi-walled carbon nanotubes followed by LC-MS/MS. Environ. Sci. Pollut. R. 24:20784-20793. http://dx.doi.org/10.1007/s11356-017-9748-0

Lam C, James JT, McCluskey R, Arepalli S, Hunter RL (2006) A Review of Carbon Nanotube Toxicity and Assessment of Potential Occupational and Environmental Health Risks. Crit. Rev. Toxicol. 36:189-217. http://dx.doi.org/10.1080/10408440600570233

Lei J, Ju H (2012) Signal amplification using functional nanomaterials for biosensing. Chem. Soc. Rev. 41:2122-2134. http://dx.doi.org/10.1039/c1cs15274b

Li H, Gui X, Ji C, Li P, Li Z, Zhang L, Shi E, Zhu K, Wei J, Wang K, Zhu H, Wu D, Cao A (2012) Photocatalytic, recyclable CdS nanoparticle-carbon nanotube hybrid sponges. Nano Res. 5:265-271. http://dx.doi.org/10.1007/s12274-012-0206-5

Li Y, Wang S, Luan Z, Ding J, Xu C, Wu D (2003) Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes. Carbon 41:1057-1062. https://doi.org/10.1016/S0008-6223(02)00440-2

Liang J, Yang Z, Tang L, Zeng G, Yu M, Li X, Wu H, Qian Y, Li X, Luo Y (2017) Changes in heavy metal mobility and availability from contaminated wetland soil remediated with combined biochar-compost. Chemosphere. 181:281-288. https://doi.org/10.1016/j.chemosphere.2017.04.081

Lisi S, Scarano S, Fedeli S, Pascale E, Cicchi S, Ravelet C, Peyrin E, Minunni M (2017) Toward sensitive immuno-based detection of tau protein by surface plasmon resonance coupled to carbon nanostructures as signal amplifiers. Biosens. Bioelectron. 93:289-292. https://doi.org/10.1016/j.bios.2016.08.078

Liu H, Vecitis CD (2012) Reactive Transport Mechanism for Organic Oxidation during Electrochemical Filtration: Mass-Transfer, Physical Adsorption, and Electron-Transfer. J. Phys. Chem. C 116:374-383. http://dx.doi.org/10.1021/jp209390b

Liu Y, Liu H, Zhou Z, Wang T, Ong CN, Vecitis CD (2015) Degradation of the Common Aqueous Antibiotic Tetracycline using a Carbon Nanotube Electrochemical Filter. Environ. Sci. Technol. 49:7974-7980. http://dx.doi.org/10.1021/acs.est.5b00870

Liu Y, Zhao Y, Sun B, Chen C (2013) Understanding the Toxicity of Carbon Nanotubes. Acc. Chem. Res. 46:702-713. http://dx.doi.org/10.1021/ar300028m

Long F, Gong JL, Zeng GM, Chen L, Wang XY, Deng JH, Niu QY, Zhang HY, Zhang XR (2011) Removal of phosphate from aqueous solution by magnetic Fe–Zr binary oxide. Chem. Eng. J. 171:448-455. https://doi.org/10.1016/j.cej.2011.03.102

Lowry GV, Gregory KB, Apte SC, Lead JR (2012) Transformations of Nanomaterials in the Environment. Environ. Sci. Technol. 46:6893-6899. http://dx.doi.org/10.1021/es300839e

Ma X, Dong Y, Li R (2017) Monitoring technology in composites using carbon nanotube yarns based on piezoresistivity. Mater. Lett. 188:45-47. https://doi.org/10.1016/j.matlet.2016.10.085

Mamba G, Mbianda XY, Mishra AK (2015) Photocatalytic degradation of the diazo dye naphthol blue black in water using MWCNT/Gd,N,S-TiO_2 nanocomposites under simulated solar light. J. Environ. Sci. 33:219-228. https://doi.org/10.1016/j.jes.2014.06.052

