

Environmental application of nanotechnology: air, soil, and water

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Abstract Global deterioration of water, soil, and atmosphere by the release of toxic chemicals from the ongoing anthropogenic activities is becoming a serious problem throughout the world. This poses numerous issues relevant to ecosystem and human health that intensify the application challenges of conventional treatment technologies. Therefore, this review sheds the light on the recent progresses in nanotechnology and its vital role to encompass the imperative demand to monitor and treat the emerging hazardous wastes with lower cost, less energy, as well as higher efficiency. Essentially, the key aspects of this account are to briefly outline the advantages of nanotechnology over conventional treatment technologies and to relevantly highlight the treatment applications of some nanomaterials (e.g., carbon-based nanoparticles, antibacterial nanoparticles, and metal oxide nanoparticles) in the following environments: (1) air (treatment of greenhouse gases, volatile organic compounds, and bioaerosols via adsorption, photocatalytic degradation, thermal decomposition, and air filtration processes), (2) soil (application of nanomaterials as amendment agents for phytoremediation processes and utilization of

stabilizers to enhance their performance), and (3) water (removal of organic pollutants, heavy metals, pathogens through adsorption, membrane processes, photocatalysis, and disinfection processes).

Keywords Nanotechnology · Nanomaterial application · Water and wastewater · Air pollution · Soil pollution

Introduction

The ongoing propagation of industrialization and urbanization processes involving transportation, manufacturing, construction, petroleum refining, mining, etc., deplete the natural resources as well as produce large amounts of hazardous wastes which cause air, water, and soil pollution and consequently threaten human public health and the environmental security. The generated wastes are released to the environment in different forms, for example atmospheric pollutants include toxic gases (nitrogen oxides, sulfur oxides, carbon oxides, ozone, etc.), suspended airborne particles, and volatile organic compounds (VOCs), while soil and water pollutants may comprise of organic substances (pesticides, insecticides, phenols, hydrocarbons, etc.), heavy metals (lead, cadmium, arsenic, mercury, etc.), as well as microbial pathogens. These environmental pollutants have a great potential to adversely influence the human health (Fereidoun et al. 2007; Kampa and Castanas 2008), since they can find their way into human body either through inhalation, ingestion, or absorption. In addition to that, some of these toxicants tend to accumulate in food chains, such as the bioaccumulation of heavy metals (Kumar et al. 2011; Smical et al. 2008; Yap et al. 2011) and persistent organic pollutants (POPs) (Bayen et al. 2005; Houde et al. 2008; Kelly et al. 2007) in biota and fishes, which poses major risks to human and wildlife. Therefore, there is an exigent

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demand for the improvement of sustainable, efficient, and low-cost technologies to monitor and properly treat toxic environmental pollutants.

One of the most promising approaches to revolutionize the environmental remediation techniques is “nanotechnology” which can be defined as a group of emerging technologies that work on nanometer scale (i.e., between 1 and 100 nm range) to produce materials, devices, and systems with fundamentally new properties and functions by controlling the size and the shape of matters (Mansoori and Soelaiman 2005; NSTC/NNI/NSET August 29 2003; Ramsden 2009). The global momentum of nanotechnology due to its potential applications that are covering many fields (e.g., medicine (Kiparissides and Kammona 2015; Müller et al. 2015; Usui et al. 2008), food industry (Duncan 2011; Shanthilal and Bhattacharya 2014), energy (Hussein 2015; Serrano et al. 2009; Zang 2011), pollution treatment (Brame et al. 2011; Karn et al. 2009)) is offering leapfrogging prospects in the improvement and transformation of conventional remediation technologies.

Different processes (including photocatalytic deposition (PD) deposition–precipitation (DP), chemical vapor decomposition (CVD), chemical solution decomposition (CSD), wet chemical method, sol–gel, ultrasonic irradiation, thermal and hydrothermal processes, etc.) (Khajeh et al. 2013) have been used to synthesize various types of nanomaterials that exhibit unique merits different from that of their bulk counterparts. The extraordinary properties such as thermal, optical, mechanical, electromagnetic, structural, and morphological properties (Loos 2015) provide the nanomaterials with advantageous features for many applications where they can be utilized as nanoadsorbents, nanosensors, nanomembrane, and disinfectants. Furthermore, many attempts were reported to synthesize more sophisticated nanostructure (e.g., nanorods, nanobelts, nanowires, nanofibers, etc.) in order to increase the versatility of nanomaterials and to overcome all the challenges that hinder their applications (Aguilar 2013). In view of the remarkable advances in nanotechnology and the urgent need to develop green, robust, and economic approaches for environmental remediation, this paper highlights the auspicious nanomaterial applications in air, soil, and water and provides a broader view on favorability of nanotechnology over the conventional technologies in wastewater treatment systems.

Air pollution

Air pollution is one of the world’s most significant problems, and it can be defined as the alteration in the natural composition of the atmosphere that is caused by the introduction of chemical, physical, or biological substances that are being emitted from anthropogenic, geogenic, or biogenic sources (Daly 2007). The poor air quality has an adverse impact on ecosystem (e.g., vegetation and living organisms) and on the

human health by possibly causing various types of diseases which can be fatal, such as cancer, respiratory, and cardiovascular diseases. The World Health Organization (WHO) in 2014 reported that around seven million people died in 2012 due to air pollution exposure.

Outdoor air pollution

The most important outdoor air pollution problem is global warming that leads to many changes in the atmosphere, land, and water sources all over the world. Greenhouse gases (GHGs) are considered the direct contributors to the global warming. The main greenhouse gases are carbon dioxide, methane, nitrous oxide, and fluorinated gases. The problem of GHG emission is exacerbating by the growing human activities (Metz et al. 2007). The majority of the greenhouse gases have persistent long-term effects on climate due to their tendency to stay in the atmosphere for hundreds of years. Many of control and treatment technologies have been developed to eliminate and monitor the emission of these gases and to eliminate their risks on human and the environment. Nanotechnology is a well-enabled treatment technology to control and remediate air pollution in several ways by taking advantage of nanomaterial properties and applying them as adsorbents, catalysts, membranes, and sensors (Zhao 2009).

As can be noticed from Fig. 1, carbon dioxide represents 75 % of GHGs in the environment; thus, several techniques have been proposed to control its emission either by separation or capturing, such as filtration, absorption in liquids, adsorption on solids, or a combination of these processes (Cheung et al. 2013). The adsorption on nanomaterials is proved to be more efficient and cost-effective process due to the high surface area of nanomaterials that can significantly enhance the adsorption capacity, as well as the availability of nanomaterials and their ability to be regenerated. The solid adsorbents for capturing carbon dioxide can be divided into three classes: (1) the high temperature adsorbents (>400 °C), (2) the intermediate temperature adsorbents (200–400 °C), and (3) the low temperature adsorbents (<200 °C) (Uppendrar et al. 2012).

Calcium (Ca)-based nano-adsorbents are used to capture carbon dioxide at high temperature based on the reversible carbonation reaction of calcium oxides (CaO). The serious disadvantage of using the high temperature adsorbents lies in their ability to aggregate easily leading to a sintering problem during the carbonation/calcination cycles (Abanades and Alvarez 2003). As a result, surface coating of the Ca-based nano-adsorbents is used to prevent the aggregation of these adsorbents and consequently avoid the sintering problem. Wang et al. (2013c) reported that titanium dioxide (TiO₂)-coated nano calcium carbonate can prevent the sintering of nano calcium carbonate and effectively capture carbon dioxide using the adsorption phase technique.

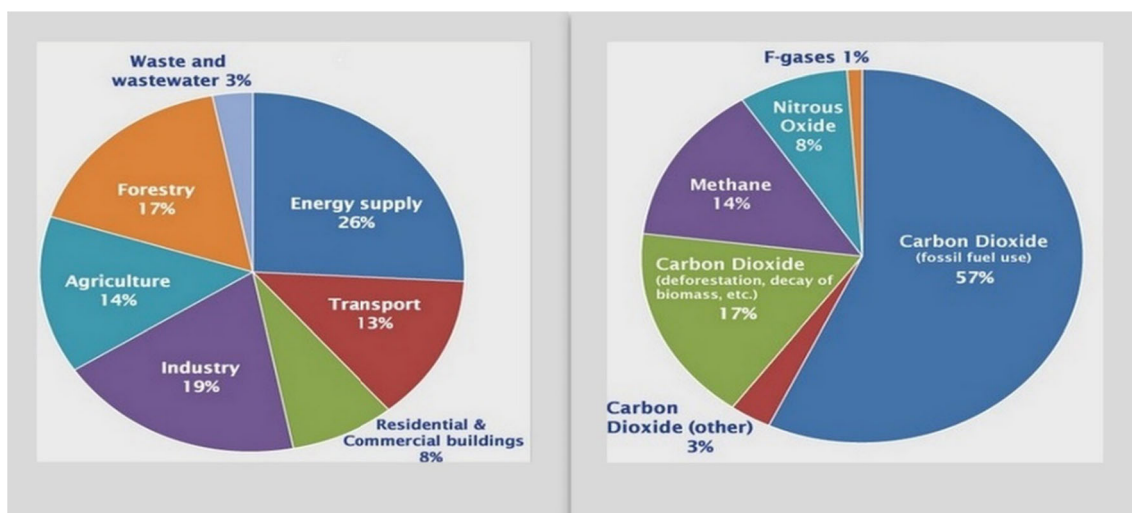


Fig. 1 Greenhouse gas emission (1) by gas and (2) by source (Metz et al. 2007)

Moreover, the treated nanoparticles with alkali metals (Li, Na, K, Cs, Fr) showed the ability to capture carbon dioxide at high temperature, for instance nano-sized citric acid pretreatment rice husk ash (CRHA) lithium ortho-silicate based (CRHA-Li₄SiO₄) adsorbents exhibited a sintering-resistant character and captured carbon dioxide (CO₂) at 700 °C (Wang et al. 2014a). Furthermore, the alkali nanotubes (e.g., potassium titanate (K-Ti-NT) and sodium titanate (Na-Ti-NT)) have been used to capture carbon dioxide at low temperature (below 200 °C) (Upendar et al. 2012). Another example of CO₂ low temperature adsorbents is carbon-based materials (CNMs). They are used widely due to their high surface and high amenability to pore structure modification and surface functionalization (Upendar et al. 2012). Functionalized carbon nanotubes (CNTs) have been successfully used to capture CO₂ and enhance the adsorption performance in the presence of moisture, which decline the adsorption capacity due to water molecules competing with CO₂ for the active adsorption sites (Jänchen et al. 2007). Su et al. (2009) pointed out that functionalization of carbon nanotubes by 3-aminopropyl-triethoxysilane (CNTs-APTS) grafted the surface of CNTs with abundant amine groups that provide numerous chemical sites for CO₂ adsorption which makes CNTs adsorb more CO₂ gases at low temperature range (20–100 °C). In addition, it was suggested that there are two possible reasons for the increase of (CNTs-APTS) adsorption capacity in the presence of moisture and they are (1) CO₂ gas may dissolve into the adsorbed water on the surface of (CNTs-APTS) and (2) the reaction between CO₂ and surface amino groups forms carbonate ions which may undergo further reaction with CO₂ and water to form bicarbonate (HCO₃⁻) (or the amino groups itself can also directly react with CO₂ and H₂O to form HCO₃) (Su et al. 2009).

As another illustration of nanotechnology role in GHG treatment, many catalytic processes have been devoted for

conversion or decomposition of methane (CH₄) and nitrous oxides (NO_x). For instance, metallic nickel nanoparticles were employed as catalysts for thermal decomposition of methane to produce hydrogen (Wang and Lua 2012), and TiO₂ coated with stainless steel web net was efficiently used for photocatalytic degradation of (CH₄) (Merajin et al. 2013). On the other hand, titanate nanotubes (TNTs) and their derivatives have been widely reported for the photocatalytic oxidation of NO_x. Many studies attempted to obtain the optimum parameters that effect the decay rate and the removal efficiency of NO_x. For example, Nguyen and Bai (2015) have proved that the surface area, the amount of crystalline, and the remnant sodium content of TNTs increased by washing at pH 3–5 and accordingly increased the removal efficiency of both NO and NO₂. Moreover, modified TiO₂ with different loads of silver was used for the photocatalytic decomposition of (N₂O) to nitrogen and oxygen (Obalová et al. 2013). The silver deposited on the surface of TiO₂ provokes a decrease in the electron-hole recombination rate (Kočí et al. 2012).

In addition to GHGs, sulfur dioxide is one of the industrial emissions that is linked to different environmental problems and serious human health risks. Nanomaterials have been used to eliminate SO₂ release to environment either by desulfurization of fossil fuel (Saleh et al. 2015) or by its removal directly from the emission source by various technologies, such as adsorption processes (Wu et al. 2011) and catalytic oxidations (Koutsopoulos et al. 2006; Rodriguez et al. 2010). Removal of SO₂ occasionally leads to some changes in the morphology or characteristics of the used materials. For instance, during the application of activated carbon with deposited iron nanoparticles as adsorbent, formation of weakly acidic groups on the adsorbent surface was involved with the SO₂ adsorption process which increases the surface acidity (Arcibar-Orozco et al. 2013). Moreover, it was proved that SO₂ adsorption process can lead to clear changes in magnetism when using magnetic

nanoparticles (MNPs). For example, SO₂ adsorption on the surface of COFe₂O₄ MNPs leads to a decrease in their saturation and remnant magnetization by approximately 20 % and a decrease in their coercivity by approximately 9 % (Glover et al. 2012). Table 1 shows more examples of nanomaterials used to treat different types of air pollutants.

Indoor air pollution

Indoor air pollution has recently become a major concern due to its direct effects on human health (MR 2009; Solomon et al. 2008). Among the indoor air pollutants are VOCs which are

believed to be the main cause of increasing childhood asthma, atopic hypersensitivity, as well as other series of symptoms, such as headache, nausea, coryza, pharyngitis, emphysema, and lung cancer (Lee et al. 2010a, b). Therefore, it is strongly required to progress an effective method to control and eradicate the emission of these VOCs (Hauptmann et al. 2004).

