Impact of nanomaterial in environmental remediation and toxicity

Jatindra N. Bhakta[1,2], Bana B. Jana[1,2], Susmita Lahiri[1], Sushil K. Mandal[1], Monoj K. Pradhan[3]

[1]*International Centre for Ecological Engineering, University of Kalyani, Kalyani 741235, West Bengal, India*
[2]*Centre for Environmental Protection and Human Resource Development (KSI), B-10/289, Kalyani 741235, West Bengal, India*
[3]*Heritage Foundation, Kolkata 700104, West Bengal, India*

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Corresponding Author:
Jatindra N. Bhakta
E–mail: lsnjbhakta@gmail.com

ABSTRACT

The air, water and soil environments are continuously contaminated by various pollutants posing tremendous hazardous impacts in environmental and human health worldwide during last few decades. Recently, nanomaterial is the significant development of nano-scaled size material with highly reactive large surface area in the material science. It offers wide range of applications in protecting environmental and human health from hazardous risks of pollutants. Considering the tremendous risks of environmental pollution and potential impacts of nanomaterials in respect to environmental pollution, the present review has attempted to draw an account on impact of nanomaterials in environmental remediation and toxicity. This review has critically dealt the significant nanoremedial characteristics of nanomaterials - iron, ferritin, copper peroxide, polymeric nanoparticles, nanotubes and nanofibres, semiconductor photocatalytic nanoparticle, nanofiltration membrane, antimicrobial nanomaterials, nanomaterial based sensor, etc. for cleaning up the polluted air, water and soil environments. In addition to remediation, environmental toxicity impacts of nanomaterials have also been briefly ellustrated herein as literatures obtained. Summarily, though nanomaterials may have adverse impacts, due to having potential nanoremediation capacity it could be considered and applied as a new and advanced remediation approach that can enhance, improve or replace the existing conventional technologies to protect the air, water and soil resources in order to achieve the environmental sustainability.

1. Introduction

In today's scientific and technological world, nanomaterial is one of the important discoveries in material science, which opens many novel avenues in its wide array of technological applications. Nanomaterials include nanoparticles which are an increasingly important synthesis of nanotechnologies. Currently, nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A lot of researches are going on concerning its beneficial application that has proved its tremendous potential in different dimensions of practical application. Consequently, nanomaterials technology is emerging as a significant technological approach applying in different domains of science, such as - environmental, human, agricultural sciences, etc.

Synthesis of nanomaterials using various easy and eco-friendly low-cost technologies is also a major breakthrough in the field of nanotechnology and has received considerable attention in last ten years due to their potentially new and varied applications in catalysis (Kamat 2001), plasmonics (Maier et al. 2001), optoelectronics (Mirkin et al. 1996), biological sensor (Han et al. 2001), antimicrobial activities (Sarsar et al. 2014), DNA sequencing (Cao et al. 2001), and surface-enhanced Raman scattering (SERS) (Matejka et al. 1992). Apart from these, nanoparticles have solved various critical problems like climate change and pollution control (Shan et al. 2009), clean water technology (Maccuen 2009), energy generation (Zach et al. 2006), information storage (Sandhu 2008) and biomedical applications (Caruthers et al. 2007). According to Global Environment Outlook (GEO) annual report by UN, nanotech-products will account for more than 14% of the total products or $2.6 trillion by 2014, up from less than 0.1% in 2004 (UNEP 2007). It is obvious that nanomaterials play a significant role in variety of industrial processes and natural phenomena including chemical industries, engineering, chemistry, physics, electronics, environmental and biotechnological engineering, public health, medical biology, etc. Furthermore, its potentiality has pronounced the major impacts in the environment (e.g. air, water and soil pollution; climate change; and green house effect), energy utilization (e.g. fossil fuel combustion, and fly ash formation), and food engineering (e.g. flavour retention). Despite above various beneficial impacts, nanomaterials generated from different sources are unintentionally and/or undesirably discharged to the environment in the form of suspension in fluids which can cause hazardous impacts in environment (Lebedev 2013).

However, as the unique characteristics of nanoparticle provide tremendous beneficial opportunity for society (Deardorff 2012), whereas, the same physical traits that give nanotechnology its economic and scientific value also unfortunately make it a dangerous form the view point of pollution in air, water and soil environments that is particularly difficult to regulate in present environmental scenario (Lebedev 2013).

These properties of merits and demerits of the nanomaterials in respect to environmental pollution, therefore, are the impetus of the present review that has been aimed to draw brief impacts of nanomaterials in remediation and toxicity of air, water and soil environments.

2. Conceptual overview: nanomaterial and nanotechnology

The nanomaterials or nanoparticles are referred to those particles which are of nano-scaled size (1 – 100 nm) with significantly enriched physical, chemical, biological properties and with a very large reactive surface area (Fig. 1). The technology involved in fabrication, characterization, manipulation and application of structures of nanomaterials by controlling shape and size at nano scale is known as nanotechnology. Furthermore, nanotechnology is defined by the United States government as “research and technology development at the atomic, molecular, or macromolecular levels using a length scale of approximately one to one hundred nanometers in any dimension (EPA 2007).

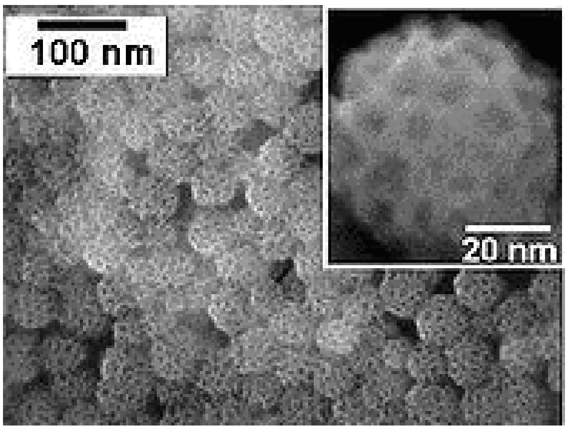

Fig. 1 Transmission electron microscopic image of nanoparticles

The characteristic behaviour of a nanoparticle of a substance becomes increasingly dependent on quantum effects that are essentially invisible on a macroscopic scale, rather than exhibiting the typical macroscopic properties of the substance utilized (http://www.nano.gov/nanotech-101/special). The properties of nanoparticles, such as melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity change as a function of the size of the particle (Lebedev 2013). Consequently, nanoparticles generally possess significantly far greater reactive properties than that of the bulk material (the non-nanoscale version of the same substance) due to an increase in surface area to volume ratio (Lebedev 2013). Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials (Buzea et al. 2007*)*. Nanoclusters are referred to the clusters which have at least one dimension between 1 and 100 nm and a narrow size distribution. Nanopowders are agglomerates of ultrafine particles, nanoparticles, or nanoclusters (Fahlman 2007). Nanometer-sized single crystals, or single-domain ultrafine particles, are often referred to as nanocrystals. Examples of advanced nanomaterials include metallic, metal oxide, polymeric, semiconductor and ceramic nanoparticles, nanowires, nanotubes, quantum dots, nanorods, and composites of these materials.

However, nanotechnology has recently been emerged as a most fascinating research area in modern materials science in order to solve the problems of diversified fields all over the world. The unique properties of nanoparticles as well as continuing advancement in nanotechnology researches represent a tremendous opportunity and impacts in various applied fields.

Recently, the synthesis and characterization of nanoparticles of different materials using technologically simple, low-cost and eco-friendly methods is gaining significant importance for applying diversified fields.