Merkoçi A, Pumera M, Llopis X, Pérez B, del Valle M, Alegret S (2005) New materials for electrochemical sensing VI: Carbon nanotubes. TrAC Trend. Anal. Chem. 24:826-838. https://doi.org/10.1016/j.trac.2005.03.019

Merli D, Ugonino M, Profumo A, Fagnoni M, Quartarone E, Mustarelli P, Visai L, Grandi MS, Galinetto P, Canton P (2011) Increasing the antibacterial effect of lysozyme by immobilization on multi-walled carbon nanotubes. J. Nanosci. Nanotechno. 11:3100-3106. http://dx.doi.org/10.1166/jnn.2011.3758

Mocan T, Matea CT, Pop T, Mosteanu O, Buzoianu AD, Suciu S, Puia C, Zdrehus C, Iancu C, Mocan L (2017) Carbon nanotubes as anti-bacterial agents. Cell. Mol. Life. Sci. 74:3467-3479. http://dx.doi.org/10.1007/s00018-017-2532-y

Mohan R, Shanmugharaj AM, Sung Hun R (2011) An efficient growth of silver and copper nanoparticles on multiwalled carbon nanotube with enhanced antimicrobial activity. J. Biomed. Mater. Res. B. 96B:119-126. https://doi.org/10.1002/jbm.b.31747

Natarajan TS, Lee JY, Bajaj HC, Jo WK, Tayade RJ (2017) Synthesis of multiwall carbon nanotubes/TiO_2 nanotube composites with enhanced photocatalytic decomposition efficiency. Catal. Today. 282:13-23. https://doi.org/10.1016/j.cattod.2016.03.018

Oh KH (2009) Standardization Trends for Carbon Nanotubes. Carbon Lett. 10:1-4. http://dx.doi.org/10.5714/CL.2009.10.1.001

Ong LC, Chung FL, Tan YF, Leong CO (2016) Toxicity of single-walled carbon nanotubes. Arch. Toxicol. 90:103-118. http://dx.doi.org/10.1007/s00204-014-1376-6

Ozdes D, Gundogdu A, Kemer B, Duran C, Senturk HB, Soylak M (2009) Removal of Pb(II) ions from aqueous solution by a waste mud from copper mine industry: Equilibrium, kinetic and thermodynamic study. J. Hazard. Mater. 166:1480-1487. https://doi.org/10.1016/j.jhazmat.2008.12.073

Paiva MC, Covas JA (2016) Carbon Nanofibres and Nanotubes for Composite Applications. In: Rana S, Fangueiro R (eds) Fibrous and Textile Materials for Composite Applications. Springer Singapore, Singapore, pp 231-260 http://dx.doi.org/10.1007/978-981-10-0234-2_7

Pan B, Xing B (2008) Adsorption Mechanisms of Organic Chemicals on Carbon Nanotubes. Environ. Sci. Technol. 42:9005-9013. http://dx.doi.org/10.1021/es801777n

Pasquini LM, Hashmi SM, Sommer TJ, Elimelech M, Zimmerman JB (2012) Impact of Surface Functionalization on Bacterial Cytotoxicity of Single-Walled Carbon Nanotubes. Environ. Sci. Technol. 46:6297-6305. http://dx.doi.org/10.1021/es300514s

Rahman MM, Balkhoyor HB, Asiri AM (2017) Phenolic sensor development based on chromium oxide-decorated carbon nanotubes for environmental safety. J. Environ. Manage. 188:228-237. https://doi.org/10.1016/j.jenvman.2016.12.008

Ren X, Zeng G, Tang L, Wang J, Wan J, Liu Y, Yu J, Yi H, Ye S, Deng R (2018) Sorption, transport and biodegradation – An insight into bioavailability of persistent organic pollutants in soil. Sci. Total. Environ. 610-611:1154-1163. https://doi.org/10.1016/j.scitotenv.2017.08.089