The most abundant airborne carbonyl chemical is formaldehyde (HCHO), which is a well-known precursor in manufacturing of more complex materials, such as phenol-formaldehyde and urea-formaldehyde resins, that are broadly used as wood-binding products and insulating foam. Several methods are used for the removal of formaldehyde, including

Table 1 Nanoparticle application in air remediation

Nanoparticles	Target pollutants	Observations	References
Silica nanoparticle (SiNPs)	Atmospheric lead (Pb)	The increased capture of Pb by SiNPs was explained by the large surface and the negative-charged groups in the SiNPs	Yang et al. (2013c)
Zn ₁₂ O ₁₂ nanocage	Carbon disulfide (CS ₂)	At the increasing number of the CS ₂ molecules, the adsorption energy of CS ₂ per molecule decreased which may be due to the steric repulsion between the CS ₂ molecules	Ghenaatian et al. (2013)
Ag/SBA-15 nanocomposites	Carbon monoxide (Co)	The silver content and dispersion of the catalyst are increased with the increase of the pH value, and it gave 98 % of CO oxidation at pH = 5 and 70 °C	Zhang et al. (2011c)
Aligned carbon nanotube	Aerosols	The filtration performance of the novel filters showed that when the number of CNTs layers increased, the filtration efficiency increased dramatically, while the pressure drop also increased	Yildiz and Bradford (2013)
Zinc oxide and zirconium hydroxide nanoparticles	Nitrogen oxide (NO ₂), sulfur oxides (SO ₂)	ZnO and Zr(OH) ₄ powders are photo luminescent, both exhibiting UV and visible emission peaks. The exposure of ZnO and Zr(OH) ₄ powders to SO ₂ and NO ₂ resulted in SO ₃ and NO ₃ chemisorption	Singh et al. (2012)
Nanosilver-decorated titanium dioxide (TiO ₂) nanofibers	Nitrogen oxide (Nox), volatile organic compounds (VOCs), microbial activity	Decomposition efficiency of nitrogen oxide (NO _x) and volatile organic compound (VOC) was 21 and 30 %, respectively. The antimicrobial activity was enhanced after nanosilver inclusion	Srisithirakul et al. (2011)
Single-walled carbon nanotubes	Nitrogen (N ₂), methane (CH ₄), carbon monoxide (CO), carbon dioxide (CO ₂)	The experimental simulated adsorption uptake of the SWCNTs was in the following order: H ₂ << N ₂ ≈ CH ₄ < CO << CO ₂	Lithoxoos et al. (2010)
Horn-shaped carbon nanotubes	Carbon dioxide (CO ₂), methane (CH ₄), carbon monoxide (CO), nitrogen (N ₂)	Horn-shaped carbon nanotubes showed good selectivity for carbon dioxide over the other gases	Sawant et al. (2012)
Ruthenium nanoparticle catalysts (Ru/γ-Al ₂ O ₃)	Nitrogen oxide (N ₂ O)	The catalyst samples exhibited high activity in N ₂ O decomposition and can retain higher than 90 % conversion of N ₂ O for long reaction times	Komvokis et al. (2011)
Mg ferrite nanospheres (MgFe ₂ O ₄)	Sulfur dioxide (SO ₂)	During the adsorption of SO ₂ , sulfate and sulfite species are formed on the surface of MgFe ₂ O ₄ , and Fe(III) is partially reduced to Fe(II)	Zhao et al. (2010a)
Titanium dioxide nanoparticles (TNPs)	Sulfur dioxide (SO ₂)	In the absence of light irradiation, the main product of SO ₂ adsorption was found to be SO ₃ ²⁻ , while light irradiation resulted in oxidation and the formation of adsorbed SO ₄ ²⁻	Baltrusaitis et al. (2011)
Titanium dioxide nanoparticles (TNPs)	VOCs (ethylene)	Sol-gel method with vortex reactor was used to synthesize novel TNPs with superior characteristics and a high bandgap energy that enhanced the photocatalytic degradation of ethylene	Hussain et al. (2010)
Electrospun nanofibers (NF) (hydroxypropyl-beta-cyclodextrin (HPβCD), NF, and hydroxypropyl-gamma-cyclodextrin (HPγCD) NF)	VOCs (aniline and benzene)	Both types of NFs efficiently entrapped the examined VOCs, due to their high porous structure, high surface area, and their molecular entrapment ability of VOCs by inclusion complexation	Celebioglu et al. (2016)

decomposition by which photocatalysts and physical adsorption by porous materials are used, as well as chemical adsorption which is considered one of the effective methods where the re-emission is excluded due to strong chemical bonding (Nuasaen et al. 2014). However, HCHO imposes great challenges for its removal. For example, conventional photochemical methods using photocatalysts are not appropriate for the indoor removal of HCHO because of the requirement of UV light irradiations and the risk of harmful ozone formation (Miyawaki et al. 2012). Moreover, hydrocarbon compounds could generate carcinogenic by-products through chains of secondary photochemical reactions (Miyawaki et al. 2012).

As a result, many attempts have been carried out to improve the removal of formaldehyde, for example, Lee et al. (2010a, b) produced electrospun polyacrylonitrile (PAN)-based carbon nanofiber (CNF) membrane with tailored microporosity and abundant nitrogen-containing functional groups as vastly effective adsorption sites. A notable amount of formaldehyde was adsorbed onto the PAN-activated carbon nanofiber (ACNF) pore surface even at a low concentration. However, air humidity reduced the life time of the nanofiber membrane to half. As a result, manganese oxide (MnO_x) catalysts were deposited on the PAN-ACNFs. The combination of MnO_x with PAN-ACNF afforded a superior formaldehyde removal performance in dry and extremely humid conditions by applying a two-stage removal process, comprised of the adsorption of formaldehyde in the PAN-ACNF micropores followed by the oxidative decomposition by MnO_x nanoparticles without any irradiation of UV light (Miyawaki et al. 2012).

An additional example on indoor air pollutants that have received social and scientific attentions is bioaerosols (aerosols of biological origin such as viruses, bacteria, and fungi) which can rapidly spread with airflow and can cause numerous diseases, including infections and allergies (Stark et al. 2003). Air filtration technology using antimicrobial materials such as silver nanoparticles, copper nanoparticles, CNTs, and natural products is considered the most applied and effective technique to remove bioaerosols through ventilation processes. Several studies have exposed that silver nanoparticles can successfully remove bacterial bioaerosols during the air filtration process. Several factors affect the antimicrobial activity of silver nanoparticles such as bacterial species, concentration, relative humidity (RH), size distribution, and exposure time of the silver nanoparticles (Lee 2008a; Lee et al. 2010a). In a like manner, the inactivation efficiency of CNTs is dependent on the loading concentration and membrane pore size, and it is low for single-walled carbon nanotubes (SWCNTs) compared to that of multi-walled carbon nanotubes (MWCNTs) (Jung et al. 2011).

Despite the efforts to improve indoor air quality (IAQ), the human exposure to nanomaterial-based filters in indoor environments may lead to variety of adverse health effects,

including peribronchial inflammation and necrosis, skin irritation, and mucosal inflammation (Lam et al. 2004; Warheit et al. 2007). In comparison to some antimicrobial materials such as silver, carbon nanotubes, and metal oxides, the antimicrobial natural products are typically considered less toxic to human and have recently been used to improve the IAQ. For example, essential oils extracted from natural products show acceptable reduction rates in bacterial inactivation; therefore, they have been applied to ventilation systems of indoor-contaminated environments (e.g., an antimicrobial filter coated with tea tree oil inactivates 99 % of bacterial aerosol on its surface within 2–8 min) (Pibiri et al. 2006; Pyankov et al. 2008). Some of natural nanoparticles (e.g., *Sophora flavescens*) have been deposited on the filter media surface using an aerosol process, yet they lost their spherical shape and coalesced on fiber filters under humid conditions (Hwang et al. 2012). In consequence, the electro-spraying method, driven by high-intensity electric fields, is used to generate the natural product nanoparticles in order to increase their morphological stability and eventually increase the produced filter efficiency for bioaerosol removal (Jung et al. 2013). Thus, the implementation of filters generated from electro-spraying natural products can be a promising new technology to control air quality.

Soil pollution

Soil contamination is caused by the existence of hazardous compounds in the natural soil environment. The common soil pollutants are heavy metals which can be presented naturally in soil but scarcely at toxic levels, and their main sources in contaminated soil are mining, manufacturing, landfill sites, particularly those that are accepting industrial wastes (e.g., paint residues, batteries, electrical wastes, etc.), and municipal or industrial sludge. Heavy metals can be considered one of the challenging soil pollutants because they are non-degradable substances, and they will stay in the contaminated environment once they are introduced to it; the only exceptions are mercury and selenium, since they can be transformed and volatilized by microorganisms. When large areas of soil are polluted, treatments can be done in situ (on-site) or ex situ (removed and treated off-site); however, the traditional treatment methods for contaminated soil are cost-prohibitive and extremely difficult (Natural Resources Conservation Service 2000). As a result, the best way to protect the environment is by preventing the contamination of heavy metals or by hindering the spreading of heavy metals in soil by immobilization technique (Ma et al. 1993).

Due to the fact that activity of heavy metals in soil is governed by sorption–desorption reactions with other constituents of soil (Singh et al. 2001), wide range of amendment agents have been used to manipulate the bioavailability of

heavy metals and to impede their diffusion in soil by inducing various sorption processes: adsorption to mineral surfaces, formation of stable complexes with organic ligands, surface precipitation, and ion exchange (Kumpiene et al. 2008). There are two types of amendment agents (Robinson et al. 2009): (1) mobilizing agents, which increase the bioavailability and mobility of heavy metals and enhance their removal through plant intake and soil washing (i.e., phytoextraction process), and (2) immobilizing amendment agents that decrease the bioavailability and mobility of heavy metals and reduce their transfer to food chain by preventing their leaching to the groundwater (i.e., phytostabilization) (Fig. 2). Both phytoextraction and phytostabilization processes are part of phytoremediation technique that is employed to manage contaminated soils (Bolan et al. 2014).

In recent years, nanoscale particles have gained a great interest for heavy metal immobilization in soil and groundwater. Two essential requirements should be met when using nanoparticles as amendment agents including the following (An and Zhao 2012): (1) they must be deliverable to the contaminated zones and, (2) when removing the external injection pressure, the delivered nanoparticles should remain within the confined domain (i.e., under natural groundwater conditions), where the delivered nanoparticles will work as an immobile sink for capturing soluble metals. However, the rapid tendency of nanoparticles to aggregate into micro- to millimeter scale aggregates results in losing their distinctive characteristics such as high specific surface area and soil deliverability. For the purpose of overcoming these problems, organic polymers such as starch (He and Zhao 2005) and carboxymethyl cellulose (CMC) (He and Zhao 2007) are often attached on the nanoparticles as stabilizers in order to prevent nanoparticle agglomeration through steric and/or electrostatic stabilization mechanisms and to improve the physical stability and mobility in soil and greater specific surface area. Liang and Zhao (2014) investigated the effectiveness of starch-stabilized

magnetite nanoparticles for in situ enhanced sorption and immobilization of arsenate As(V); the results indicated that water-leachable As(V) was greatly reduced as well as the toxicity characteristic leaching procedure (TCLP) leachability of As(V) was decreased.

Phosphate compounds can be used as effective agents for in situ immobilization of heavy metals in contaminated soils, as demonstrated by immobilization of lead (Pb) where phosphate was commonly applied to soil either in its soluble forms such as phosphoric acid or solid forms such as synthetic apatite, natural phosphate rocks, and even fishbone (with apatite being the effective composition) (Yang et al. 2001). Therefore, a new type of apatite nanoparticles was synthesized using CMC as a stabilizer in order to increase the dispersion rate of phosphate and immobilize lead in soil. It was suggested that the carboxyl and hydroxyl groups in cellulose molecules played an important role in inhibiting further agglomeration of nanoparticles; moreover, in producing a stable lead phosphate compound, that is widely recognized as pyromorphite (Liu and Zhao 2013).

Zerovalent iron (ZVI) nanoparticles are also used widely for in situ reductive immobilization of heavy metals in soil. The main drawback of ZVI nanoparticles that are prepared using traditional methods is their ability to agglomerate rapidly or react quickly with the surrounding media (e.g., dissolved oxygen or water), resulting in losing in their reactivity and mobility in soil. The agglomerated ZVI particles are often in the range of micron scale; therefore, they are not transportable or deliverable in soils, and thus, they are not applicable for in situ treatments. Accordingly, various ZVI particle-stabilizing strategies have been reported including modification of nZVI with several types of organic coatings, such as starch (Reyhanitabar et al. 2012), polyvinylpyrrolidone (PVP), (Fang et al. 2011a) and sodium CMC (He and Zhao 2007). Cetylpyridinium chloride has also been used to control ZVI nanoparticle agglomeration (Chen et al. 2004). Another problem that is limiting the engineering

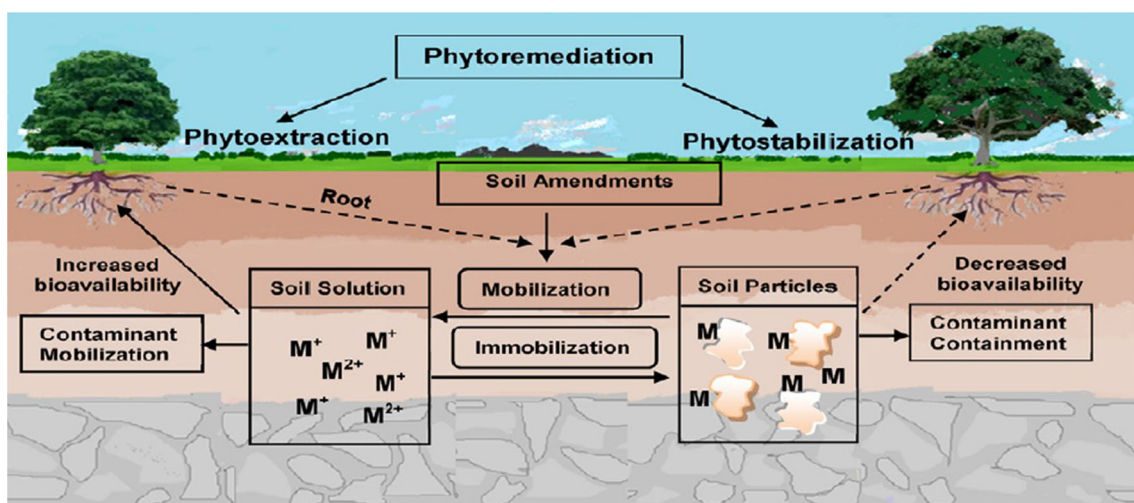


Fig. 2 Schematic diagram illustrating the link between (im)mobilization, bioavailability, and remediation of heavy metal (Bolan et al. 2014)

applications of iron-based materials is the cost factor due to the large amount of chemical reagents such as ferrous sulfate and ferrous chloride that are consumed during the material conventional preparation technologies (Fang et al. 2011b). With intention to reduce the cost, Wang et al. (2014c) successfully prepared CMC-stabilized nanoscale zerovalent iron from steel pickling waste liquor to remove Cr(VI) from contaminated soil, and the results revealed that TCLP leachability of Cr(VI) reduced by 100 %. Moreover, Table 2 displays some of used nanomaterials to remove different types of soil contaminants.