The several methods including mechanical (attrition), pyrolysis, chemical/electrochemical, hydrothermal synthesis, thermal/laser ablation, green synthesis, etc. are used to synthesize nanoparticles (Ahmed et al. 2016). Some methods for synthesizing the nanoparticles are described herein as follows: (1) In mechanical process, attrition method is used, where the nanoparticles are synthesized by grinding macro- or micro-scale particles in a ball mill, a planetary ball mill, or other size-reducing mechanism. The resulting particles are air classified to recover nanoparticles. (2) In the method of pyrolysis, a vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting solid (a version of soot) is air classified to recover oxide particles from by-product gases. (3) The radiation chemistry is a relatively simple method employed to synthesis nanoparticles using a minimum number of chemicals. Radiolysis from gamma rays can create strongly active free radicals in solution. This technique requires water, a soluble metallic salt, a radical scavenger (often a secondary alcohol), and a surfactant (organic capping agent). High gamma doses on the order of 10^4 Gray are required. In this process, reducing radicals will drop metallic ions down to the zero-valence state. A scavenger chemical will preferentially interact with oxidizing radicals to prevent the re-oxidation of the metal. Once in the zero-valence state, metal atoms begin to coalesce into particles. A chemical surfactant surrounds the particle during formation and regulates its growth. In sufficient concentrations, the surfactant molecules stay attached to the particle. This prevents it from dissociating or forming clusters with other particles. Formation of nanoparticles using the radiolysis method allows for tailoring of particle size and shape by adjusting precursor concentrations and gamma dose (Belloni et al. 1998). (4) The sol-gel process for nanoparticles synthesis is a wet-chemical technique using the method of chemical solution deposition. Recently, it is widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (*sol*), which acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers (Brinker and Scherer 1990). (5) In addition, the organic chemicals [derived from bacteria (Nanda and Saravanan 2009), fungi (Bhainsa and D'Souza 2006), and plants (Kulkarni; et al. 2011)] mediated nanoparticles synthesis is recently developed as an environmental friendly and sustainable technique. In this process, the presence of a large of phytochemicals, enzymes, proteins and other reducing agents with electron-shuttling compounds is usually involved in the synthesis of nanoparticles.

The morphological structure of nanoparticles is characterized by using light-based and non-light-based techniques. The spectroscopic, X-ray diffraction (XRD) measurements, transmission electron microscopy (TEM), scanning electron microscopy (SEM), Dynamic Light Scattering (DLS), Atomic Force Microscopy (AFM), Confocal Microscopy etc. are used in the process of light-based characterization. The non-optical nanoparticle characterization technique called Tunable Resistive Pulse Sensing (TRPS) has been developed that enables the simultaneous measurement of size, concentration and surface charge for a wide variety of nanoparticles (Anderson et al. 2013).

3. Historical account

Although, nanomaterials or nanoparticle is generally considered a discovery of modern research, it actually has a long ancient history. Nanoparticles were used by artisans from far back as in the ninth century in Mesopotamia for generating a glittering effect on the surface of pots (Gunter and Andreas 2010; Khan 2012). The distinct gold- or copper-coloured and glittering effect of pottery made by craftsmen making metallic film in the eras of Middle and Renaissance are still found to be remained unchanged. The lustre originated within the film containing silver and copper nanoparticles dispersed homogeneously in the glassy matrix of the pottery. These nanoparticles were created by the artisans by adding copper and silver salts and oxides together with vinegar, ochre, and clay on the surface of pottery. Although the craftsmen had no idea about the nanoparticles, they had a rather sophisticated empirical knowledge of materials and its application in ancient period.

Michael Faraday firstly described, in scientific terms, the optical properties of nanometer-scale metals in his classic 1857 paper. In the 1959, the American physicist Richard Feynman delivered lecture on "There's Plenty of Room at the Bottom," at an American Physical Society meeting at Caltech, which is often held to have provided inspiration for the field of nanotechnology.

In 1974, the Japanese scientist, Norio Taniguchi, Tokyo University of Science was the first to use the term "nano-technology" in a conference (MacNaught and Wilkinson, 1997) to describe semiconductor processes such as thin film deposition and ion beam milling exhibiting characteristic control on the order of a nanometer.

In the 1980s the idea of nanotechnology as a deterministic, rather than stochastic, handling of individual atoms and molecules was conceptually explored in depth by K. Eric Drexler, who promoted the technological significance of nano-scale phenomena and devices through speeches and two influential books.

In the 1981, the emergence of nanotechnology was caused by the convergence of experimental advances such as the invention of the scanning tunneling microscope and the discovery of fullerenes in 1985, with the elucidation and popularization of a conceptual framework for the goals of nanotechnology beginning with the 1986 publication of the book "Engines of Creation".

In the 1970-80s, the first thorough fundamental studies with "nanoparticles" were underway in the USA (Granqvist et al. 1976) and Japan, within an ERATO Project (Hayashi et al. 1997) they were called "ultrafine particles" (UFP). However, during the 1990s before the National Nanotechnology Initiative was launched in the USA, the new name, "nanoparticle," had become fashionable.

In early 2000s, the nanotechnology field was subject to growing public awareness and controversy with prominent debates about both its potential implications as well as the feasibility of the applications envisioned by advocates of molecular nanotechnology, and with governments moving to promote and fund research into nanotechnology. The early 2000s also saw the beginnings of commercial applications of nanotechnology, although these were limited to bulk applications of nanomaterials rather than the transformative applications envisioned by the field. Currently, nanoparticle is a significant area of intense scientific research with a wide variety of potential applications.

4. Nanomaterial for environmental remediation

In today's world, the process of advanced industrialization, modernized urbanization and tremendous population explosion are principal sources for emitting massive amount of various kinds of pollutants which are mostly found to mix in the air (atmosphere), water (hydrosphere) and soil (lithosphere) and are responsible for damaging the total environment. For example, carbon monoxide (CO), chlorofluorocarbons (CFCs), heavy metals (arsenic, chromium, lead, cadmium, mercury and zinc), hydrocarbons, nitrogen oxides, organic compounds (volatile organic compounds and dioxins), sulfur dioxide, particulates, etc. Some of them are known as deadly dangerous pollutants always discharging, introducing and contaminating the environment. Additionally, oil, coal and gas combustion is directly responsible for causing air pollution (EDF 2006), whereas including waste disposal, oil spills, leakage of fertilizers, herbicides and pesticides, by-products of industrial processes and combustion, extraction of fossil fuels etc. are directly responsible for polluting the water environment (Krantzberg et al. 2010).

In this respect, therefore, a promising technology is necessary to monitor, detect and, if possible, to clean the contaminants from the air, water and soil. Nanotechnology offers a phenomenon to control matter at the nanoscale by producing nanomaterials that have specific properties with a specific function (Roco et al. 1999). Currently, it has also been evidenced by several studies that nanotechnology using specific properties of nanoparticle offers a wide range of capabilities and technologies for remediation of environmental pollutions as well as to improve the quality of existing environment. Thus, remediation process of nanomaterials for treating and cleaning the polluted air, water and soil environments is known as Nanoremediation. It is estimated that there are between 45 to 70 sites have used nanoremediation technologies for cleaning up the environment around the world, predominantly in the United States (Barbara et al. 2012; Muelleret al. 2010; Bardos et al. 2014; PEN 2015). Surveys from selected European Union (EU) media show relatively high optimism with respect to the chances/risk ratio associated with nanotechnology (Fig. 2), where most of them have been attributed to the prospect of improvement in the quality of life and health (European Commission 2010; Yunus et al. 2012).