Robel I, Bunker BA, Kamat PV (2005) Single-Walled Carbon Nanotube–CdS Nanocomposites as Light-Harvesting Assemblies: Photoinduced Charge-Transfer Interactions. Adv. Mater. 17:2458-2463.

http://dx.doi.org/10.1002/adma.200500418

Roozban N, Abbasi S, Ghazizadeh M (2017) Statistical analysis of the photocatalytic activity of decorated multi-walled carbon nanotubes with ZnO nanoparticles. J. Mater. Sci.: Mater. El. 28:6047-6055. https://doi.org/10.1007/s10854-016-6280-9

Seyed Dorraji MS, Amani-Ghadim AR, Rasoulifard MH, Taherkhani S, Daneshvar H (2017) The role of carbon nanotube in zinc stannate photocatalytic performance improvement: Experimental and kinetic evidences. Appl. Catal. B: Environ. 205:559-568. https://doi.org/10.1016/j.apcatb.2017.01.002

Shao D, Hu J, Wang X (2010) Plasma Induced Grafting Multiwalled Carbon Nanotube with Chitosan and Its Application for Removal of UO_2^{2+}, Cu^{2+}, and Pb^{2+} from Aqueous Solutions. Plasma Process. Polym. 7:977-985. https://doi.org/10.1002/ppap.201000062

Siegrist M, Cousin M-E, Kastenholz H, Wiek A (2007) Public acceptance of nanotechnology foods and food packaging: The influence of affect and trust. Appetite. 49:459-466. https://doi.org/10.1016/j.appet.2007.03.002

Song B, Xu P, Zeng G, Gong J, Wang X, Yan J, Wang S, Zhang P, Cao W, Ye S (2018) Modeling the transport of sodium dodecyl benzene sulfonate in riverine sediment in the presence of multi-walled carbon nanotubes. Water Research 129:20-28. https://doi.org/10.1016/j.watres.2017.11.003

Song B, Zeng G, Gong J, Zhang P, Deng J, Deng C, Yan J, Xu P, Lai C, Zhang C, Cheng M (2017) Effect of multi-walled carbon nanotubes on phytotoxicity of sediments contaminated by phenanthrene and cadmium. Chemosphere 172:449-458. http://dx.doi.org/10.1016/j.chemosphere.2017.01.032

Song B, Zhang C, Zeng G, Gong J, Chang Y, Jiang Y (2016) Antibacterial properties and mechanism of graphene oxide-silver nanocomposites as bactericidal agents for water disinfection. Archives of biochemistry and biophysics 604:167-176. http://dx.doi.org/10.1016/j.abb.2016.04.018

Sun W, Jiang B, Wang F, Xu N (2015) Effect of carbon nanotubes on Cd(II) adsorption by sediments. Chem. Eng. J. 264:645-653. http://dx.doi.org/10.1016/j.cej.2014.11.137

Tamayo FG, Turiel E, Martín-Esteban A (2007) Molecularly imprinted polymers for solid-phase extraction and solid-phase microextraction: Recent developments and future trends. J. Chromatogr. A. 1152:32-40. https://doi.org/10.1016/j.chroma.2006.08.095

Tan X, Liu Y, Zeng G, Wang X, Hu X, Gu Y, Yang Z (2015) Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere. 125:70-85. https://doi.org/10.1016/j.chemosphere.2014.12.058

Tang D, Tang J, Su B, Chen G (2010) Ultrasensitive Electrochemical Immunoassay of Staphylococcal Enterotoxin B in Food Using Enzyme-Nanosilica-Doped Carbon Nanotubes for Signal Amplification. J. Agr. Food. Chem. 58:10824-10830. http://dx.doi.org/10.1021/jf102326m

Tang WW, Zeng GM, Gong JL, Liang J, Xu P, Zhang C, Huang BB (2014) Impact of humic/fulvic acid on the removal of heavy metals from aqueous solutions using nanomaterials: A review. Sci. Total. Environ. 468-469:1014-1027. https://doi.org/10.1016/j.scitotenv.2013.09.044