However, the immobilization technique to remediate the contaminated soil imposes many problems. Firstly, despite of both soluble and solid phosphates being reported as highly effective for heavy metal in situ stabilization on the laboratory scale, adding large amounts (e.g., 3 % PO_3^{-4} dosage) of very soluble phosphoric acid or phosphate salts into the subsurface is limited not only by the cost of materials but also by the secondary contamination problems that arise due to the high solubility of phosphate which may lead to the contamination of groundwater and surface waters in the affected area by excessive nutrient input (eutrophication) (Park et al. 2011). Secondly, Xu and Zhao (2007) stated that the CMC stabilizer is vulnerable to hydrolysis and, once it decomposes, its particle-stabilizing ability ceases and the fine residual

precipitates end up in the soil phase. Finally, Wang et al. (2014b) investigated the ecotoxicity of the immobilized chromium by CMC-stabilized ZVI nanoparticles prepared from steel pickling waste. The results suggested that such remediation exerted an inhibitory effect on plant growth, which might be related to specific physicochemical properties of nZVI. There are several possible mechanisms by which fresh nZVI could enhance Fe uptake into plants; one possibility is that they penetrate the seed coat and are assimilated by the seed embryo (Wang et al. 2014b). Another expected way for nZVI to enter the plant is via root epidermal cells by endocytosis (Slomberg and Schoenfisch 2012). Moreover, it was confirmed that carbon nanotubes are also able to penetrate the seed coat while supporting and allowing water uptake inside the seeds (Khodakovskaya et al. 2009).

Water pollution

One of the major challenges that is facing the globe is providing a convenient access to clean and affordable water that can keep up with rapidly growing demands. Population growth, global climate change, and water pollution are the highest challenges that increase the struggles faced by water supply

Table 2 Nanoparticle application in soil remediation

Nanoparticle	Target pollutants	Observations	References
Iron sulfide (FeS)	Mercury (Hg^{2+})	Using carboxymethyl cellulose (CMC) as stabilizer, and it was able to immobilize in situ mercury ions	Xiong et al. (2009)
Ni/Fe bimetallic	Decabromodiphenyl ether (BDE209)	Ni/Fe bimetallic nanoparticles were able to degrade BDE209 in soil at ambient temperature, and the removal efficiency can reach 72 %	Xie et al. (2014)
Emulsified nanoiron	Trichloroethylene (TCE)	Electro-osmotic flow played a basic role in removing TCE from the soil matrix to the cathode reservoir	Yang and Chang (2011)
Nano zerovalent iron (nZVI)	Organochlorine insecticides (DDT)	1 g nZVI kg^{-1} was efficient for DDT degradation in spiked soil, while a higher concentration was applied for the treatment of aged contaminants in soil	El-Temseh and Joner (2013)
Nanocrystalline hydroxyapatite (nHA)	Cadmium and lead	(nHA) significantly formed Pb/Cd phosphate (e.g., hydroxypyromorphite-like mineral) that was able to reduce water-soluble, bioaccessible, and phytoavailable Pb/Cd	He et al. (2013)
Iron phosphate (vivianite)	Copper (Cu(II))	Sodium carboxymethyl cellulose (NaCMC) was used to prepare iron phosphate (vivianite) nanoparticles. It was observed that the availability of Cu in soil was decreased by the formation of copper phosphate minerals through precipitation and adsorption	Liu and Zhao (2007a)
Nanoscale zerovalent iron	Hexavalent chromium (Cr(VI))	Green tea extract was used to stabilize the zerovalent iron (GT-nZVI), and it was not that successful in treating Cr(VI) because the strongly sorbed Cr(VI) was progressively releasing in soil, followed by an increase in pH and the dissolution of PbCrO_4	Chrysochoou et al. (2012)
Iron phosphate (vivianite)	Lead (Pb^{2+})	The TCLP-leachable Pb^{2+} in soils was decreased resulting in the formation of chloro-pyromorphite minerals due to the addition of chloride in the treatment	Liu and Zhao (2007b)
Nano zerovalent iron (nZVI)	Chromium (Cr(VI))	Carboxymethyl cellulose was used to stabilize (nZVI) and the complex depicts a significant reactivity and reaction kinetics for reductive immobilization of Cr(VI)	Xu and Zhao (2007)

systems. In both developing and industrialized countries, water scarcity is exacerbated by human activities that play the greatest role in contaminating the natural water resources by releasing energy, chemicals, and other pollutants that deteriorate the water quality for other users. In addition, nature itself can be one of the contamination sources such as water storm runoff, animal wastes, etc. The United States Environmental Protection Agency (EPA) classifies water pollution into the following six categories: (1) plant nutrients, (2) biodegradable waste, (3) heat, (4) sediment, (5) hazardous and toxic chemicals, and (6) radioactive pollutants. Thus, water pollutants include organic pollutants, pathogens, industrial discharge containing heavy metals and different anions, etc. (Goyal et al. 2013) that are added to the water and cannot be naturally broken down and they tend to change the properties of the water body.

Essentially, the wastewater treatment involves physical, chemical, and biological technologies and it usually occurs in four stages: (1) preliminary, (2) primary, (3) secondary, and (4) tertiary advanced treatment. The technologies that are generally used for water purification are coagulation and flocculation, sedimentation, dissolved air flotation, filtration, steam distillation, ion exchange, deionization, reverse osmosis, and disinfection (Shon et al. 2007). Materials usually used in these technologies are sediment filters, activated carbon, coagulants, ion exchangers, ceramics, activated alumina, organic polymers, and many hybrid materials (Hotze and Lowry 2011). However, the conventional water treatment procedures might be costly and could release secondary toxic contaminants into the environment (Gaya and Abdullah 2008a).

Nanotechnology enables extremely efficient, flexible, and multifunctional processes that can provide a promising route, in order to retrofit aging infrastructure and to develop high performance, inexpensive treatment solutions which depend less on large infrastructures (Qu et al. 2013b). The current advancements in nanotechnology spot the light on great opportunities to develop the next generation of water supply systems and expose the possibilities to expand the water supplies by affording new and cost-effective treatment capabilities that can overcome the major challenges faced by the current treatment technologies (Qu et al. 2013a).

Adsorption

Compared to the limited active site surface area and low efficiency of the conventional adsorbents, the nano-adsorbents offer a considerable advancement with their high adsorption kinetics as demonstrated by their extremely high specific surface area and associated sorption sites, short intraparticle diffusion distance, and tunable pore size and surface chemistry (Qu et al. 2013a) that provide useful features for effective adsorption. Their great adsorption capacity is mainly because of their high specific area and the highly active adsorption sites that are

created by high surface energy and size-dependent surface structure at the nanoscale (Auffan et al. 2008). The nanoadsorbents are effectively used in the removal of organic compounds, and metal ions and their selectivity toward particular pollutants can be increased by functionalization.

Nanoscale metal oxides, such as titanium dioxides, iron oxides, zinc oxides, alumina, etc., have been explored as low-cost, effective adsorbent for water treatment offering a more cost-efficient remediation technology due to their size and adsorption efficiency (Engates and Shipley 2011; Zhang 2003). The adsorption is chiefly controlled by forming a complex with the surface of nanoscale metal oxides and undergoing one electron oxidation reaction under visible irradiation (Peng et al. 2012a). Among the nanoscale metal oxides, the magnetic nanoparticles have drawn a considerable concern because of their potential application (Xin et al. 2012) and their exhibition of interesting magnetic properties (e.g., super paramagnetism, strong magnetic response under low applied magnetic fields (Fig. 3) (Kilianová et al. 2013). Table 3 shows the applications of nanoscale metal oxides as adsorbents.

Not to mention that CNTs, including single-walled CNTs and MWCNTs, have lately drawn significant attention because of their mechanical, electrical, optical, physical, and chemical properties (Kozioł et al. 2007). Since CNT discovery by Iijima in 1991 (Iijima 1991), they have been recognized as alternates for activated carbon as they exhibit remarkable adsorption competency for gas and liquid phases, such as organic vapors, inorganic pollutants, and several heavy metal ions (Luo et al. 2013a) due to their binding sites that are more available than those on activated carbon (Ji et al. 2009).

In comparison to other carbon-based adsorbents, CNTs is the super organic adsorbent for environmental remediation; they behave as flexible porous materials toward the organic pollutants. CNTs have shown remarkable adsorption capability and high removal efficiency for various organic pollutants (Table 4), including organic dyes (e.g., cationic, azoic, reactive, basic and acid dyes, etc.) (Bazrafshan et al. 2012; Gao et al. 2013; Geyikçi 2013; Gong et al. 2009; Gupta et al. 2013; Madrakian et al. 2011; Moradi 2013), pharmaceuticals (e.g., cephalixin, tetracycline (TC), olaquinox, carbamazepine, etc.) (Cai and Larese-Casanova 2014; Jafari and Aghamiri 2011; Zhang et al. 2011a, b), pesticides (Chen et al. 2011a; Deng et al. 2012), phenolic compounds (Abdel-Ghani et al. 2014; Chen et al. 2009b; Lin and Xing 2008; Pacholczyk et al. 2011; Sheng et al. 2010b), and other toxic organics. Apul and Karanfil (2015) and Yu et al. (2014) reported the adsorption of many different types of organic compounds on carbon nanotubes. The dominate adsorption mechanisms by which CNTs adsorb organic compounds consist mainly of physical processes and are affected by the properties of the compound of interest (Pan and Xing 2008). Lin and Xing (2008) and Ren et al. (2011) stated that the aromatic compounds have relatively higher sorption affinity toward CNTs than non-aromatics.

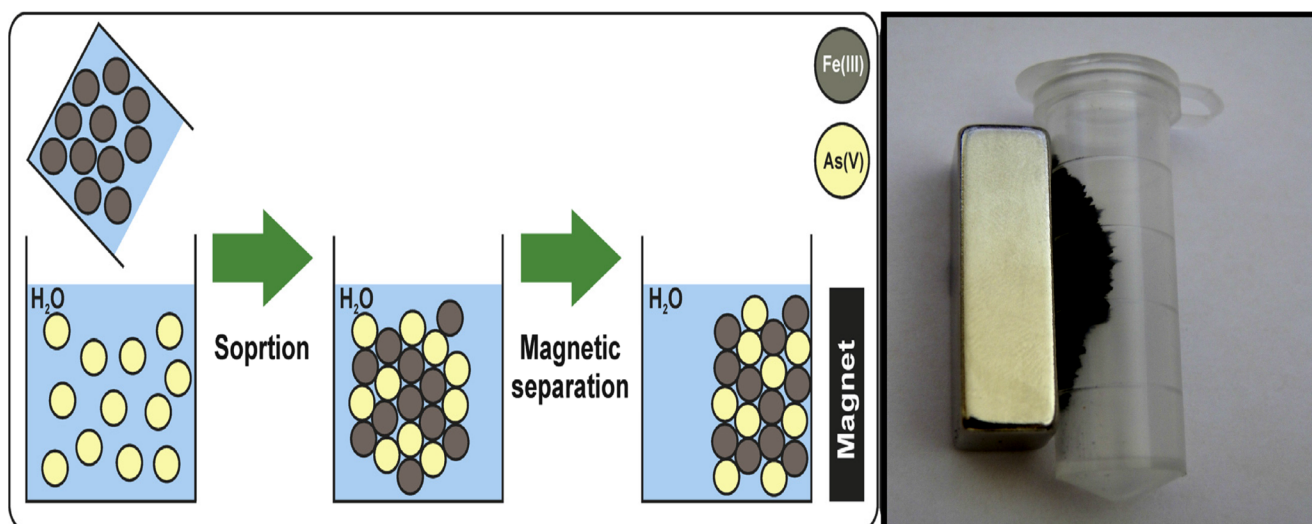


Fig. 3 Schematic aggregation of carbon nanotubes which monomers form small aggregates first and then big aggregates (Yang and Xing 2010)

Furthermore, organic compounds which have $-\text{COOH}$, $-\text{OH}$, and $-\text{NH}_2$ functional groups could also form hydrogen bond with the graphitic surface of CNTs (Yang et al. 2008). In short, during organic compound–CNT interactions, different mechanisms may take place simultaneously such as hydrophobic interactions, π – π bonding, electrostatic interactions, and covalent and hydrogen bonding (Gupta et al. 2013; Pan and Xing 2008; Yang and Xing 2010).

On the other hand, CNTs have shown great capabilities for the adsorption of heavy metals from natural waters and wastewater streams and that is of great environmental relevance due to the high toxicity and non-biodegradability of compounds which are generally considered as carcinogenic (Luo et al. 2013a). Many researches have investigated the mechanisms of heavy metal ion adsorption on CNTs which appear to be very complicated and attributable to physical adsorption, electrostatic attraction, precipitation, and chemical interaction between the heavy metal ions and the surface functional groups of CNTs (e.g., carboxyl, hydroxyl, lactones, and phenol) (Ren et al. 2011), whereas the chemical interaction between the heavy metal ions and the surface functional groups of CNTs is the main adsorption mechanism and that reflects that the sorption of metal ions onto CNTs is chemisorption process rather than physisorption process and strongly depends upon CNT surface total acidity (Lu et al. 2006; Lu and Liu 2006; Rao et al. 2007). The adsorption of the heavy metals might be influenced by the presence of some organic compounds, for instance, the adsorption of copper(II) is significantly influenced by humic acid (HA), fulvic acid (FA), and hydroxylated and carboxylated fullerenes (Sheng et al. 2010a; Wang et al. 2013a). The order of binding of heavy metal ions by CNTs is widely studied. Stafiej and Pyrzyńska (2007) reported the adsorption characteristics of certain divalent metal ions (i.e., Cu, Co, Cd, Zn, Mn, and Pb) by MWCNTs and found that the affinity of metal ions for MWCNTs followed the order Cu(II)

$> \text{Pb(II)} > \text{Co(II)} > \text{Zn(II)} > \text{Mn(II)}$. Meanwhile, Li et al. (2003a) studied the competitive adsorption of Pb(II), Cu(II), and Cd(II) ions by oxidized MWCNTs and found that the adsorption capacities of MWCNTs for the three metal ions were in the following sequence: Pb(II) $>$ Cu(II) $>$ Cd(II). Table 5 represents carbon nanotube as heavy metal adsorbent.