However, as literature available environmental remediation potentiality of nanomaterials has been taken into consideration in air, water and soil environments as follows:

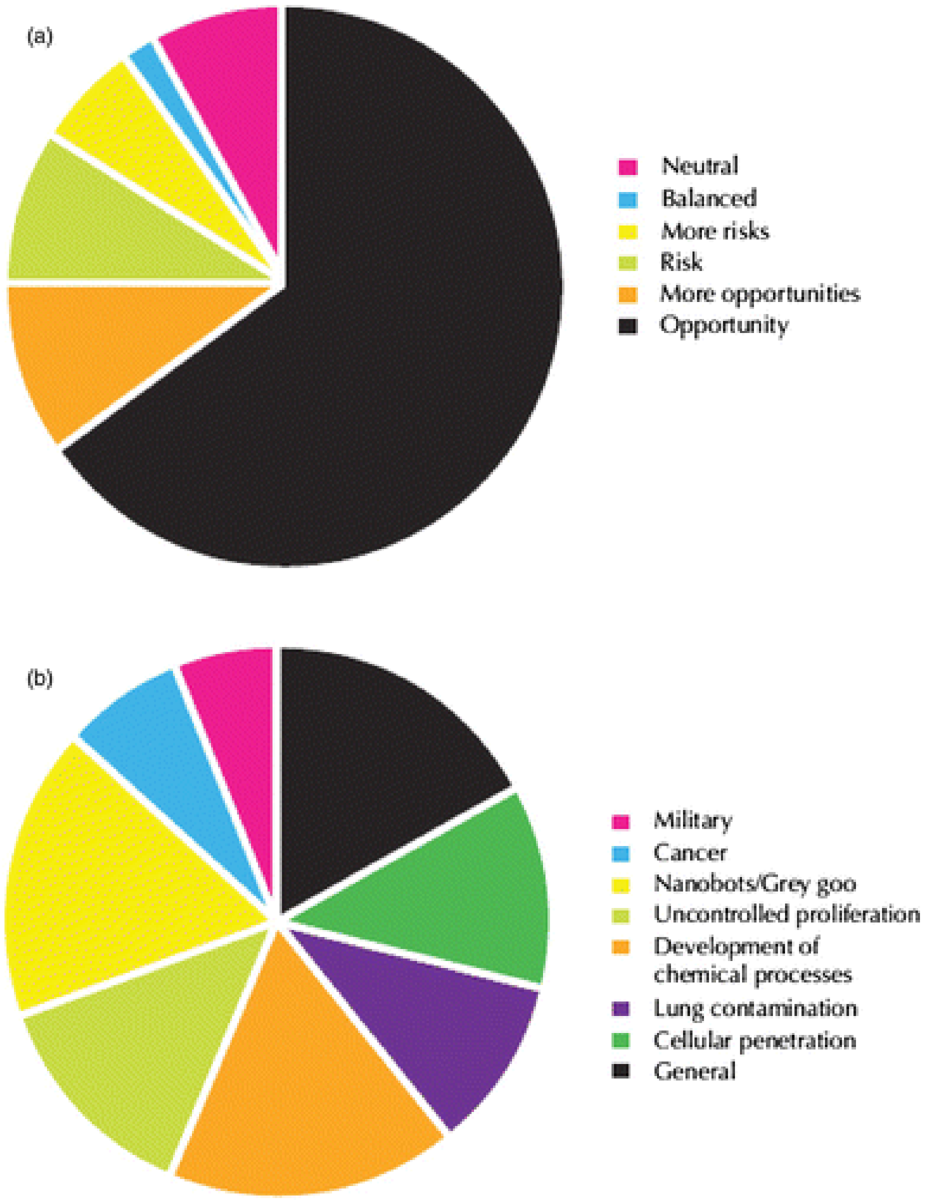

Fig. 2 Survey result of European Union (EU 2010): (a) balance between perceptual opportunities and risks of nanotechnology and (b) hypothetical risks of nanotechnology development (EU 2010)

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4.1. Nanomaterials for remediation of air

Air pollution can be controlled using nanotechnology. Nanomaterials have ability to purify and decontaminate the polluted air by means of sorption and transformation mechanisms. It is suspended in air/gas fluids and can absorb the toxic gas pollutants from the ambient air. Nanoparticles (1 – 100 nm) are generally present in trace quantities as suspended form in the air/atmosphere along with other particles. These nanoparticles play a central role in the formation of cloud droplets, precipitation, atmospheric visibility, ozone depletion in the stratosphere, and radiation balance of the earth (Wang et al. 2005). Therefore, nanoparticles are not only employed in water and soil remediation, it can also be effectively applied in cleaning toxic gases in the ambient air. Nanomaterials generally can remediate air in following ways:

(i) Nano-catalysts approach – The nano-catalyst contains increased surface area. The increased surface area of nano-catalysts speeds up the chemical reactions of gases which is associated with the high rate transformation of harmful gases generated from cars and industrial plants into harmless gases. Catalysts currently in use include a nanofiber catalyst made of manganese oxide that removes volatile organic compounds from industrial smokestacks.

(ii) Nanostructured membranes approach – It is still in developing stage. It has pores small enough to separate methane or carbon dioxide from exhaust (Jhu et al. 2008). Currently, research is going on for developing carbon nanotubes (CNT) in order to trapping greenhouse gas emissions caused by coal mining and power generation in University of Queensland. CNTs consist of a hexagonal arrangement of carbon atoms in graphene sheets that surround the tube axis. The gas trapping capacity of CNTs is hundred times faster than other methods. It is mainly depended on the pore structure and the existence of a broad spectrum of surface functional groups of CNTs. This new technology both processes and separates large volumes of gas effectively, unlike conventional membranes that can only do one or the other effectively (Pandey and Fulekar 2012). Single walled nanotubes (SWNTs) and multiple walled nanotubes (MWNTs) are the other advancement in this respect. Since, SWNTs and MWNTs can also be used as hydrogen storage, whereas only SWNTs have been reported to be a chemical sensor for NO_2 and NH_3. In addition, CNTs have been used as quantum nanowires, electron field emitters, catalyst supports, etc.

However, it is obvious that their unique electronic properties and structures have attracted the interest of researchers in developing the advanced nanomaterials and enhancing the potential applications for remediation of various air pollutants as follows:

Nanomaterials in dioxins adsorption

Dioxin and its related compounds (e.g. polychlorinated dibenzofuran and polychlorinated biphenyls) are stable and highly toxic pollutants are mainly generated from the combustion of organic compounds in waste incineration which are known to be carcinogenic to humans and also affect the immune and endocrine systems and foetal development. Dibenzo-p-dioxins are a family of compounds consisting of two benzene rings which are joined by two oxygen atoms. It is generally necessary to reduce dioxin concentrations to below 1 ng/m^3 due to its lethal toxicity. Study revealed that dioxin removal efficiency of activated carbon is much higher than other adsorbents because the bond energy between dioxin and activated carbon is higher than with other adsorbents, such as clay, γ-Al_2O_3 and zeolites (Cudahy and Helsel 2000). It has also found that CNTs have greater dioxin removal efficiency compared to that of the activated carbon, since there is a strong interaction between the two benzene rings of dioxin and the surface of CNTs. Long and Yang (2001) found that the interaction of dioxin with CNTs is nearly three times stronger than the interaction of dioxin with activated carbon. This improvement is probably due to the nanotube curved surface compared with those for flat sheets that gives stronger interaction forces between dioxin and CNTs (Bhushan 2010). Owing to the dioxin decontamination potentiality of CNTs, it is obvious that nanoparticles have strong ability to detoxify dioxin in air.