Tang WW, Zeng GM, Gong JL, Liu Y, Wang XY, Liu YY, Liu ZF, Chen L, Zhang XR, Tu DZ (2012) Simultaneous adsorption of atrazine and Cu (II) from wastewater by magnetic multi-walled carbon nanotube. Chem. Eng. J. 211:470-478. https://doi.org/10.1016/j.cej.2012.09.102

Tian Y, Jiang H, Anoshkin IV, Kauppinen LJI, Mustonen K, Nasibulin AG, Kauppinen EI (2015) A reference material of single-walled carbon nanotubes: quantitative chirality assessment using optical absorption spectroscopy. RSC Advances 5:102974-102980. http://dx.doi.org/10.1039/C5RA23326G

Tuzen M, Saygi KO, Soylak M (2008) Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes. J. Hazard. Mater. 152:632-639. https://doi.org/10.1016/j.jhazmat.2007.07.026

Vecitis CD, Schnoor MH, Rahaman MS, Schiffman JD, Elimelech M (2011) Electrochemical multiwalled carbon nanotube filter for viral and bacterial removal and inactivation. Environ. Sci. Technol. 45. http://dx.doi.org/10.1021/es2000062

Velzeboer I, Peeters ETHM, Koelmans AA (2013) Multiwalled Carbon Nanotubes at Environmentally Relevant Concentrations Affect the Composition of Benthic Communities. Environ. Sci. Technol. 47:7475-7482. http://dx.doi.org/10.1021/es400777j

Wan J, Zeng G, Huang D, Hu L, Xu P, Huang C, Deng R, Xue W, Lai C, Zhou C, Zheng K, Ren X, Gong X (2018) Rhamnolipid stabilized nano-chlorapatite: Synthesis and enhancement effect on Pb-and Cd-immobilization in polluted sediment. J. Hazard. Mater. 343:332-339. https://doi.org/10.1016/j.jhazmat.2017.09.053

Wang P, Cao M, Wang C, Ao Y, Hou J, Qian J (2014) Kinetics and thermodynamics of adsorption of methylene blue by a magnetic graphene-carbon nanotube composite. Appl. Surf. Sci. 290:116-124. https://doi.org/10.1016/j.apsusc.2013.11.010

Wang X, Chen Y, Zheng B, Qi F, He J, Yu B, Zhang W (2017) Significant enhancement of photocatalytic activity of multi-walled carbon nanotubes modified WSe_2 composite. Mater. Lett. 197:67-70. https://doi.org/10.1016/j.matlet.2017.03.150

Wang Y, Zhu J, Huang H, Cho HH (2015) Carbon nanotube composite membranes for microfiltration of pharmaceuticals and personal care products: Capabilities and potential mechanisms. J. Membrane. Sci. 479:165-174. https://doi.org/10.1016/j.memsci.2015.01.034

Wu H, Lai C, Zeng G, Liang J, Chen J, Xu J, Dai J, Li X, Liu J, Chen M (2017) The interactions of composting and biochar and their implications for soil amendment and pollution remediation: a review. Crit. Rev. Biotechnol. 37:754-764. http://dx.doi.org/10.1080/07388551.2016.1232696

Wu H, Shi H, Zhang H, Wang X, Yang Y, Yu C, Hao C, Du J, Hu H, Yang S (2014) Prostate stem cell antigen antibody-conjugated multiwalled carbon nanotubes for targeted ultrasound imaging and drug delivery. Biomaterials. 35:5369-5380. https://doi.org/10.1016/j.biomaterials.2014.03.038

Xu P, Zeng GM, Huang DL, Lai C, Zhao MH, Wei Z, Li NJ, Huang C, Xie GX (2012) Adsorption of Pb(II) by iron oxide nanoparticles immobilized Phanerochaete chrysosporium: Equilibrium, kinetic, thermodynamic and mechanisms analysis. Chem. Eng. J. 203:423-431. https://doi.org/10.1016/j.cej.2012.07.048