The main drawback of CNTs is the poor dispersion in the aqueous phase that significantly hinders the application of CNTs because of the hydrophobicity of their graphitic surface and the strong intermolecular van der Waals interaction between tubes, which can lead to the formation of loose bundles/aggregates (Fig. 4) that contain interstitial spaces and grooves which are reported to be high adsorption energy sites for organic molecules (Pan et al. 2008), and despite of that, it was suggested that those aggregates reduce the effective surface area of CNTs (Vuković et al. 2010a). In order to overcome this drawback and enhance the CNT performance, it can be functionalized in different ways, for example formation of chemical bonds between the modifier and CNT surfaces or physical adsorption of the modifying species to the surface of CNTs and all the ways lead to the addition of functional groups on the surface of the CNTs improving their efficiency, selectivity, and sensitivity (Ghaedi and Kokhdan 2012; Han et al. 2006; Liu et al. 2008; Perez-Aguilar et al. 2011; Tasis et al. 2006; Wildgoose et al. 2006). The acid treatment produces carboxylic and hydroxylic group (COOH , OH , $\text{C}=\text{O}$, and OSO_3H) on the external surface of the CNTs (Vuković et al. 2010a) as shown in Fig. 5. The hydrophilic groups (i.e., carboxylic groups) can be introduced onto the sidewall of CNTs, as a result improving the solubility and dispersion of CNTs in aqueous solutions (Liu et al. 1998). Functionalization of CNTs via oxidizing and reducing chemicals such as HNO_3 , KMnO_4 , H_2O_2 , NaClO , H_2SO_4 , KOH , and NaOH has been widely reported (Li et al. 2010; 2003b; Raymundo-Piñero et al. 2005).

Table 3 Nanoscale metal oxides as adsorbents

Adsorbents	Modification/synthesis	Target pollutants	Performance	Adsorption isotherm	Remarks	References
Magnetite (Fe ₃ O ₄)	Zirconium (IV)-metalloporphyrin	Fluoride	The percentage of the extracted fluoride ions was 92.0 ± 1.7 % (contact time 20 min, pH 5.5)	–	These modified nanoparticles were separated by an external magnetic field	Poursaberi et al. (2012)
Magnetite (Fe ₃ O ₄)	Amino-functionalized (1,6-hexadiazine)	Cu(II)	The maximum adsorption capacity was 25.77 mg g ⁻¹ at pH 6 and 298 K	Langmuir	Adsorption process was spontaneous, endothermic, and chemical in nature coexisted ions; Ca ²⁺ and Mg ²⁺ have no influence on the removal efficiency of Cu ²⁺ with MNP-NH ₂	Hao et al. (2010)
Magnetite (Fe ₃ O ₄)	Polymer-modified nanoparticles (3-aminopropyltriethoxysilane (APS) and copolymers of acrylic acid (AA) and crotonic acid (CA))	Cd(II), Zn(II), Pb(II), Cu(II)	95 % of the metal ions were adsorbed at about 30 min at pH 5.5	Langmuir	The adsorption capacity remained almost constant for the 4 cycles; the adsorption capacity of Cu ²⁺ decreased with increasing coexisting ions (Na ⁺ , K ⁺ , or Mg ²⁺)	Ge et al. (2012)
Titanate nanotube (TNTs)	Hydrothermal method from TiO ₂ nanoparticles	Pb(II), Cd(II), Cu(II), Cr(II)	TNTs followed the sequence of Pb ²⁺ (2.64 mmol g ⁻¹) > Cd ²⁺ (2.13 mmol g ⁻¹) > Cu ²⁺ (1.92 mmol g ⁻¹) > Cr ³⁺ (1.37 mmol g ⁻¹)	–	TNTs can be considered as good adsorbents for heavy metals as they can effectively adsorb cations via ion exchange due to their low point of zero charge (pHPZC) and abundant hydroxyl groups (OH) on the surface	Liu et al. (2013b)
Titanate nanoflowers (TNF)	–	Cd(II), Ni(II), Zn(II), Pb(II)	The maximum adsorption capacity for Pb(II), Cd(II), Ni(II), and Zn(II) ions were 1.47, 0.73, 0.33, and 0.44 mmol/g, respectively	Langmuir	High selectivity in the removal of Cd(II) than less toxic ions (Zn(II) and Ni(II))	Huang et al. (2012)
Iron oxide–alumina (Fe ₂ O ₃ –Al ₂ O ₃)	–	Cu(II), Pb(II), Ni(II), Hg(II)	Maximum sorption capacities were found to be 4.98 mg/g for Cu ²⁺ , 32.36 mg/g for Ni ²⁺ , 23.75 mg/g for Pb ²⁺ , and 63.69 mg/g for Hg ²⁺ ions	Langmuir	The removal percentage was in the order of Cu ²⁺ < Pb ²⁺ < Ni ²⁺ < Hg ²⁺	Mahapatra et al. (2013)
Titanium dioxide	–	Pb(II), Cu(II), Zn(II)	Largest adsorption capacity (2312.18 μmol/g) with Pb, while the smallest adsorption capacity (40.10 μmol/g) with Cu	Freundlich	Desorption was pH dependent and that more than 98 % of all metals desorbed at pH 2 adsorption affinity to be Pb > Zn > Cu	Hu and Shipley (2012)
Titanium dioxide	–	Pb, Cd, Cu, Ni, Zn	TiO ₂ nanoparticles removed Pb, Cd, and Ni from solution with similar adsorption at 0.1 and 0.5 g/L	Langmuir	The high surface area of TiO ₂ nanoparticles results in their large adsorption capacities making them better sorbents when compared to bulk particles	Engates and Shipley (2011)
Hydrous cerium oxide (SCO)	(SCO) was synthesized by integrating CeO ₂ nanoparticles into silica monoliths	As	Treatment met the maximum contaminant level of arsenic at 10 g/L for drinking water	–	The silica monolith substrate was used to enhance the stability of SCO during the water treatment and preventing the leakage of CeO ₂ nanoparticles into the treated water	Sun et al. (2012b)
Magnetite (Fe ₃ O ₄)	Synthesized with high specific area by the aerosol-assisted chemical vapor deposition method	As	100 % removal efficiency before 1 min of contact	–	The fast removal of arsenic means that the affinity of arsenic by the iron is very strong	Monárrez-Cordero et al. (2014)
Magnetite (Fe ₃ O ₄)	Amine-functionalized	Pb(II), Cd(II), Cu(II)	Equilibrium within 120 min at pH 7.0. AF-Fe ₃ O ₄ was able to remove over 98 % of Pb(II), Cd(II), and Cu(II)	Langmuir	Affinity Pb > Cu > Cd, separation by magnetic field	Xin et al. (2012)
NiO nanoparticles	–	Cd(II) and Pb(II)	The maximum adsorption capacity for Cd(II) and Pb(II) ions were 909 and 625 mg/g, respectively	Langmuir	The adsorption was endothermic and spontaneous in nature and followed boundary layer diffusion or external mass transfer effects	Sheela and Nayaka (2012)
Mixed maghemite-magnetite nanoparticles (γ-Fe ₂ O ₃ -Fe ₃ O ₄)	–	Cd(II)	About 40 % of total Cd(II) was removed within 5 min. Thereafter, the adsorption capacity remained constant after the contact time of 2 h	Langmuir	Upon exposure to mixed maghemite-magnetite, Cd ²⁺ ions may go through oxidation-reduction reactions or may become fixed by complexation with oxygen atoms in the oxy-hydroxy groups at the shell surface of the iron oxide nanoparticles	Chowdhury and Yanful (2013)
Iron oxide nanoparticles (magnetite and maghemite)	Iron oxide nanoparticle was produced by employing electrical wire explosion (EWE)	As(III) and As(V)	Q _{max} for As(III) and As(V) was 2.90 and 3.05 mg/g, respectively	Langmuir	The sorption capacity values are lower than those of the commercial ones	Song et al. (2013)
Magnetic iron oxide nanoparticles (MION-Tea) Fe ₃ O ₄	Synthesized using tea waste	As(III) and As(V)	High adsorption capacity of 188.69 mg/g for arsenic(III) and 153.8 mg/g for arsenic(V)	Langmuir	Thermodynamics revealed the endothermic nature of adsorption MION-Tea can be reused up to 5 adsorption cycles and recycled using NaOH	Lunge et al. (2014)
Graphene oxide-hydrated zirconium	Prepared by hydrothermal co-precipitation method	As(III) and As(V)	Adsorption capacity of 95.15 and 84.89 mg/g for As(III) and As(V)	Langmuir	GO-ZrO(OH) ₂ was successfully regenerated with a stable adsorption capacity for 5 cycles	Luo et al. (2013b)

Table 3 (continued)

Adsorbents	Modification/synthesis	Target pollutants	Performance	Adsorption isotherm	Remarks	References
nanocomposite (GO-ZrO(OH) ₂) Magnetite (Fe ₃ O ₄)	–	Pb(II)	Equilibrium was achieved in less than 30 min. Maximum removal was observed at pH 5.5	Freundlich	Pb(II) removal efficiency was not affected by the add addition coexisting cations such as Ca ²⁺ , Ni ²⁺ , CO ₃ ²⁺ , and Cd ²⁺	Nassar (2010)
Iron(III) oxide (γ-Fe ₂ O ₃)	Wet chemical method	As(V)	100 % removal of As(V) is achieved at pH from 5 to 7.6 with Fe/As = 20/1	Freundlich	The strong magnetic interactions they developed between nanoparticles develop a mesoporous nature of nanoparticle arrangement which is responsible for enhancement of adsorption capacity	Kilianová et al. (2013)
Magnetic nanoparticle (Fe ₃ O ₄) impregnated onto activated maize cob powder (Fe ₃ O ₄ -MCP)	–	Methylene blue (MB)	The highest percentage for dye concentration removal was 93.11 % at pH 6.0	–	The electrostatic attraction between the negatively charged Fe ₃ O ₄ -MCP surface and the positively charged cationic dyes is the key mechanism of the adsorption process	Tan et al. (2012)
Guar gum-nano zinc oxide (GG/nZnO)	–	Cr(VI)	98.63 % Cr(VI) was removed with a contact time of 50 min, pH 7, and an adsorbent dose 1.0 g/L	Langmuir and Freundlich	Both liquid-film and intraparticle diffusions dominated the overall kinetics of the adsorption process	Khan et al. (2013)
Hydrous aluminum oxide embedded with Fe ₃ O ₄ nanoparticle (Fe ₃ O ₄ @Al(OH) ₃ NPs)	–	Fluoride		–	The advantage of this adsorbent is a combination from magnetic nanoparticle and hydrous aluminum oxide flocc, with magnetic separability and high affinity toward fluoride	Zhao et al. (2010b)
Nano-sized superparamagnetic zirconia (ZrO ₂ /SiO ₂ /Fe ₃ O ₄ , SPMZ)	–	Fluoride	The sorption capacity amount was 14.7 mg/g at pH = 4	Langmuir and Freundlich	SPMZ possesses a considerable selectivity for fluoride which allows its preferred sorption from multicomponent systems	Chang et al. (2011)
Magnetite nanoparticles Fe ₃ O ₄	Direct attachment of reactive blue-19 onto the surface of magnetite nanoparticles	Pb(II)	Adsorption of Pb ²⁺ takes place at 3.0 < pH < 5.5 range with a maximum capacity factor for Pb ²⁺ ion on the RB-MNPs was 79.3 mg g ⁻¹	Langmuir	Ion exchange mechanism is mainly responsible for the removal of lead, while the electrostatic attraction force probably has slight influence on the removal process	Madrakian et al. (2013)
PVA/TiO ₂ /APTES nanohybrid	Functionalized with amine groups	Cd(II), Ni(II), and U(VI)	The maximum sorption capacities were 49.0, 13.1, and 36.1 mg g ⁻¹ for Cd(II), Ni(II), and U(VI) ions with pH of 5.5, 5, and 4.5, respectively	Freundlich	The sorption process was ideal at higher temperature with affinity order for heavy metal ions is as follows: Cd(II) > U(VI) > Ni(II)	Abbaszadeh et al. (2014)
Amorphous zirconium oxide (am-ZrO ₂)	–	As(III) and As(V)	The adsorption capacities of am-ZrO ₂ nanoparticles on As(III) and As(V) at pH 7 are (83.2) and 32.5 mg/g, respectively	–	Am-ZrO ₂ nanoparticles immobilized on glass fiber cloth showed an even better removal effect than am-ZrO ₂ nanoparticles dispersed in water, which reduces the possible dispersion of nanoparticles into the environment	Cui et al. (2012a)
Amorphous zirconium oxide (am-ZrO ₂)	–	Phosphate	Adsorption capacity was about 99.01 mg/g at pH 6.2	Langmuir	Hydroxyl groups on the surface played a main role in the phosphate adsorption. am-ZrO ₂ nanoparticles could be easily regenerated using a 0.1 M NaOH	Su et al. (2013)
Fe ₃ O ₄ nanoparticles	Coated with ascorbic acid	As	Maximum adsorption capacity of 16.56 mg/g for arsenic(V) and 46.06 mg/g for arsenic(III)	Langmuir	The use of the ascorbic acid enhanced the suspension of Fe ₃ O ₄ nanoparticles and effectively inhibited the leaching of Fe into the solution	Feng et al. (2012)
Single-phase α-MnO ₂ nanorod sand δ-MnO ₂	–	As(V)	α-MnO ₂ , pH 6.5, maximum removal capacity 19.41 mg g ⁻¹ δ-MnO ₂ , pH 6.5, maximum removal capacity 15.33 mg g ⁻¹	Langmuir	Electrostatic force and the ligand exchange (ligand exchange with –OH) phenomenon are the two factors that play an important role in the adsorption of arsenate species onto Mn-oxide surface	Singh et al. (2010)
CeO ₂ , TiO ₂ , and Fe ₃ O ₄	–	Pb(II)	The adsorption capacity obtained for the NPs was 189 mg Pb/g NPs CeO ₂ , 83 mg Pb/g NPs Fe ₃ O ₄ and 159 mg Pb/g NPs TiO ₂	–	The toxicity issue of these NPs is also assessed in this study, and the result showed that the CeO ₂ NPs had high phytotoxicity while TiO ₂ and Fe ₃ O ₄ NPs did not exhibit any toxicity	Recillas et al. (2011)
Magnesium and zinc oxide (MgO and ZnO)	–	Cu(II)	The maximum adsorption capacities obtained for ZnO and MgO are 226 and 593 mg/g, respectively, at initial pH of 3–4	Freundlich	MgO has better adsorption potential as compared to ZnO	Rafiq et al. (2014)
Nano ZnO	Gel combustion	Pb(II)	Nano ZnO shows almost complete Pb adsorption at lower initial	Langmuir and Freundlich	The surface area of the powder was 80.425 m ² g ⁻¹ , large surface area compared to normal zinc oxide	Venkatesham et al. (2013)