There is a strong interaction between the two benzene rings of dioxin and the surface of CNTs. In addition, dioxin molecules interact with the entire surface of nanotubes with a porous wall, i.e. 2.9 nm, and the possibility of overlapping events that increase the adsorption potential inside the pores. Strong oxidation resistance of CNTs has also been beneficial for the regeneration of the adsorbent at high temperatures.

Nanomaterials in nitrogen oxides (NO_x) adsorption

Nitrogen oxides (NO_x, mixture of NO and NO_2), an indirect greenhouse gases having substantial impact on global warming by producing the tropospheric greenhouse gas 'ozone' via photochemical reactions in the atmosphere. Several advanced technologies have been developed in order to eliminate the emissions of NO_x from fossil fuel combustion. Amongst different removal processes, the adsorption has commonly showed the reliable method using adsorbents, activated carbon, zeolites, etc. to remove NO_x at low temperatures. NO_x can be effectively adsorbed to activated carbon due to the reactivity of surface functional groups, although the amount of adsorbed species is still not significant.

Recently, nanotechnology pronounced important roles in this concern by producing NO_x removal nanoparticles and nanotubes. The CNTs could be used as an adsorbent for the removal of NO_x from air (Long and Yang 2001) (Fig. 3). It has also been observed that NO_x absorption of CNTs was approximately 78 mg/g CNTs which was influenced by the unique structures, electronic properties and surface functional groups of CNTs (Long and Yang 2001, Mochida et al. 1997).

Nanomaterials in carbon dioxide (CO_2) adsorption

Carbon dioxide (CO_2) is one of the primary green house gases directly responsible for causing global warming. The capture and storage of carbon dioxide (CO_2) produced from fossil-fuelled power plants have received significant attention since the Kyoto Protocol came into force on 16

February 2005. Among various investigated CO_2 capture technologies - sorption, cryogenic, membrane filtration (White et al. 2003, Aaron and Tsouris 2005), absorption evidenced potential CO_2 elimination capacity using sorbents, activated carbon, zeolite, silica adsorbents, SWNTs and nanoporous silica-based molecular baskets. The carbon nanoparticles and nanotubes (Fig. 3) have a good potential to capture the greenhouse gas CO_2 (Yunus et al. 2012).

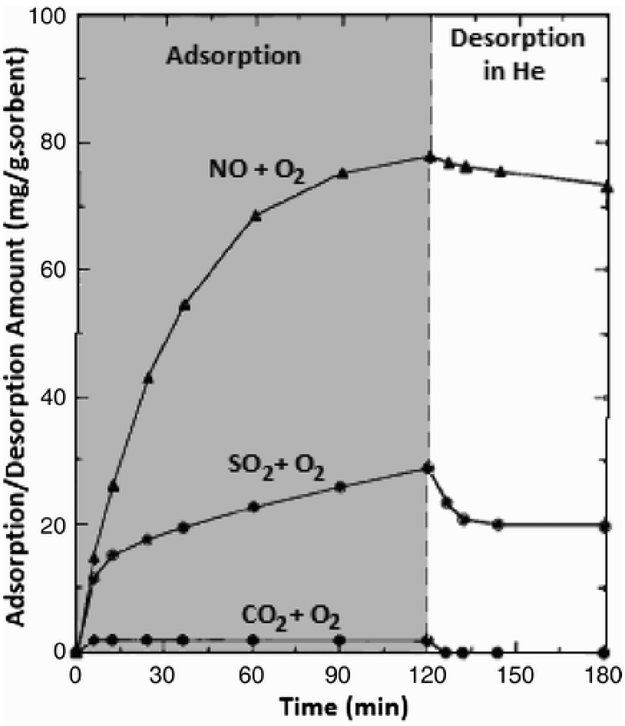

Fig. 3 Adsorption/desorption profile of CO_2, NO_x and SO_2 on carbon nanotubes at 25°C (Long and Yang 2001)

Nanomaterials in volatile organic compounds (VOCs) removal

In addition to dioxine, NO_x, CO_2 and SO_2, other many chemicals such as soot (Indarto 2009), nitrous acid (Indarto 2012), polyaromatic compounds (Santiago and Indarto 2008, Natalia and Indarto 2008, Indarto et al. 2009) and volatile organic compounds (VOCs) are synthesized by atmospheric reactions which are potentially damaging the environmental and human health. To purify the contaminated air, the conventional technologies, photocatalysts, adsorbents such as activated carbon or ozonolysis are commonly used in most of the cases, which have no substantial potentiality to get rid of organic pollutants in air at room temperature. Currently, nanomaterials directly and indirectly have shown high potential in removing VOCs from air. For example, highly porous manganese oxide with gold nanoparticles can effectively remove VOCs, nitrogen and sulfur oxides from air at room temperature (Sinha and Suzuki 2007). In this context, Sinha and Suzuki (2007) conducted a study using this gold catalyst with three major components of organic indoor air pollutants: acetaldehyde, toluene and hexane to determine the effectiveness of catalyst and observed that all three pollutants in the air were effectively removed and degraded by this catalyst. The main reason in support of higher removal of these gases are the presence of gold nanoparticles those helps to reduce the barrier of radical formation that is usually very high in addition to large surface area of porous manganese oxide. This process has opened the possibility for nanoparticles of other metal components can be applied. Shahzad et al. (2012) applied nanoparticles of TiO_2 in removing H_2S from air at high temperatures. The simultaneous destruction of this gas using nanoparticles of TiO_2 has been investigated for brick kilns, power generation and gasification processes which are carried out at high temperatures.

4.2. Nanomaterials for water remediation

The ocean holds about 97% of the Earth's water; the remaining 3% is distributed in many different places, including glaciers and ice, below the ground, in rivers and lakes, and in the atmosphere, whereas only 0.08% of it is clean water (http://water.usgs.gov/edu/earthwherewater.html, Shiklomanov 1993). In recent years, water has become an important issue, since the precious water body is tremendously polluted by numerous hazardous pollutants generated from various anthropogenic and geogenic activities as well as by various microbial contaminants. Several traditional methods such as extraction, adsorption, oxidation and biological degradation are generally used in remediation of polluted water. Most of them are less effective, expensive and time consuming, although the biological degradation process of pollutants is environmentally friendly and inexpensive, but it is very time consuming and has limitations in case of non-biodegradable substances.

The development of nanotechnology recently has opened a new and advanced approach in water treatment that can be used to improve water quality. The polluted and contaminated waters are treated using various forms of nanomaterials or nanoparticles and nanotechnologies (Araújo et al. 2015) such as - iron nanomaterial, ferritin, polymer nanoparticles, bioactive nanoparticles, nanofibres and nanobiocides, nanofiltration. Zeolites, carbon nanotubes (CNTs) (Sharmaa et al. 2009), self-assembled monolayers on mesoporous supports, biopolymers, single-enzyme nanoparticles, nanoparticles of zero valent iron (ZVI), etc. The advantages of using nanomaterials are their higher reactivity, larger surface contact and better disposal capability. The nanomaterials are currently used in groundwater remediation which is the most common commercial application of nanoremediation technologies (Bardos et al. 2014; USEP 2014). The use of various nanomaterials, including carbon nanotubes and TiO_2, shows promise for treatment of surface water, including for purification, disinfection, and desalination (Theron et al. 2008). Nanoparticles may assist in detecting trace levels of contaminants in field settings, contributing to effective remediation.