Yang L, Chu D, Wang L, Wu X, Luo J (2016) Synthesis and photocatalytic activity of chrysanthemum-like Cu_2O/Carbon Nanotubes nanocomposites. Ceram. Int. 42:2502-2509. https://doi.org/10.1016/j.ceramint.2015.10.051

Zardini HZ, Amiri A, Shanbedi M, Maghrebi M, Baniadam M (2012) Enhanced antibacterial activity of amino acids-functionalized multi walled carbon nanotubes by a simple method. Colloid. Surface. B. 92:196-202. https://doi.org/10.1016/j.colsurfb.2011.11.045

Zhang C, Lai C, Zeng G, Huang D, Yang C, Wang Y, Zhou Y, Cheng M (2016) Efficacy of carbonaceous nanocomposites for sorbing ionizable antibiotic sulfamethazine from aqueous solution. Water. Res. 95:103-112. https://doi.org/10.1016/j.watres.2016.03.014

Zhang L, Lei C, Chen J, Yang K, Zhu L, Lin D (2015a) Effect of natural and synthetic surface coatings on the toxicity of multiwalled carbon nanotubes toward green algae. Carbon 83:198-207. http://dx.doi.org/10.1016/j.carbon.2014.11.050

Zhang P, Mo Z, Han L, Wang Y, Zhao G, Zhang C, Li Z (2015b) Magnetic recyclable TiO_2/multi-walled carbon nanotube nanocomposite: Synthesis, characterization and enhanced photocatalytic activity. J. Mol. Catal. A: Chem. 402:17-22. https://doi.org/10.1016/j.molcata.2015.03.005

Zhang Q, Huang JQ, Zhao MQ, Qian WZ, Wei F (2011) Carbon Nanotube Mass Production: Principles and Processes. ChemSusChem 4:864-889. http://dx.doi.org/10.1002/cssc.201100177

Zhang Y, Zeng GM, Tang L, Chen J, Zhu Y, He XX, He Y (2015c) Electrochemical Sensor Based on Electrodeposited Graphene-Au Modified Electrode and NanoAu Carrier Amplified Signal Strategy for Attomolar Mercury Detection. Anal. Chem. 87:989-996. http://dx.doi.org/10.1021/ac503472p

Zhao X, Jia Q, Song N, Zhou W, Li Y (2010) Adsorption of Pb(II) from an aqueous solution by titanium dioxide/carbon nanotube nanocomposites: kinetics, thermodynamics, and isotherms. J. Chem. Eng. Data 55:4428-4433. https://doi.org/10.1021/je100586r

Zhou C, Lai C, Huang D, Zeng G, Zhang C, Cheng M, Hu L, Wan J, Xiong W, Wen M, Wen X, Qin L (2018) Highly porous carbon nitride by supramolecular preassembly of monomers for photocatalytic removal of sulfamethazine under visible light driven. Appl. Catal. B: Environ. 220:202-210. https://doi.org/10.1016/j.apcatb.2017.08.055

Zhou W, Shan J, Jiang B, Wang L, Feng J, Guo H, Ji R (2013) Inhibitory effects of carbon nanotubes on the degradation of ^{14}C-2,4-dichlorophenol in soil. Chemosphere. 90:527. http://dx.doi.org/10.1016/j.chemosphere.2012.08.022

Zhu R, Zhou G, Tang F, Tong C, Wang Y, Wang J (2017) Detection of Cu^{2+} in Water

Based on Histidine-Gold Labeled Multiwalled Carbon Nanotube Electrochemical Sensor. Int. J. Anal. Chem. 2017:1-8. http://dx.doi.org/10.1155/2017/1727126

Zolfonoun E, Yousefi SR (2016) On-line extraction and determination of uranium in aqueous samples using multi-walled carbon nanotubes-coated cellulose acetate membrane. Int. J. Environ. An. Ch. 96:203-211. http://dx.doi.org/10.1080/03067319.2015.1137909