Table 4 Carbon nanotubes as organic compound adsorbent

Organic pollutant type	Examples	CNT modification	Adsorption isotherm	Remarks	References
Pharmaceuticals	Epirubicin (EPI)	Carboxylized with HNO ₃	Freundlich	CNTs were able to form supramolecular complexes with EPI via π - π stacking and possessed favorable loading properties as drug carriers	Chen et al. (2011c)
	Ciprofloxacin (CPI)	Graphitized (MG), carboxylized (MC), and hydroxylized (MH)	Freundlich and Dubinin-Astakhov (DA)	The π - π electron donor-acceptor interactions were the reason for higher sorption on MH than MC	Li et al. (2014a)
	Tetracycline (TC)	Treated by heating and trace metals by sodium hypochlorite	Freundlich	The aqueous solution chemistry played a significant role in tetracycline adsorption on carbon nanotubes	Ji et al. (2010)
	Sulfamethoxazole (SMX)	Graphitized (MG), carboxylized (MC), and hydroxylized (MH)	Dubinin-Astakhov	The π - π electron donor-acceptor interactions are responsible for high SMX adsorption at low pHs and resulting in the following adsorption sequence: MH > MG > MC	Zhang et al. (2010)
	Norfloxacin (NOR)	Graphitized (MG), carboxylized (MC), and hydroxylized (MH)	Freundlich	The sorption process is affected by the properties of CNT surface; therefore, the functionalized carbon nanotubes show great sorption affinity and capacity for NOR	Wang et al. (2010b)
	Ofloxacin (OFL)	Graphitized (MG), carboxylized (MC), and hydroxylized (MH)	Freundlich	The high sorption of OFL was through several mechanisms including electrostatic interactions, cationic exchange, and hydrogen bond	Peng et al. (2012b)
	Ibuprofen (IBU)	Oxidized with HNO ₃ (O-MWCNTs)	Polanyi-Manes model	The adsorption capacity of CNTs for IBU was dependent upon the oxygen content of CNTs, resulting in less adsorption capacity for O-MWCNTs than that of pristine MWCNTs	Cho et al. (2011)
Organic dyes	Methylene blue (MB)	Loaded with magnetite (M-MWCNTs)	Langmuir	The electrostatic attraction and π - π stacking interactions between (M-MWCNTs) and (MB) was responsible for the high adsorption capacity	Ai et al. (2011)
	Methyl orange (MO)	Purified with acid washing and oxidation in diluted air	Langmuir	Dye molecule diffusion to the surface of CNTs was inhibited by the increased viscosity as the CNT dosage was increased	Yao et al. (2011)
	Alizarin red S (ARS) and Morin	–	Langmuir	The adsorption capacity of both of the dyes was increased at low pH due to the electrostatic interaction between negatively charged adsorbent surface and these charged dye cations	Ghaedi et al. (2011)
	Reactive red M-2BE (RRM)	–	Liu isotherm	The maximum adsorption capacities were 335.7 mg/g, and the loaded CNTs with RRM dye can be efficiently regenerated using a mixture of methanol + 4 mol L ⁻¹ NaOH	Machado et al. (2011)
	Reactive blue 4 (RB4)	–	Liu isotherm	At high temperature, CNT adsorption capacity increased because of enhancing the rate of intraparticle diffusion	Machado et al. (2012)
	C.I. Direct Yellow 86 (DY86) and C.I. Direct Red 224 (DR224)	–	Freundlich (DY86), D-R isotherm (DR224)	The affinity between DY86 and CNTs was less than that between DR224 and CNTs, and the adsorption process was physisorption and can be characterized as ion exchange process	Kuo et al. (2008)
Pesticides	Diuron and dichlobenil	–	Polanyi-Manes	The main adsorption mechanism was hydrogen bonding, and the adsorption was diminished by increasing the oxygen-containing groups	Chen et al. (2011a)
	Atrazine	–	Polanyi-Manes	Hence, the adsorption of atrazine was at external surface of CNTs and no closed interstitial spaces in CNT aggregates were formed; reversible adsorption of atrazine was observed	Yan et al. (2008)
	Diuron, fluridone, and norflurazon	Purified by a mixed HNO ₃ and H ₂ SO ₄	Freundlich model and Dubinin-Astakhov (DA)	The adsorption mechanism was mainly controlled by hydrogen bonding and hydrophobic interactions	Sun et al. (2012a)
Phenolic compounds, benzene derivatives, and other toxic organics	1,2-Dichlorobenzene (1,2 DCP)	Graphitized (MG)	Freundlich	At pH above 10, the adsorption capacity of CNT decreased because of the formation of water clusters on the oxygen groups	Peng et al. (2003)
	2,4,6-Trichlorophenol (TCP)	Treated with HNO ₃	Polanyi-Manes	Oxidation treatment of CNTs increased the adsorption capacity for TCP due to the increased surface area and hydrophilic carboxylic groups	Chen et al. (2009b)
	Benzene, toluene, ethylbenzene, and <i>p</i> -xylene	Oxidized by sodium hypochlorite (NaOCl)	Langmuir and Freundlich	The adsorption performance was enhanced by oxidation due to the increased of purity, carboxylic groups, negative surface charge, and carbon containing defects	Su et al. (2010)
	Pentachlorophenol (PCP)	Oxidized by HNO ₃ , H ₂ O ₂ , and KMnO ₄	Langmuir and Freundlich models, Radke-Prausnitz model, and Fritz-Schlünder model	The more oxygen-containing groups were introduced (carboxylic, phenolic, and lactic), the lower the adsorption of PCP to CNTs became	Abdel Salam and Burk (2008)
	Naphthalene with 2,4-dichlorophenol and 4-chloroaniline	–	Dubinin-Astakhov (DA)	The adsorption of 2,4-dichlorophenol and 4-chloroaniline was suppressed by added naphthalene	Yang et al. (2010b)
Natural organic matters (NOMs)	Fulvic acid (FA)	Purified by mixed HNO ₃ and H ₂ SO ₄ solutions	Freundlich	As the pH increased, the adsorption of fulvic acids was decreased because of increasing repulsive interaction	Yang and Xing (2009)
	Humic acid (HA)	Purified by mixed HNO ₃ and H ₂ SO ₄ solutions	Langmuir	Adsorption of HA with high polarity could efficiently stabilize MWCNTs in water	Lin et al. (2012)

Table 5 Carbon nanotube as heavy metal adsorbent

Modification	Target pollutants	Adsorption isotherm	Remarks	References
Oxidized with H ₂ O ₂ , KMnO ₄ , and HNO ₃	Cadmium(II)	–	Many functional groups have been introduced to the surface of the CNTs, which are responsible for the increase of cadmium(II) adsorption capacities	Li et al. (2003b)
Manganese dioxide (MnO ₂)	Cadmium(II)	Langmuir	The mechanism of cadmium adsorption onto the MnO ₂ /O-MWCNTs may include both physical and chemical adsorptions and appeared to be influenced by external mass transfer, intraparticle diffusion, and chemical adsorption	Luo et al. (2013a)
Iron oxide magnetic	Nickel (Ni(II)) and strontium (Sr(II))	Langmuir	Both adsorption capacities of MWCNTs and iron oxides are much less than that of the magnetic composites. The separation of the composites from the treated solution can be achieved by a magnetic process	Chen et al. (2009a)
Acidified by concentrated nitric acid	Lead (Pb(II))	Langmuir	Salt or complex deposited on the surface of MWCNTs due to reaction between Pb(II) and the oxygenous functional groups formed on the surface of acidified MWCNTs and increased adsorption capacity	Wang et al. (2007b)
Purified by sodium hypochlorite solution	Zinc (Zn(II))	Langmuir	Structure and nature of the surface were significantly enhanced after purification which made CNTs become more hydrophilic and proper for adsorption of Zn ²⁺	Lu and Chiu (2006)
Alumina	Lead (Pb(II))	–	The coated nanotubes demonstrated better removal ability over uncoated where the removal ratio of lead increased from 20 % to around 99 %	Liu and Zhao (2013)
KMnO ₄ (98 % concentration) and 0.4 M HNO ₃ (68 % concentration)	Zinc (Zn(II))	Langmuir and Freundlich	The removal percentage of Zn ²⁺ was more than 99 %	Mubarak et al. (2013)
Silver nanoparticles	Copper (Cu(II)) and cadmium (Cd(II))	Langmuir	The adsorption process was spontaneous and exothermic	Venkata Ramana et al. (2013)
Sodium hypochlorite (NaClO)	Zinc (Zn(II))	Langmuir	CNTs could be efficiently regenerated by a 0.1 mol/L HNO ₃ solution, and the sorption capacity was maintained after 10 cycles of the sorption/desorption process	Lu et al. (2006)
Manganese oxide (MnO ₂)	Lead (Pb(II))	–	The mechanism of adsorption mainly controlled by a liquid film diffusion and the results showed that most of the lead could be removed from a solution at a pH between 7.0 and 9.0 and within a few minutes	Salam (2013)
Sodium hypochlorite (NaClO)	Nickel (Ni(II))	–	The oxidation process significantly improved the hydrophilicity of CNTs and as a result more Ni(II) was adsorbed	Lu and Liu (2006)
Manganese oxide (MnO ₂)	Lead (Pb(II))	Langmuir	After the loading of MnO ₂ , smaller pore width (2.6 nm) and larger surface area (275 m ² /g) were observed	Wang et al. (2007c)
Amino modified (ethylenediamine, diethylenetriamine, and triethylenetetramine)	Lead (Pb(II)) and cadmium (Cd(II))	Langmuir	The surface basicity of treated MWCNT was increased offering numerous adsorption sites and thus enhancing the adsorption capacity. The adsorption affinity of the heavy metals to MWCNTs followed the sequence Pb ²⁺ > Cd ²⁺ .	Vuković et al. (2011)
8-Hydroxyquinoline (C ₉ H ₇ NO)	Copper (Cu(II)), lead (Pb(II)), cadmium (Cd(II)), and zinc (Zn(II))	–	The competition between the target heavy metals was in the order of Cu(II) > Pb(II) ≈ Zn(II) > Cd(II) for % adsorption	Kosa et al. (2012)
Oxidation (O-CNT)	Anionic chromate (CrO ₄ ⁻²)	–	Excellent adsorption was attributed to interaction of the CrO ₄ ⁻² with the surface oxygen-containing functional groups on the modified CNTs	Xu et al. (2011)
Ethylenediamine	Cadmium (Cd ²⁺)	Langmuir	The mechanism of which may include both of physisorption and chemisorption mechanisms	Vuković et al. (2010a)
Nitric acid (HNO ₃)	Lead (Pb(II))	–	The main adsorption mechanism was chemisorption and/or chemical complexation	Xu et al. (2008)
Nitric acid (HNO ₃)	Lead (Pb(II))	–	The maximum adsorption capacity of 6-h-acidified MWCNTs for Pb(II) is 91 mg/g, which is more than 10 times greater than that of untreated MWCNTs for Pb(II) (7.2 mg/g)	Wang et al. (2007a)
Poly(vinylpyridine) and ferrocenic oxide	Divalent metal ion (M ²⁺) (such as Zn ²⁺ , Cu ²⁺ , and Pb ²⁺)	–	Formation of insoluble bundles in which the divalent metals remain trapped through pyridyl–M ²⁺ –pyridyl interactions. Adsorbate-loaded CNTs can be	Maggini et al. (2013)

Table 5 (continued)

Modification	Target pollutants	Adsorption isotherm	Remarks	References
Ammonium iron(II) sulfate and ammonium iron(III) sulfate	Copper (Cu (II))	Langmuir	separated using magnetic filtration and recycled by acid treatment The main adsorption mechanism of Cu(II) was by physical force, while the chemisorption played a small role due to a few oxygen-containing functional groups on MWCNT	Tang et al. (2012)
Nanoscale zerovalent iron (nZVI)	Chromium (Cr(VI))	–	The adsorption process, stimulated by electrostatic, hydrophobic, and hydrogen-bond interactions, depends strongly on pH value	Lv et al. (2011)
Diamine-modified mesoporous silica	Copper (Cu(II)), lead (Pb(II)), zinc Zn(II), and nickel (Ni(II))	Langmuir	The order of removal percentage for metal ions is Pb(II) > Cu(II) > Zn(II) > Ni(II)	Yang et al. (2013b)
Chitosan (polysaccharide biopolymer)	Copper, zinc, cadmium, and nickel ions	–	The order of metal ion removal from aqueous solution was Cu(II) > Cd(II) ≈ Zn(II) > Ni(II) due to the competition for the binding sites at the surface of MWCNTs/CS nanocomposite	Salam et al. (2011)
Mercapto-propyl triethoxysilane, thiol-functionalized (MPTS-CNTs/Fe ₃ O ₄)	Mercury (Hg ²⁺) and lead (Pb ²⁺)	Langmuir	The maximum adsorption capacity for Hg ²⁺ is 65.52 and for Pb ²⁺ is 65.40 mg/g	Zhang et al. (2012)

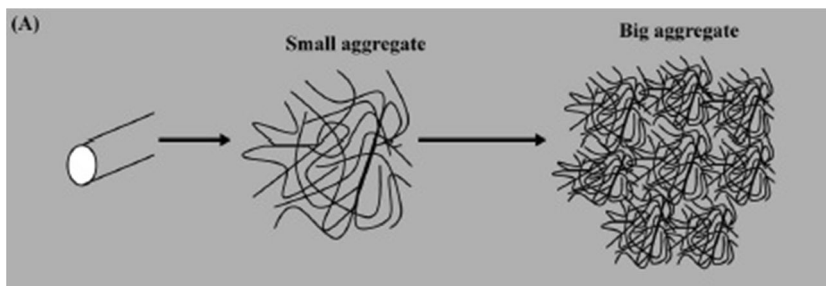
Another essential point is the separation of CNTs from the treated medium that may cause considerable inconvenience in their practical application. In order to cope with this problem, magnetic CNTs have been prepared by association of CNTs with magnetic nanoparticles and they can be well dispersed in the water as well as can be simply manipulated by external weak magnetic field that permits their easy separation from water (Peng et al. 2005; Qu et al. 2008). Thus, it was demonstrated that combining the magnetic properties of the iron oxides with the adsorption properties of CNTs is an effective and rapid method for the separation of the magnetic adsorbents from aqueous solutions (Gong et al. 2009; Gupta et al. 2011; Lu et al. 2011). Despite of that, the magnetic phase can be leached out in acidic media because they are placed within the pores which do not protect them from contact with solution. Bystrzejewski and Pyrzyńska (2011) pointed out that carbon-encapsulated magnetic nanoparticles (CEMNPs) are free of this disadvantage, because they comprise of uniform spherical nano-crystallites firmly covered by tight carbon coatings. The role of the coatings is to protect the encapsulated nanoparticles from agglomeration and corrosion and to provide a scaffold for introducing surface acidic groups that are

important to bind the metal ions (Bystrzejewski et al. 2009; Pyrzyńska and Bystrzejewski 2010).