However, the different application approaches of nanotechnology, nanomaterials and nanoparticles for remediation of precious water resources have been concisely accounted as below:

Iron nanomaterial

Iron nanomaterial is effectively used in treating the contaminated water in last decades. The ZVI are employed as a filter material of permeable reactive barrier (PRB) to remove hazardous contaminants in water in large quantities (Uyttebroek et al. 2010). Zero-valent iron (ZVI) is generally injected into a site to degrade the contaminant either by forming PRB of particles that cleans water as it passes through it, or by using mobile particles small enough to travel through the pores in the soil (Fig. 4, Crane and Scott 2012). In this respect, a common system which is known as a 'pump and treat' system has been developed using PRB for water remediation (Fig. 5, Tratnyek and Johnson 2006). In addition to the use in PRB, the small nanoparticles of iron have multifunctional use for remediation purposes, such as nanoparticles can also be used via direct mixing in wastewater to form slurry, injection into the solid waste, etc. and for treating the ground water. Nano zero-valent iron (nZVI) appears to be useful for degrading organic contaminants, including chlorinated organic compounds such as polychlorinatedbiphenyls (PCBs) and trichloroethene (TCE), as well as immobilizing or removing metals (Karn et al. 2009; Theron et al. 2008). Once injected, the nanoparticles will remain in the form of a suspension and a treatment zone will be formed or is attached to a solid matrix such as activated carbon which has proven quite effective in treating the pollutants. Iron nanoparticles can effectively remove arsenic and chromium from contamination (Mosaferi et al. 2014; Rashmi et al. 2013).

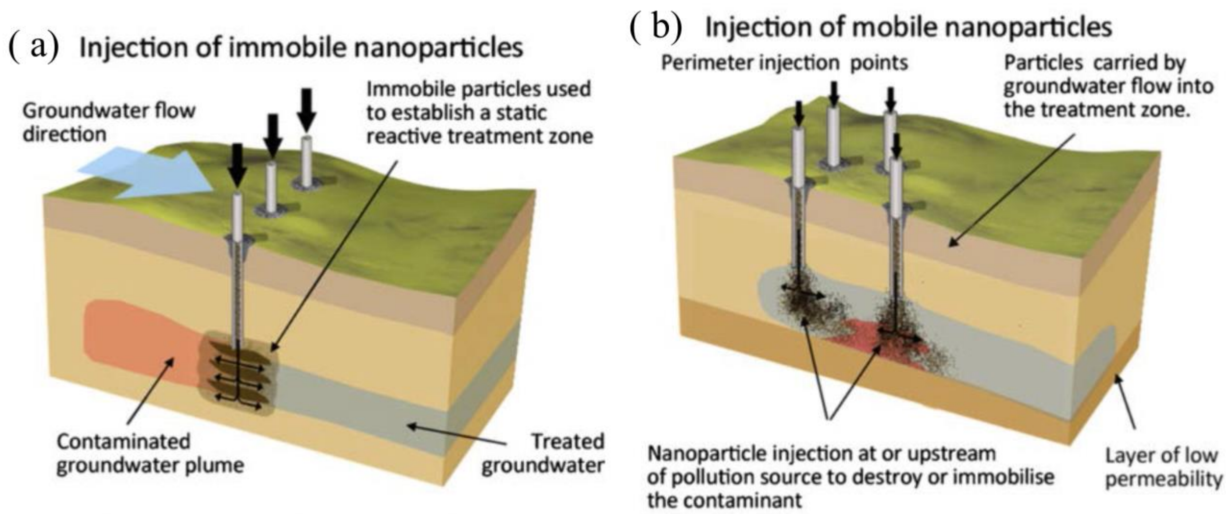

Fig. 4 Schematic representation of nanoparticle application showing how (A) immobile nanoparticles and (B) mobile nanoparticles are injected into the subsurface for groundwater treatment (modified from Crane and Scott 2012) (Grieger et al. 2015)

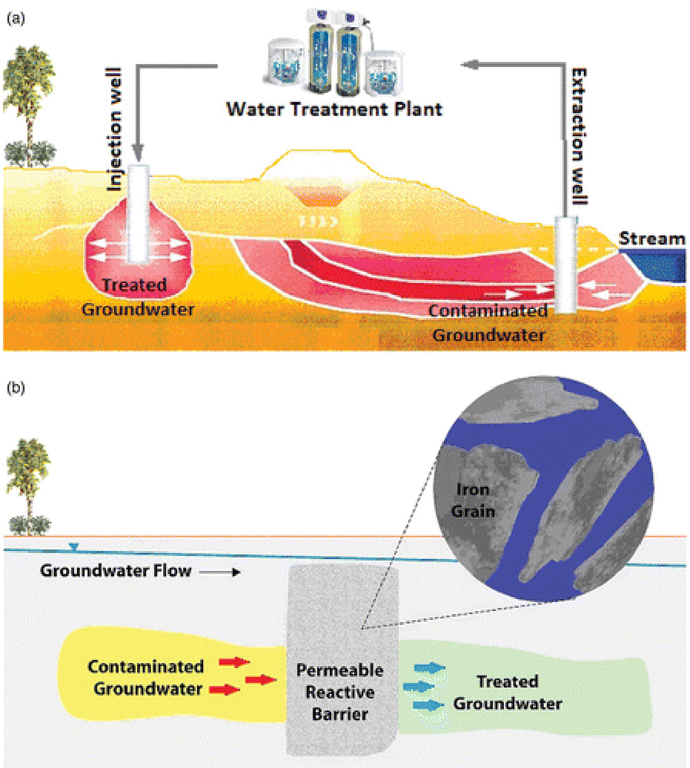

Fig. 5 A schematic diagram of (a) pump and treat system and (b) permeable reactive barrier (PRB) application made with millimeter-sized construction-grade granular iron (Tratnyek and Johnson 2006)

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Ferritin nanoparticle

Ferritin is an iron-containing protein structure of 24 structurally identical polypeptides, where the mineralization process transforms iron molecules into ferrihydrite nanoparticles, found in animals and plants associated with iron storage activities in cell. Several studies reported that ferritin has the ability to detoxify the toxic effects of metals and chlorocarbon under visible light or solar radiation (Moretz 2004). Transformation of chromium Cr(VI) into Cr(III) (Watlington 2005; USEPA 1998) is one detoxification evidence of ferritin nanostructure.

Copper nanoparticles

It has well known that both sulphur dioxide (SO_2) and NO_2 are the major green house gases have significant contribution towards global warming. Additionally, SO_2 can be detrimental to ecosystems, harming aquatic animals and plants, and can be damaging to a wide range of terrestrial plant life as well as NO_2 and O_3 have significant impacts in environment as discussed earlier. To control these hazardous problems, the metal nanomaterials can be applied as effective agent to remove these green house gases from aqueous environment. For example, copper nanoparticles and copper immobilized beads are able to remove the SO_2 and NO_2 from water (Sirisha et al. 2014).

Nanoscale calcium peroxide

Nanoscale calcium peroxide has recently been used for the clean-up of oil spills (Mueller and Nowack 2013; Karn et al. 2009) and it is claimed to be highly efficient in removing aromatics and is also used in enhanced bioremediation. The oxygen produced in the reaction of calcium peroxide with water leads to an aerobic environment that supports natural bioremediation by aerobic. Several concerning projects have been conducted in New Jersey, USA.

Semiconductor photocatalytic nanoparticle

Studies revealed that nanoparticles of some materials such as titanium dioxide (TiO_2), zinc oxide (ZnO), iron oxide (Fe_2O_3) and tungsten oxide (WO_3) act as photocatalysts and serve as environmental cleaners as well as antimicrobial agents. These photocatalysts are capable to oxidize toxic organic pollutants to nontoxic substances and hence such types of catalysts can be employed in water remediation. The advantages of TiO2 for applying in the remediation of water are low levels of toxicity, high photoconductivity, high photostability, and that it is an easily available and inexpensive material. Semiconductor photocatalyst has been applied for water remediation under the United States Environmental Protection Agent (USEPA) SITE program (Watlington 2005). In a pilot scale, it was also found that TiO_2 was capable of eliminating benzene, toluene, ethylbenzene and xylene (BTEX) contents from groundwater. The surface of TiO_2 catalysts which can be developed using nanotubes is shown to be more effective for eliminating the material in comparison with the usual structure of TiO_2 powder (Liang et al. 2010). During laboratory experiments, a ZnO photocatalyst was successfully used to detect and eliminate 4-chlorocatechol (Kamat et al. 2002).

Polymer nanoparticle

Polymer nanoparticles have amphiphilic properties as that of micelles i.e., each molecule has hydrophobic and hydrophilic parts. The polymer forms a polymer cell with a diameter of several nanometres having the hydrophobic part inside and the hydrophilic part outside in aqueous medium. The stability of polymer nanoparticles depends on formation of crosslink prior to the aggregation of particles. Polymer nanoparticles have multipurpose applications, including water treatment and sunscreen. It offers a solution for commonly used conventional surfactants to enhance remediation of hydrophobic organic contaminants using a pump and treat system. For example, amphiphilic polyurethane nanoparticles have good prospects as a remediation agent. Tungittiplakorn et al. (2004) used a polyurethane acrylate anionomer and poly(ethylene glycol)-modified urethane acrylate as the reactant/precursor chains. However, application of the polymer nanoparticle is in preliminary stage so far and needs more studies considering its various relevant aspects.

Nanofiltration membrane

Nanofiltration membrane is a kind of membrane of nanomaterials having high capacity to treat the polluted water in order to improve the water quality. Currently, it has evolved as a newest and most leading-edge technology in water treatment which is widely using in home, business or manufacturing facility. The mechanism of filtration uses pressure as the driving force. Nanofiltration membranes provide higher thrust or rejection of multivalent ions, pesticides and heavy metals compared with conventional treatment methods. Some important investigations concerning the performance of nanofiltration membrane have been reported Bruggen et al. (2008) and Hilal et al. (2004). Nanofiltration membranes can effectively be modified according to different target molecules to be treated.

Antimicrobial nanomaterials

Microbial contamination of water is a serious and growing problem worldwide damaging large number of lives every year worldwide by causing various kinds of water born diseases. Although several conventional technologies are employed to control this problem, nanotechnology recently provides a potential alternative solution to clean up germs in water. Several studies using antimicrobial nanomaterials obtained satisfactory results in controlling the microbial contamination in water (Li et al. 2008; Mamadou et al. 2009). According to Li et al. (2008), several nanomaterials pronounced potential antimicrobial properties through the following diverse mechanisms: (1) photocatalytic reaction for producing reactive oxygen species that damage cell components and viruses (e.g. TiO_2, ZnO and fullerol), (2) impairment of membrane function (e.g. peptides, chitosan, carboxyfullerene, CNTs, ZnO and silver nanoparticles), (3) inhibition of energy transduction (e.g. Ag and aqueous fullerene nanoparticles), (4) protein dysfunction and loss of enzyme activity, (5) competitive inhibition of nutrient assimilation and (6) genotoxicity (e.g. chitosan). Due to aqueous stability, nontoxic when ingested and low cost properties, TiO_2 has been considered to be the best candidate among different nanomaterials in this respect.

Nanofibres and nanobiocides are the kinds of antibacterial surface-modified nanomaterials of water filtration membranes (du Plessis 2011). They can protect bacteria fouling by inhibiting their growth in the water which reduce the quality of water. For example, nontoxic and biodegradable synthetic polymer silver nanoparticles containing polyvinyl alcohol and polyacrylonitrile nanofibres have excellent (about 91% - 100%) antimicrobial activity (du Plessis 2011).

Other nanotechnologies for water remediation

In addition to above, various other types of nanomaterials are applying in water remediation processes. Such as, metal alloys – iron and iron–nickel–copper have been employed to degrade trichloroethene and trichloroethane (O'Carroll et al. 2012). The commonly used other metals are palladium, silver, platinum, cobalt, copper and gold, while aluminum is used as an inert. Self-assembled monolayers on mesoporous silica, dendrimers or dendritic polymers, single nanoparticle enzyme, tunable biopolymers, nanocrystalline zeolites, etc. are some other examples of nanotechnologies used in water remediation.

4.3. Nanomaterial for soil remediation

Likewise air and water environments, manomaterials are potentially used in remediation of contaminated soil. The soil nanoremediation of various contaminants such as heavy metals, other inorganic contaminants, organic contaminants and emerging contaminants, as pharmaceutical and personal care products has been reported in several recent studies (Araújo et al. 2015; Mueller and Nowack 2010). The properties of highly reactive and great sorption capacity of nanomaerials are significantly effective in soil remediation. However, technical challenges, such as the delivery of the particles to the target polluted area of soil, have to be solved. There are also concerns regarding the release of large quantities of manufactured nanoparticles into the soil prior to extensive human and ecological toxicity testing. Metal based nanomaterials, such as silver, zinc, titanium dioxide, iron oxide are used in soil nanoremediation. Two American companies are using nano-sized calcium peroxide as an oxidant in the remediation of soils containing various organic contaminants, such as gasoline, heating oil, methyl tertiary butyl ether (MTBE), ethylene glycol and solvents (Mueller and Nowack 2010).

In remediation process, the nanoparticles are applied via direct injection into the soil to remove the pollutants from soil (Latif 2006). Based on the applied methods and information obtained by Latif (2006), the nanoscale site remediation does not appear to pose a threat to humans and the environment. Transport data indicate that nanoscale particle plumes may travel slightly faster than the natural migration rate of contaminant plumes (Latif 2006). In situ applications, it seems to be most promising as they are in general less costly. It is necessary to create either an in situ reactive zone with relatively immobile nanoparticles or a reactive nanoparticle plume that migrates to contaminated zones in case of in situ application (Mueller and Nowack 2010). For applications in topsoil, nanoparticles can be worked into the surface of the contaminated soil using conventional agricultural practices (Mueller and Nowack 2010). So far zero valence iron is the only application of nanomaterials in soil and groundwater remediation that has been successfully commercialized in the United States. Possibly in a few years, remediation with nanoscale calcium peroxide will also be a common method in this regard.