Membrane processes

Membrane process has been proven to be an effective way for water remediation because of its high separation efficiency, easy operation where no chemical addition or thermal input is required, and it does not lead to secondary pollution as well as no regeneration of spent media is required (Balamurugan et al. 2011; Buonomenna 2013; Pendergast and Hoek 2011). The performance of the membrane system is basically influenced by the membrane material, which affords an inherent tradeoff between membrane selectivity and permeability. The common membrane materials applied for water treatment are polymers, for instance cellulose acetate (CA), polyacrylonitrile (PAN), and polyamide (PA) (Yang et al. 2009a). Based on the pore size and filtration application, the membrane process can be classified as microfiltration (MF) for suspended solids, protozoa, and bacteria removal, ultrafiltration (UF) for virus and colloid removal, nanofiltration (NF) for hardness, heavy metals, and dissolved organic matter removal, and for

Fig. 4 Schematic presentation of functional groups of H₂SO₄/HNO₃-oxidized CNT surface (Vuković et al. 2010b)



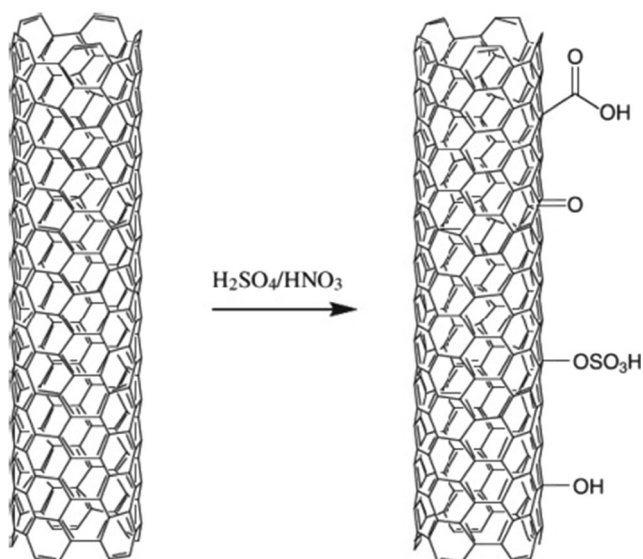


Fig. 5 Illustrative photo of magnetic nanoparticles of iron oxide nature interacting with a simple hand magnet (Kilianová et al. 2013)

desalination, water reuse, and ultrapure water production (reverse osmosis (RO) and forward osmosis (FO)) (Balamurugan et al. 2011; Bernardo et al. 2009; Ulbricht 2006).

Over the past decade, nanotechnology has led to new water treatment membranes by incorporation of nanomaterials into membranes either by blending or surface grafting for producing membranes with desirable structure and new functionality such as high permeability, catalytic reactivity, contaminant degradation, and self-cleaning (Pendergast and Hoek 2011), moreover, controlling membrane fouling due to nanoparticles functional groups and their hydrophilic properties (Vatanpour et al. 2012).

Nanofibrous membranes

Polymer or composite nanofibrous membranes can be generated using electrospinning method which is versatile and efficient technique to compose ultra-fine fibers using various materials (e.g., polymers, ceramics, or even metals) with diameters in the range of 20–2000 nm (Cloete 2010; Li and Xia 2004; Li et al. 2013; Yang et al. 2009a). Electrospun nanofibrous membranes have large specific surface area (Balamurugan et al. 2011), fine tunable pore size (Ramakrishna et al. 2006), as well as high water flux that attracted both industry and academic researchers to study their application for MF and UF (Gopal et al. 2006, 2007). The researches revealed that nanofiber membranes can sufficiently remove micron size particles from aqueous solutions at high rejection rate and without a significant fouling; therefore, the membrane could be successfully recovered upon cleaning (Ramakrishna et al. 2006).

The electrospun nanofibers can be simply manipulated for particular application and used as affinity membrane to

remove heavy metals and organic pollutants during filtration by the introduction of certain functional groups (Li and Xia 2004; Li et al. 2013; Qu et al. 2013a). The nanofibers are functionalized by covalently attaching ligands onto the surface, for example, using cibacron blue to functionalize cellulose nanofiber membranes for albumin purification (Ma et al. 2005), functionalization of polymer nanofibers membranes with a ceramic nanomaterials such as hydrated alumina/alumina hydroxide and iron oxide for removal of heavy metal ions by adsorption/chemisorption and electrostatic attraction mechanisms (Ramakrishna et al. 2006), and introduction of cyclodextrin into a poly(methyl methacrylate) nanofiber membrane to enhance their affinity for organic waste removal (KAUR et al. 2006).

Nanocomposite membranes

Although the membrane separation technology plays a remarkable role in water and wastewater treatment, membrane fouling is still the main shortcoming that reduces the lifetime of the membrane and limits its application due to the increasing of energy consumption, operating costs, and difficulty of process operation (Balta et al. 2012). The membrane fouling can be classified into organic fouling and biological fouling and both are responsible for the flux decline in the membrane processes (Meng et al. 2009). The main reason of membrane organic fouling is the abundance of natural organic matters (NOM) in water that are adsorbed and deposited on the surface of the membrane leads to the blockage of the pores forming a cake layer on the surface (Lee et al. 2004; Meng et al. 2009). Next, the leading cause of the biological fouling is the adhesion of bacteria to the membrane surface producing a sticky biofilm composed of polysaccharide, organic chemicals, and a complex community of microbial cells resulting in biofouling which is considered a serious problem due to the ability of bacteria to reproduce at the surface of the membrane, forming biofilms and producing an additional fouling which is difficult to be removed (Bjørkøy and Fiksdal 2009; Ciston et al. 2009; Herzberg and Elimelech 2007; Sawada et al. 2012; Wang et al. 2005). With regards to the causes of both organic and biological membrane fouling and their severe consequences, it is important to improve the antifouling and antibacterial properties of the membranes.

The fouling of the membranes is affected by their morphology, charge, as well as the hydrophobicity of the membranes (Gray et al. 2008; Sun et al. 2009; Weis et al. 2005). Many studies have proven that the membrane shows stronger resistance to substance adsorption when increasing its surface hydrophilicity; therefore, modifying the membrane hydrophobicity can be an effective technique to improve its organic antifouling (Arahman et al. 2009; Rahimpour and Madaeni 2007; Wang et al. 2006).

Many efforts have been devoted to study a number of modification methods in order to improve the hydrophilicity and reduce membrane fouling, involving coating (Razmjou et al. 2011b), grafting (Rahimpour 2011), and blending with hydrophilic metal oxide nanoparticles which is proven to be an effective method to obtain nanocomposite membranes without complicated operation process (Yu et al. 2013). The blending of metal oxide nanoparticles includes alumina (Maximous et al. 2010b; Yan et al. 2006), zirconium dioxide (Bottino et al. 2002; Maximous et al. 2010a; Pang et al. 2014), silica (Bottino et al. 2001; Jin et al. 2012; Shen et al. 2011; Yu et al. 2013), zeolites (Pendergast et al. 2010), and titanium dioxide (Rahimpour et al. 2008; Razmjou et al. 2011a, 2012). It was highlighted that the addition of metal oxides nanoparticles does not affect the membrane structure, while it obviously enhances the performance of the membrane (Shen et al. 2011) as well as its thermal stability (Ebert et al. 2004; Pendergast et al. 2010). Additionally, functionalized MWCNTs were successfully blended with polymer membranes. The membrane, permeability, hydrophilicity, and fouling resistance were significantly improved by the functional groups on MWCNTs which are embedded in membrane nanocomposite (Choi et al. 2006b; Daraei et al. 2013).

Another prerequisite argument is preventing the development of biofilms on membrane surface; thus, many antimicrobial nanoparticles have been studied to endow the membrane with a self-antimicrobial property. For example, silver nanoparticles (nano-Ag) have been exploited to inactivate viruses (De Gusseme et al. 2011), mitigate the bacterial growth, and inhibit biofilm formation (Mauter et al. 2011; Zodrow et al. 2009) not only by being coated or grafted on the surface of the membranes but also by being blended in the membrane fabrication process (Zodrow et al. 2009). Ag-nanocomposite membranes showed significant antibacterial properties toward *Escherichia coli* (Zodrow et al. 2009) (Obalová et al. 2013), with antibacterial efficiency about 99.999 % (Sawada et al. 2012). Another nanomaterial integrated into membranes as antimicrobial agent is SWCNTs. The antibacterial activity of SWCNTs-nanocomposites was investigated, and the results exposed that high bacterial inactivation (>90 %) was attained by the SWCNTs-nanocomposites reducing the growth of biofilms on the surface of the membranes (Ahmed et al. 2011).

It is important to point out that photocatalytic nanoparticles, namely TiO_2 which has drawn a significant attention due to its stability and promising applications as photocatalysis (Cao et al. 2006), have been used to develop photocatalytic nanocomposite membranes (reactive membranes) with higher hydrophilicity (Li et al. 2014b), improved fouling resistance, and thermal stability (Wu et al. 2008) coupled with their ability to combine their function of physical separation and the reactivity of a catalyst toward pollutants degradation (Bae and Tak 2005; Choi et al. 2006a; Kim et al. 2003). In addition to that, metallic/bi-metallic nanoparticles precisely nano

zerovalent iron (nZVI) which serves as electron donor and catalyst (Qu et al. 2013a; Wang et al. 2013b) have also been integrated into membranes for reductive dechlorination of contaminants mainly chlorinated organic compounds (COCs) (Wu and Ritchie 2008; Wu et al. 2005). Finally, although nanoparticles are very effective for environmental remediation and enhancement of the performance of membrane process, they tend to leach out and aggregate especially if they were grafted on the membrane without surface protection and that might complicate the operation and decrease the contaminant degradation. Consequently, many studies have investigated the possibilities to employ mediation (Li et al. 2014b) or solid supports (Wang et al. 2008b) for immobilization of the nanoparticles in order to overcome the aforementioned shortcomings.

Osmotic membranes

Both RO and FO exploit semi-permeable membrane for water purification and desalination processes, and their performances are defined by their salt rejection and energy consumption not to mention their antifouling property. RO membranes are easy to be designed and operated as well as they can produce high quality clean water (Greenlee et al. 2009; Tarboush et al. 2008) by employing a high hydraulic pressure to force the water through the semi-permeable membrane (Liu et al. 2011). RO membranes with an active layer on the top are called thin film composite (TFC) (Fathizadeh et al. 2011). The standard material for this active layer is polyamide (Tiraferri et al. 2011), and it employs the diffusion mechanism to separate the water from the pollutants (Paul 2004).

The primary disadvantages of RO membranes are high energy consumption (Liu et al. 2011) and irreversible membrane fouling (Chung et al. 2012); in addition to that, the polyamide tends to degrade in the presence of the chemical oxidants that are used for mitigation of the microbial growth (Tiraferri et al. 2011). Consequently, many attempts have been proposed utilizing nanoparticles to functionalize the active layer to improve TFC membrane application. Modification methods include incorporation of nanomaterial into the active layer of TFC (Lee et al. 2011) to evolve new polyamide-nanoparticle (NP) membranes which are called thin film nanocomposite (TFN) membranes with increased fouling resistance, higher permeability, and improved salt rejection (Fathizadeh et al. 2011). Figure 6 shows the difference between TFC and TFN. The most prominent nanoparticles being researched for integration into the active layer are nanozeolites that proved to maintain the solute rejection and resulted in thicker, more permeable, and hydrophilic negatively charged active layer (Jeong et al. 2007; Lind et al. 2009). Also, TiO_2 increased the water flux and led to organic degradation and microbial inactivation upon ultraviolet (UV) irradiation due to its photocatalytic attributes (Chin et al. 2006).

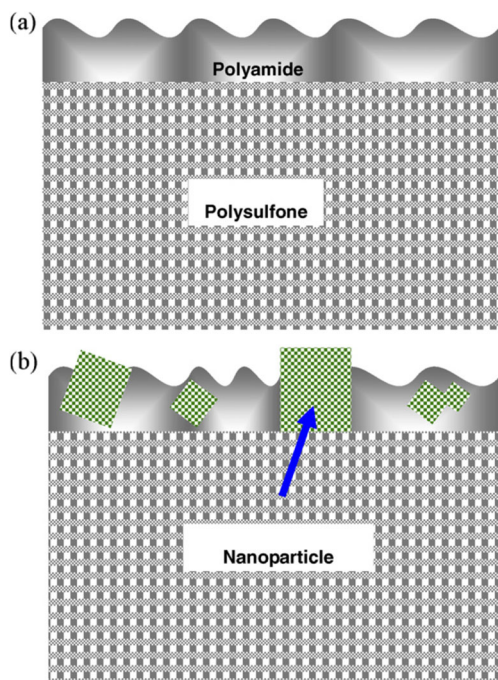


Fig. 6 Conceptual illustration of **a** TFC and **b** TFN membrane structures (Jeong et al. 2007)

Finally, silver nanoparticle-TFN membranes exhibited an obvious antibiofouling influence on *Pseudomonas* (Lee et al. 2007), while unaligned SWCNTs were covalently bound to the TFC membrane surface and inactivated 60 % of *E. coli* bacteria attached to the membrane within 1 h of contact time resulting in moderate biological antifouling membrane (Tiraferri et al. 2011).