Once nanoparticles are entered into the soil, they are subject to reactions with the soil solution as well as with the (mobile and stationary) solid phase. In soils, stability of nanoparticle is affected by various processes and environmental factors (Klitzke et al. 2015). According to Paula et al. (2012), the characteristics of nanoparticles (e.g., size, shape and surface charge) and soil (e.g., pH, ionic strength, organic matter and clay content) will affect physical and chemical processes, resulting in nanoparticles dissolution, agglomeration, and aggregation in soil environment.

However, on account of the above discussion, it is obvious that nanomaterial is one of the important agents in soil remediation process.

5. Nanomaterial based sensor in environmental monitoring

In spite of these, it is very much important to mention herein that application of nanomaterials for the above purposes are greatly responsible for causing adverse and hazardous impacts due to mixing of nanoparticles into the air, water and soil environments. Besides, nanoparticles are suspended in fluids during production, handling, processing, and by unintentional and/or undesired release to the environment may cause dangerous pollutions and damages in different domains of environments, such as - air, water and soil. Environmental pollution of various particulate hazardous and toxic pollutants poses serious environmental and human health risks. It has been found that long-term exposure to particulate matter and heavy metal pollution can cause severe health problems such as dysfunction of heart, kidney and liver, lung cancer, neural disorders etc. In urban areas, particulate sizes are typically in the range of 100–300 nm in diameter (Johnston 2002) while heavy metals could be found in various ranges of concentration. A highly sensitive, rapid and precise sensor can detect and monitor the pollutants and contaminants (Masciangioli and Zhang 2011) at the molecular level which may able to protect the sustainability of human health and the environment. To solve the problems, nanotechnology offers highly precise, miniature, automatic, ultrasensitive and also inexpensive sensors (Ambrosi et al. 2008; Gomez et al. 2008; Kerman et al. 2008; Algar et al. 2009), miniaturization of electronics, and advancements in wireless communication technology have shown the emerging trend towards environmental sensor networks that continuously and remotely monitor environmental parameters (Huang et al. 2001; Burda et al. 2005; Blasco and Pico' 2009; Zhang et al. 2009). Nanomaterials have also been used for the development of gas sensors (Gouma et al. 2006; Jimenez-Cadena et al. 2007; Milson et al. 2007). The specific properties of nanomaterials offer a wide range of opportunities for the detection of environmental contaminants and toxins in addition to their remediation (Vaseashta et al. 2007; Khan and Dhayal 2008; Thompson and Bezbaruah 2008; Andreescu et al. 2009; Bezbaruah and Kalita 2010) characteristics. The following are the examples of some sensors:

a. Nanocontact sensor – It has potentiality to detect some metal ions without preconcentration required and can be used for the onsite detection of heavy metal ions, including radioactive elements. Nanocontact sensors can be made in miniature size with automatic device in low-cost for easy handling in onsite (Tao 2002).

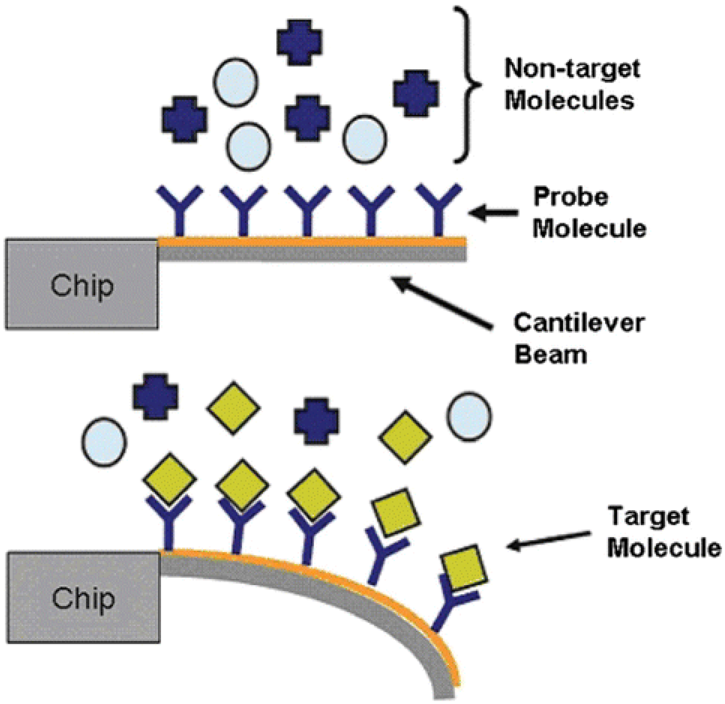
b. Nanomaterial-based biosensors – It is developed by nanoparticle using electrochemical immunoassay method and is employed to detect people who have been exposed to chemicals (Staiano et al. 2020; Liu et al. 2007). A nanoparticle 'label' that is able to enhance the ability of sensors to detect and interpret biomarker signals has been produced by Wang et al. (2007). The approach includes the electrochemical immunoassay method and specific antibodies to attract the biomarkers of disease.

c. Nanowires and nanotube-based sensors – It provides tremendous capabilities as materials for chemical and biological sensors (Smart et al. 2006). Single-walled nanotubes (SWNTs) have shown a faster response and higher sensitivity than the conventional probes that are currently used in the detection of gas molecules such as NO_2 and NH_3.

d. Cantilever sensors – A cantilever sensor is a device made of a silicon cantilever array coated with nano-coating that is sensitive to specific pollutants (Filipponi and Sutherland 2010). A cantilever is typically 10–500 µm in length, but it has a thickness of less than several micrometres. Interactions between pollutants with the nano-coated cantilever array cause the array to bend as a result of changes in surface pressure. The small bending will be measured by a laser beam which can result in the quantitative measurement of the detected mass of pollutants. Cantilever sensors have been developed to detect VOCs, heavy metals, pesticides and harmful bacteria such as salmonella. Figure 6 shows a schematic diagram of cantilever-based biosensors. In Figure 6, the molecular probe is only appropriate for the target molecule. When the target molecule is attached, the cantilever arm will bend and react. Thus, the reaction will detect and signal the presence of target molecules.

e. Molecular imprinted polymer sensors (MIPs) – Recently, MIPs are used for environmental remediation and to detect amino acids, enzymes, antibodies, pesticides, proteins, vitamins, etc. They are synthesized using template (target) molecules which are cross-linked into a monomer with template specific. The target-monomer complex is then polymerized and the template molecules are removed to leave the polymer matrix with ''holes'' specific to the target molecules (Fig. 7).

Fig. 6 Schematic diagram of how cantilever-based biosensors work: (a) before and (b) after interaction between target molecule and probe. (Picture courtesy of www.nmji.in)



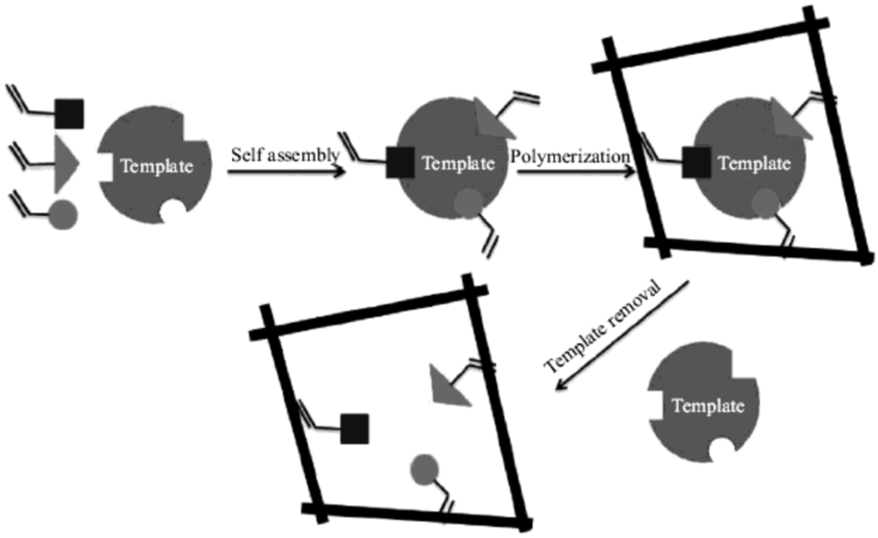


Fig. 7 Schematic representation of molecular imprinted polymer showing capturing mechanism of target molecules from sample (Shelke et al. 2008)

f. Other nanosensors - Some other nanosensors are listed as follows (Berger 2008):

(i) Functionalized-tetraphenylsilole nanoparticle sensors can detect the carcinogenic substances, Cr(VI) and Ar(V) at very low concentrations forming anionic oxidants bonding.