Comparing to conventional RO membrane, FO membrane is considered less prone to fouling (Ge et al. 2010; Holloway et al. 2007; Niksefat et al. 2014) and does not consume energy (Cornelissen et al. 2008) for it is exploiting the osmotic pressure gradient as the driving force for the separation process and draws water from a low osmotic pressure solution, referred to as “feed” to a high osmotic pressure one, often referred to as “draw solute” (Buonomenna 2013; Liu et al. 2011). However, the product of FO membranes (the diluted draw solution) usually requires a second separation step (Chung et al. 2012) to generate pure water either by applying RO or thermal treatment and both have high-cost and energy-intensive operations. To address this challenge, it is recommended to have a high osmolality draw solution that can be separated easily from water (Ge et al. 2010) as well as applying a low-cost separation technology. Recently, nanoparticles have been discovered as a new draw solution and used to develop a novel draw solution recovery system. For instance, hydrophilic coated magnetic nanoparticles have been explored as new, easily separable, and reusable draw solution with high osmotic pressure that improved FO membrane performance (Ge et al. 2010). Moreover, magnetic nanoparticles have been applied to recover draw solutes

without any intensive energy input where their negatively charged surface facilitated the recovery process through coagulation (Liu et al. 2011).

In the light of FO process disadvantages, it is important to mention that the main obstacle of FO application is the accumulation of the rejected feed solutes in the support layer resulting in what is known as internal concentration polarization (ICP) (Loeb et al. 1997; Tang et al. 2010). This phenomenon causes an intense loss in the osmotic driving force (McCutcheon and Elimelech 2008), and since it occurs in the support layer, it cannot be removed by increasing the flow rate turbulence (Zhao et al. 2012a). With the intention to minimize the ICP problem, it was suggested that the fabrication of appropriate FO membranes with small structure parameter for the support layer had improved the membrane behavior (Liu et al. 2011). In recent times, developments of nanotechnology have led to fabrication of novel groups of FO membranes inspired by the thin film nanocomposite reverse osmosis (TFN-RO) membranes. The nanostructured FO membranes, synthesized with metal oxide nanoparticles or carbon nanotubes, demonstrated considerably enhanced membrane properties like selectivity, permeability, and stability in different separation processes (Amini et al. 2013). After all, nanotechnology has contributed in eco-sustainable membrane processes for wastewater treatment, producing pure drinking water without any wastes.

Disinfection and pathogen control

Disinfection process is applied to inactivate various types of microbial pathogens including viruses, bacteria, protozoa, and other microorganisms that often found in water from sewage discharges or runoff from animal feedlots into the water bodies. Although the current conventional disinfectants such as chlorine, chloramines, ozone, chlorine dioxide, and chlorine gas (Savage and Diallo 2005) can effectively control the microbial growth, they have short-lived reactivity and can be problematic due to formation of toxic disinfection by-products (DBPs) (Li et al. 2008b). These DBPs are formed by the reaction between the aforesaid conventional oxidizing disinfectants with various constituents (e.g., NOMs) in water (Hossain et al. 2014). More than 600 DBPs have been acknowledged all over the world (Richardson et al. 2007) and most of which are considered carcinogenic. This dilemma is aggravated when high dosages of the oxidizing disinfectant are required to kill highly resistant pathogens such as *Cryptosporidium* and *Giardia* (Li et al. 2008b). These limitations provoke an urgent need to balance the risks of microbial pathogens and formation of toxic DBPs. Therefore, it is important to provide an innovative alternative technique that can effectively prevent DBP formation and improve the reliability of disinfection by using harmless, non-corrosive, water-soluble disinfectants (Rutala et al. 2008).

The rapid development of nanotechnology has encouraged a significant concern in studying the antimicrobial characteristics of several nanomaterials (NMs) and applying them for water disinfection processes. These NMs have shown a promising approach to be utilized as alternatives for conventional disinfectants (Li et al. 2008b) as well as to be associated with other existing technologies to enhance the disinfection efficacy such as photo-excitation due to the ability of the NMs to be excited under solar light illumination (Hossain et al. 2014). Accordingly, many NPs have suggested to control the microbial growth and inactivate different types of microorganisms in water, such as metal and metal oxide nanoparticles (Dizaj et al. 2014; Vargas-Reus et al. 2012) (e.g., TiO₂ (Dimitroula et al. 2012; Mayer et al. 2014), magnesium oxide (MgO) (Jin and He 2011), zinc oxide (ZnO) (Gordon et al. 2011), nanosilver (nAg) (Kaegi et al. 2011), nZVI (Crane and Scott 2012; Lee et al. 2008a, b)), carbon nanotubes (Ahmed et al. 2013; Vecitis et al. 2011), chitosan (Badawy et al. 2005; Chirkov 2002; Kong et al. 2010; Qi et al. 2004), and fullerene NPs (nC₆₀) (Aquino et al. 2010; Dizaj et al. 2015; Lyon et al. 2008).

The abovementioned nanoparticles have shown good antimicrobial properties without strong oxidation, employing diverse mechanisms to disinfect water. Several antimicrobial mechanisms have been proposed for various nanoscale metal oxides, for instance, it was confirmed that the surface of zerovalent iron nanoparticles (ZVI) corrode and create more metal oxides that could inactivate waterborne viruses by carrying out two critical mechanisms: irreversible adsorption and inactivation of viruses by direct contact (You et al. 2005). Another example on nanoscale metal oxides is ZnO that demonstrated as a strong antibacterial effect on different types of bacteria (Adams et al. 2006; Aruoja et al. 2009; Sawai and Yoshikawa 2004). The main antibacterial mechanism of ZnO is the photocatalytic generation of hydrogen peroxide (H₂O₂) from ZnO surface (Sawai and Yoshikawa 2004; Yamamoto 2001) followed by cell envelop penetration and accumulation of ZnO nanoparticles in membranes and cytoplasm of bacteria leading to bactericidal cell damage and inactivation or inhabitation of bacterial growth (Brayner et al. 2006; Huang et al. 2008; Jones et al. 2008). Additionally, it was verified that due to the photoreactivity and visible light response of TiO₂, it can inactivate microorganisms under UV/solar irradiation by generating hydroxyl radical (OH[•]), superoxide radical (O₂^{•-}), and hydrogen peroxide H₂O₂ as reactive oxygen species (ROS) (Cho et al. 2005; Li et al. 2008b). Besides, it was concluded that the photocatalytic inactivation of bacteria (Page et al. 2007; Pratap Reddy et al. 2007) and viruses (Kim et al. 2006) was improved by doping TiO₂ with silver; thus, (Ag/TiO₂) shows a great potential as a photocatalytic material. By the same token, the antimicrobial mechanism of the widely used silver nanoparticles stems from the release of silver ions (Ag⁺) which accounts for the biological response even at low concentration (Xiu et al. 2011, 2012). Silver ions inactivate

the respiratory enzymes of bacteria by binding to thiol group in proteins (Liau et al. 1997) and result in production of ROS. In addition to that, Ag⁺ interacts with DNA preventing its replication and forming structural changes in the cell envelope (Matsumura et al. 2003; Qu et al. 2013a).

On the other hand, the cytotoxicity of carbon-based nanomaterials (CBNs) (e.g., CNTs, fullerene, etc.) to bacteria in aqueous solution is a complex function of solution chemistry, transport behavior, and physiochemical properties of the nanomaterials (Kang et al. 2009). The antibacterial activity of CNTs starts with an initial contact between the bacteria and CNTs followed either by physical perturbation of cell membrane or by disruption of particular microbial process through oxidizing of vital cellular structure/component (Vecitis et al. 2010) and both cases lead to bacterial cell death. One of the main factors governing the antibacterial activity of CNTs is their size (diameter) (Liu et al. 2009). Therefore, the small-diameter, short-length SWCNTs with surface groups of –OH and –COOH demonstrate the strongest antibacterial activity (Arias and Yang 2009; Kang et al. 2007; Yang et al. 2010a). Figure 7 shows the antibacterial effects of SWCNTs on *E. coli* bacteria. Another illustration for CNM antibacterial mechanism is fullerene NP (nC₆₀) mechanism to kill bacteria which is mostly assigned to its ability to produce ROS resulting in various types of cell damage including DNA damage, lipid peroxidation, protein oxidation, as well as interruption of cellular respiration (Fang et al. 2007; Lyon and Alvarez 2008). Fullerene mechanism requires a direct contact between the nanoparticles and bacteria cells which makes it different from previously reported mechanisms of nanomaterial that involve ROS generation (metal oxides) or release of toxic elements (silver nanoparticles). Finally, chitosan, derived from shells of shrimp and other sea crustaceans (Shahidi and Synowiecki 1991), at its nanoscale has long been noted for its antimicrobial activity. The main proposed antimicrobial mechanism for chitosan is that the positively charged chitosan particles interact with negatively charged bacteria increasing the

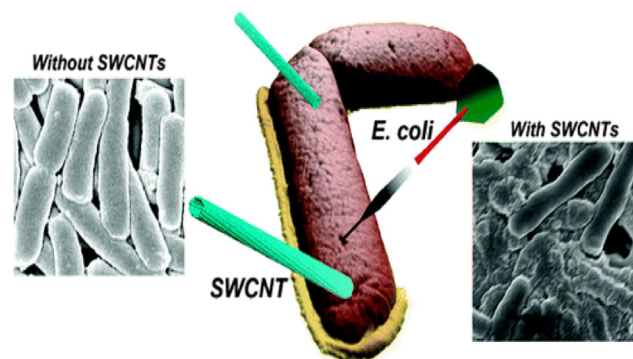


Fig. 7 SEM images of *E. coli* after incubation with saline solution for 2 h without SWCNTs and after incubation with SWCNTs dispersed in the Tween-20 saline solution (0.1 wt% Tween-20 and 0.9 wt% NaCl) for 2 h (Liu et al. 2009)

permeability of cell membranes and eventually leak the cell substances (Holappa et al. 2006; Qi et al. 2004). In short, nanomaterial had proven to be good disinfecting agents for water treatment systems by employing diverse antibacterial mechanisms (Fig. 8) as well as they successfully overcome the limitations that hindered the viability of conventional disinfection (Mahendra et al. 2014).

Photocatalysis

The main problems that are affecting the water treatment competence are removing of non-biodegradable organic pollutants which are resistant to conventional treatment methods, as well as killing waterborne pathogens without the formation of harmful DBPs from disinfection process. Addressing these problems calls for an imperative need to develop an innovative, low-cost, and eco-friendly technology that can destroy these pollutants with less energy consumption and less chemical utilization. Therefore, research activities have focused on advanced oxidation processes (AOPs) as alternative robust methods that are capable of oxidizing and mineralizing wide range of organic chemicals (Comminellis et al. 2008) due to their highly potent and strongly oxidizing radicals (Gaya and Abdullah 2008b).

Photocatalysis, a well-known AOP, has been established as an efficient method to enhance the biodegradability of persistent organic contaminants and to remove the current and emerging microbial pathogens. Photocatalytic oxidation comprises a class of reactions which use a catalyst activated by solar, chemical, or other forms of energy (Augugliaro et al. 2006; Bahnemann 2004; Kudo et al. 2003) and relies on generation of strong reactive radical species such as H_2O_2 , $\text{O}_2^{\cdot-}$, O_3 (Pera-Titus et al. 2004), and mostly hydroxyl radical (OH^\cdot) (Huang et al. 2000), which is a strong oxidizing agent that non-selectively destroys all organic molecules in water (Wang and Xu 2012).

The main source for the generation of (OH^\cdot) is the conventional oxidants H_2O_2 and O_3 (Karci 2014). Different methods have been reported to photolyze these oxidants, facilitating compliance with the specific treatment requirements and improve the versatility of AOPs (Malato et al. 2009). Methods are based on UV (Goi and Trapido 2002) and combination of UV light and oxidants (H_2O_2 , $\text{O}_2^{\cdot-}$, O_3 , etc.) (Karci 2014; Malato et al. 2009). In addition to those methods that involve catalysts, homogeneous photocatalysis method which is based on the addition of H_2O_2 to dissolved iron salts can be classified into two types of reaction: Fenton reaction that does not involve any light irradiation and photo-Fenton reaction that reacts up to a light wavelength of 600 nm (Chong et al. 2010). Moreover, heterogeneous photocatalysis methods use wide-band gap semiconductors in contact with water (e.g., TiO_2 (Fujishima et al. 2008; Gaya and Abdullah 2008b; Wang and Jing 2014), tungsten trioxide (WO_3) (Liu et al. 2013a; Zhao et al. 2012b), ZnO (Kaur and Singhal 2014; Yassitepe et al. 2008), tin dioxide (SnO_2) (Al-Hamdi et al. 2015; Jana et al. 2014), cadmium sulfide (CdS) (Chronopoulos et al. 2014; Upadhyay et al. 2012), etc.), and they are photoexcited by light in the presence of oxygen (Malato et al. 2013). Table 6 shows different methods that are used to produce hydroxyl radicals.

Both homogeneous (photo-Fenton) and heterogeneous photocatalysis methods are considered of great interests because they can either use UV light (Pera-Titus et al. 2004) or solar light (Malato et al. 2013; Maldonado et al. 2007) for irradiation. Although photo-Fenton photocatalysis has higher reactivity than heterogeneous photocatalysis, its operation is complex and expensive due to pH rectification that is required to control the formation of photoactive iron complexes (De Laat et al. 2004). Accordingly, heterogeneous photocatalysis proved to be a promising water treatment technology for elimination of persistent organic pollutants as well as for water sterilization.

Fig. 8 Various mechanisms of antimicrobial activities exerted by nanomaterials (Li et al. 2008b)

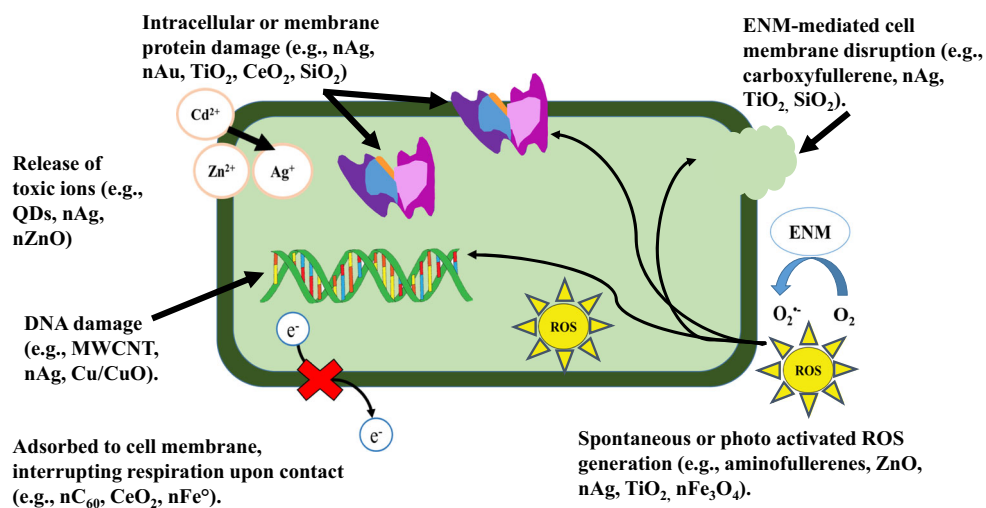


Table 6 AOPs using radiation for the generation of hydroxyl radicals (Malato et al. 2013)

AOP	Key reaction	Wavelength
UV/H ₂ O ₂	H ₂ O ₂ (aq) + hν → 2HO•	λ < 300 nm
UV/O ₃	O ₃ (aq) + hν → O ₂ (aq) + O(¹ D)O(¹ D) + H ₂ O → 2HO•	λ < 310 nm
UV/H ₂ O ₂ /O ₃	O ₃ (aq) + H ₂ O ₂ + hν → O ₂ (aq) + HO• + HO• ₂	λ < 310 nm
	TiO ₂ (s) + hν → TiO ₂ (e ⁻ + h ⁺)	
UV/TiO ₂	TiO ₂ (h ⁺) + HO ⁻ _{ad} → TiO ₂ (s) + HO• _{ad}	
Fenton	Fe ²⁺ (aq) + H ₂ O ₂ (aq) → Fe ³⁺ (aq) + HO• + HO ⁻	λ < 390 nm
Photo-Fenton	Fe ³⁺ (aq) + H ₂ O + hν → Fe ²⁺ (aq) + H ⁺ + HO•	λ < 580 nm

Among the abovementioned semiconductors, TiO₂ has drawn a special attention in the water treatment research including photodegradation of numerous organic pollutants, photoreduction of inorganic contaminants, and inactivation of microorganisms (Chong 2010; Kurniawan and Sillanpää 2011), due to its environmentally benign merits such as low toxicity, high photoconductivity, chemical stability, as well as its low cost and commercial availability (Choi et al. 2014; Fujishima et al. 2000; Xiao et al. 2015). The photocatalysis mechanism of (TiO₂) that relies on the formation of active oxygen species such as hydroxyl radicals, superoxide, hydrogen peroxide, singlet oxygen, etc. may participate in organic pollutant photodegradation or disinfection process (Fujishima et al. 2008). The mechanism consists of several steps (Berger et al. 2006; Chong 2010; Fujishima et al. 2000; Fujishima et al. 2008; Gaya and Abdullah 2008b; Krishna et al. 2006; Mayer et al. 2014) starting with photoexcitation in order to induce series of reductive and oxidative reaction on the surface of (TiO₂) photocatalyst through irradiation by an adequate wavelength (usually with photon energy (hν) greater than or equal to the band gap energy). Since the band gap of (TiO₂) is about 3.0 eV, wavelengths shorter than ~400 nm can excite the lone electron from the valance band to the empty conduction band in femtoseconds resulting in the generation of electron-hole pair. Super oxide radical anions (⁻O₂) and hydroxyl radicals (OH•) are then generated through reaction between photogenerated electrons and molecular oxygen and between photogenerated holes and water, respectively. Hydroxyl radicals are considered the major species responsible for decomposition of organic pollutants (Zhang et al. 2009) into water and carbon dioxide. Figure 9 represents the mechanism steps of TiO₂ photocatalysis.

However, several disadvantages of nanocrystalline TiO₂ powders in water system have been identified, such as agglomeration, difficult recovery, and short activity which could restrain its application in wastewater treatment (Baolong et al. 2003; Xi and Geissen 2001). For the purpose of overcoming the mentioned drawbacks and developing highly active catalyst to be exploited for large scale applications, the morphological, crystallographic, and electronic properties of TiO₂ material should be controlled through alternative synthesis procedures (Choi et al. 2010). The most common investigated methods to

prepare TiO₂ are sol-gel method (Caratto et al. 2012), which is used to fabricate highly pure with a relatively low temperature nanosized titanium dioxide and hydrothermal method (Jing et al. 2011), that works in synthesizing high crystalline titanium dioxide with controlled size and shape. Thereupon, three main approaches that are aimed to modify titanium dioxide (Xiao et al. 2015) have been highlighted in Table 7. Development of TiO₂ composites codoped with two or more of nonmetals such as S, N, F, and C (Banerjee et al. 2014; Fagan et al. 2016; Likodimos et al. 2013) is considered one of the promising strategies that have been suggested to reduce the band gap and improve the visible light (VIS) responsive photocatalytic activity. For instance, N-F-codoped TiO₂ under VIS has successfully been used for photocatalytic degradation of bisphenol A (BPA) due to its high surface area-to-volume ratio, enrichment of surface oxygen vacancies by F- and N-doping, improved surface acidity by F-doping, as well as enhancement of VIS absorption by N-doping (He et al. 2016). Moreover, carbon-doped TiO₂ composites under VIS have been used for the degradation of some occurring algal toxins in water (e.g., cyanotoxins, microcystin-LR (MC-LR), and cylindrospermopsin (CYN)), and the resulting intermediate products from the toxins degradation process were attributed to a peroxide that was formed through the action of O₂^{-•} (Fotiou et al. 2016). In short, photocatalytic process of nonmetal doped TiO₂ has shown large potential as a renewable water

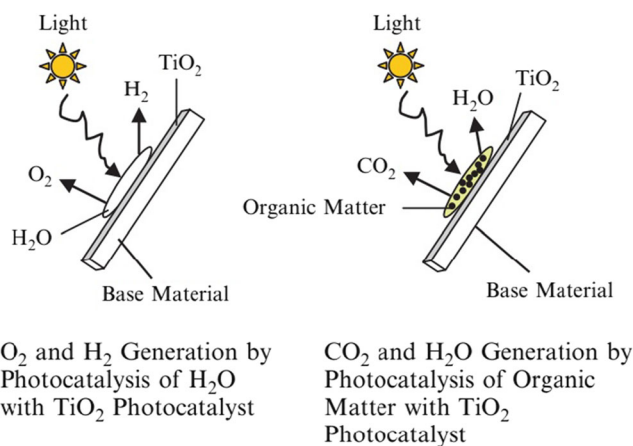


Fig. 9 Light absorption by TiO₂ photocatalyst (Ohama and Van Gemert 2011)

Table 7 Common strategies to modify titanium dioxide (TiO₂)

Approach	Remark	Examples	References
Control the size and morphology of titanium dioxide (TiO ₂)	Increase the exposed photo-reactive sites	TiO ₂ quantum dots (QDs) TiO ₂ nanotubes TiO ₂ nanosheets TiO ₂ nanowires TiO ₂ mesoporous hollow shells	Pan et al. (2014) Roy et al. (2011), Xing et al. (2014) Pan et al. (2013), Yang et al. (2009b) Pu et al. (2014), Wu et al. (2012) Cui et al. (2010), Joo et al. (2013), Moon et al. (2014)
Doping (TiO ₂) with metal or non-metals/compounding (TiO ₂) with charge transfer materials	Improve charge separation or boarding the absorption spectrum	Metal-doped TiO ₂ Non-metal-doped TiO ₂ Deposited TiO ₂ (e.g., TiO ₂ –carbon nanotubes and TiO ₂ –grapheme composites)	Kim et al. (2005), Suri et al. (2012), Wang and Jing (2014) Cong et al. (2007), Dong et al. (2008), Lin et al. (2014), Sathish et al. (2009) Saleh and Gupta (2012), Wang et al. (2008a), Williams et al. (2008), Woan et al. (2009), Yang et al. (2013a)
Mixed-phase samples of anatase and rutile TiO ₂	Enhance the quantum yield and photocatalytic reactivity	Build anatase–rutile (A–R) phase junction of TiO ₂	Jiang et al. (2007), Liu et al. (2014), Scanlon et al. (2013)

treatment process and it is considered a more eco-friendly approach compared to the photocatalytic process of metal-doped TiO₂, for the latter is vulnerable to photocorrosion and potential metal problems (Zhang et al. 2014).

Sensing and monitoring systems

A major challenge for environmental remediation management is monitoring the emission of toxic substance (i.e., organic and inorganic pollutants, pathogens, and hazardous atmospheric pollutants), coupled with accurately assessing the extent and composition of these contaminants. Therefore, various analytical techniques have been employed in environmental pollution detection and monitoring, for instance surface plasmon resonance (SPR) (Homola 2006; Salah et al. 2014; Shankaran et al. 2007), high-performance liquid chromatography (HPLC) (Shintani 2014), gas chromatography–mass spectrometry (GC-MS) (Tranchida et al. 2015), supercritical fluid chromatography (SFC) (Ishibashi et al. 2015), capillary electrophoresis (CE) (Sánchez-Hernández et al. 2014), flow injection analysis (FIA) (Gerez et al. 2014), etc. Nevertheless, these techniques are inappropriate for routine environmental detection because of their high cost and time consumption in addition to their complicated requirements (Su et al. 2012).

The growing advances in nanoscience and nanotechnology are having a remarkable influence on the field of environmental monitoring and sensing, where a large number of nanoparticles have been introduced for detection and remediation of wide range of contaminants (Andrescu et al. 2009; Theron et al. 2008, 2010) in both gaseous and aqueous mediums. Many investigations have been carried out to develop high selectivity and sensitivity nanosensors for monitoring different types of gases in the ambient air (Zhou et al. 2015) in order

to prevent potential explosion or poisoning, particularly for odorless, colorless, and tasteless hazardous gases such as hydrogen (Baik et al. 2009; Lupan et al. 2008) and for poisonous and irritant gases such as nitrogen dioxide (NO₂) (Beheshtian et al. 2012; Young et al. 2005). Similarly, the application of nanomaterial-based sensors is widely studied for water quality monitoring by detection of organism fecal pollution (Savichtcheva and Okabe 2006) such as fecal coliforms, total coliforms, *E. coli*, enterococci bacteriophages, and disease-causing viruses and parasites (Theron et al. 2010) and detection of different types of trace contaminants (such as pesticides, phenolic compounds, inorganic anions, heavy metals) (Govindhan et al. 2014).

As any other chemical sensors, nanoparticle-based sensors usually consist of two components: the receptor, which enhances the detection sensitivity, and the transducer, a chemical or physical sense component (nanomaterial), that works with electrochemical, thermal, optical, and other detection principles (Su et al. 2012). The operating mechanism involves a charge transfer that occurs between pollutant molecules and the receptors, resulting in an electrical and/or optical signal that is related to the molecule type and number (Di Francia et al. 2009). Not to mention that in the case of bio-nanosensors, recognitions agents (e.g., antibodies (Kalele et al. 2006; Volkert and Haes 2014), carbohydrates (Chen et al. 2011b; Haseley 2002), aptamers (Li et al. 2009; So et al. 2005), and antimicrobial peptides (AMPs) (Arcidiacono et al. 2008; Cui et al. 2012b)) are presented as a third components and specifically provide the selectivity by interacting with antigens or other epitopes on the pathogens surface (Vikesland and Wigginton 2010). Moreover, to obtain nanosensors with high sensitivity and fast response time, nanostructures such as nanorods, nanobelts, and nanowires were functionalized (Kanade et al. 2007). For instance, tungsten oxide nanowires (WO₃-NWs) were functionalized with

palladium for hydrogen gas detection (Chávez et al. 2013) and with copper oxide for high-performance hydrogen sulfide sensor (Park et al. 2014).

As a matter of fact, nanomaterial-based sensors have shown great potential in the chemical and biological detection researches due to their physical, chemical, optical, catalytic, magnetic, and electronic properties as well as their high selectivity and sensitivity (Qu et al. 2013a; Wang et al. 2010a). Some examples of widely used nanomaterials in sensors technology include quantum dots (QDs) which can be benefited from their fluorescence properties to detect heavy metals, toxic gases, cyanotoxins, and pathogens (Feng et al. 2014) (Hahn et al. 2005; Koneswaran and Narayanaswamy 2009; Li et al. 2008a; Ma et al. 2009; Wu et al. 2010). Metal nanoparticles such as silver and gold nanoparticles rely on the changes in their color for pollutant detection (McFarland and Van Duyne 2003; Saha et al. 2012). Furthermore, CNMs are facilitating the electron transfer between electrodes and electro-active species (Su et al. 2012), and they have been employed for monitoring of different pollutants and toxins. For instance, SWCNT and MWCNT were effectively used to develop electrochemical systems for monitoring of MC-LR in water below its WHO provisional concentration limit (Han et al. 2013; Wang et al. 2009). The specificity of MWCNT biosensor was improved by adding monoclonal antibodies specific to MC-LR in the incubation solutions, and the performance of MWCNT array biosensor was enhanced by electrochemical functionalization of MWCNT in alkaline solution to enrich its surface with oxygen containing functional groups that permit the immobilization of MC-LR onto MWCNT array electrodes (Han et al. 2013).

Conclusion

The exacerbated human activities are convulsing the ecosystem balance by feeding the environment with large amounts of anthropogenic hazardous toxicants that pollute soil, water, and atmosphere and consequently threaten human public health. As an attempt to adopt a compatible treatment technology for cleaning up all the wastes that are left behind the industrial revolution, this account simply compared the application of propitious nanotechnology to conventional technologies in environmental remediation. Moreover, this paper highlighted the hurdles that limit the application of nanomaterials and suppress the advantages of their unrivaled merits; such hurdles include conditions of surrounding environment (e.g., humidity, temperature, acidity, etc.), particle agglomeration, and separation difficulties. It has been shown that nanotechnology exhibits remarkable features for advanced, robust, and multi-functional treatment processes that can enhance pollution monitoring, treatment performance, as well as overcome all the aforementioned barriers. In brief, nanotechnology has the

potential to improve the environmental remediation system by preventing the formation of secondary by-products, decomposing some of toxic pollutants by zero waste operations, and prohibiting further soil contamination by converting the pollutants from labile to non-labile phases. Finally, nanotechnology will pave the way for versatile and vibrant systems which involve the cutting edge techniques in sensing and monitoring of varieties of harmful chemicals and toxins in different environmental media.

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