(ii) Peptide nanoelectrodes sensor is based on the concept of thermocouple to identify the metal ions. A peptide molecule is placed to form a molecular junction in a 'nano-distance' separation gap. When a specific metal ion is bound to the gap, the electrical current will result conductance in a unique value and thus, the metal ion is identified.

(iii) Composite electrode sensor is a mixture of nanotubes and copper employed to detect substances such as organophosphorus pesticides, carbohydrates and other woods pathogenic substances in low concentrations.

(iv) Polymer nanospheres can be used as nanosensors to measure organic contaminants in very low concentrations, i.e. parts per billion concentrations.

6. Environmental risk of nanomaterials

Although nanomaterials have potential and diversified applications with rapid advances, these nanomaterials may also cause unintended risk effects on environment and human health. The surveys from selected European Union (EU) media show relatively high optimism with respect to the chances/risk ratio associated with nanotechnology have shown in Figure 1 (European Commission. 2010; Yunus et al. 2012). It is known that decreasing particle size and increasing reactivity are properties that may render a substance more toxic, even though studies reported that materials those are harmless in bulk forms can become highly toxic at the nanoscale (Oberdörster et al. 2007; Mueller and Nowack 2010; Karlsson et al. 2009). Because of technologically interesting nano-size properties, nanomaterials or nanoparticles may place them in a novel category of potentially toxic substances for causing hazardous and risk impacts in environment and human health (Mueller and Nowack 2010). Unintentional and undesirable introduction of nanomaterials into the environments during processing may cause tremendous hazard due to the same traits that make nanoparticles useful. Many studies have demonstrated the toxic effect of nanoparticles on living organisms both in vitro and in vivo conditions (Chen et al. 2006). The smaller size of nanoparticles often allows them to be absorbed by living cells with greater rate than that of the larger particles (Helland 2004).

As previously mentioned the nanoparticles are commonly present in the atmosphere along with other particles and is associated with beneficial as well as adverse impacts (Wang et al. 2005). Both natural and anthopogenic sources are responsible for releasing nanoparticles and polluting the environment. The nanoparticles naturally derived from biogenic, geogenic (soil dust, volcanic ash), oceanogenic (primarily sea sprays), and astrogenic (burning of falling meteoroids) sources, whereas industrial operations, farming, motor vehicles, ships, jet planes and solid fuel rockets are the major anthropogenic origin of nanoparticles. Nucleation and coagulation are major mechanisms in the formation and dynamics of nanoparticles. The stable nuclei are produced in air by cooling the supersaturated vapors or chemical reactions and these particles collide due to their Brownian motion resulting in the formation of larger particles and a decrease in the total particle number concentration. These mechanisms result in ambient ultrafine particles (nanoparticles) of different morphological properties and may be present as liquid droplets, compact solid particles, and agglomerates (Mädler and Friedlander 2007). The nanoparticles are suspended in air fluids with high density due to its small size and pollute air. In polluted air, the particle concentration can be higher than 10^4 per cm^3 being a major component that causes adverse effects on human health, materials, vegetation, and ecosystems (Seinfeld and Pandis 1998; Mädler and Friedlander 2007). Because of extreme small size, the nanoparticles can cause hazardous for human's health by penetrating deeper into the lungs than larger particles, as the results, it increases the risk of cardiovascular and pulmonary diseases. Sea traffic has high rate of nanoparticles emission which may pose high health risk. Particles from sea traffic in North Sea the Baltic Sea are expected to contribute to 10000 premature deaths every year, but some scientists doubt this value (Edward 2015). The inhalation of airborne nanoparticles and the impact upon lung disease is a specific concern, with recent studies showing a similar response by the human body to some forms of CNTs as to asbestos particles, if inhaled in sufficient quantities (Buzea et al. 2007).

Nanoparticles may be ingested, inhaled or taken up through the skin. Several studies have shown that nanosized particles can be taken up by a wide variety of mammalian cell types (Oberdörster et al. 2007, Mueller and Nowack 2010). Tratnyek and Johnson (2006) have concluded that exposure to nZVI will be minimal due to rapid agglomeration of the particles, limited particle mobility and fast oxidation to iron oxide. Li et al. (2009) found that nano-iron can induce oxidative damage in fish embryos and disturb the antioxidative balance in fish adults. Phenrat et al. (2009) investigated this nZVI “ageing” effect and found that 11-month-old nZVI was less toxic to rodent microglia (a type of cell in the brain and spinal cord) and neurons than fresh nZVI. A study of nanoparticle ecotoxicity considering biota including plant, earthworm and nematode in soil environment were thoroughly analyzed and concluded the vigorous research is required in this respect demonstrating the inconsistent results (Lee 2010).

However, the issue of toxicity and ecotoxicity of nanomaterials is especially important for environment because in most of them free nanoparticles are released in the environment, and thus environment is definitely exposured. The risk associated with nanomaterials is not only on its toxicity but also on the extent of exposure.

7. Conclusion

The clean environment is essentially important for us as we depend on clean air to breathe, clean water to drink or use in agriculture with soil and industry. Presently, the environment unfortunately is not in clean conditions due to pollution caused by various pollutants. From the pollution viewpoint of environment, nanomaterials very recently has evolved as an important candidate by pronouncing diversified promising roles for cleaning up the air, water and soil environments by applying a number of nanotechnologies as discussed in the present review. In addition to the beneficial impacts, nanomaterials also pose some adverse impacts in the environments as hazardous materials due to its characteristics of highly active nano scale size. Although nanomaterials exhibit both beneficial and risk impacts, the significantly potential beneficial applications are substantially higher than adverse impacts as discussed from available literatures in this review. Since, the environmental remediation capacity of nanomaterials in air, water and soil compartments is significantly greater rather than other conventional technology employed so far, which has been evidenced by several studies as elucidated herein. On account of the above discussion, it is also apparent that there is insufficient research regarding the environmental toxicity of nanomaterials which is unable to draw clear picture in this respect. Although several concerned scientists are immensely engaged to find out the toxicity impacts of nanomaterials in environment, a substantial amount of research work is still necessary in this support. However, developed nanomaterial technologies have substantial capability to enhance and improve the conventional technologies and new technologies which replace the conventional technologies. Furthermore, the nanomaterials have been evolved as a potential candidate for nanoremediation technological approach effectively capable to protect the air, water and soil environmental resources in order to achieve the purpose of maintaining environmental sustainability.

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