9 Application of Nanotechnology in the Environment Biotechnology

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Abstract

With the increasing industrialization and urbanization, the environment is getting polluted. Conventional techniques such as filtration, centrifugation and biological treatment are expensive and not efficient one. Therefore, there is a need for the development of recent and efficient techniques for environmental monitoring and treatment. Nanotechnology is the solution to the abovesaid problems. Nanoparticles, nanomembranes, nanofilters, and nanocatalysts have been developed for wastewater treatment. These have smaller size (1–100 nm) and higher surface area to volume ratio. Due to these properties, they provide more reaction surface which results in increased efficiency and selectivity. With the some issues solved, nanotechnology will answer all the environmental problems.

Keywords

Nanotechnology • Nanoparticles • Environment • Contaminants

9.1 Introduction

With increase in industrialization, the pollution level in the environment is also increasing. The environment is being contaminated using heavy metals (cadmium, zinc, arsenic, mercury and lead), sulfur dioxide, carbon monoxide, nitrogen oxide, chlorofluorocarbons (CFCs), dioxins, volatile organic carbons (VOCs) etc.

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(Environmental Defence Fund 2006). Due to the excessive burning of coal, oil, and gas, the amounts of nitrogen and sulfur oxide have increased in the environment which lead to acid rain. Water pollution is caused by a lot of factors including the leakage of herbicides, pesticides, oil spills in the water bodies, and also the release of by-products of industrial processes and fossil fuel extraction and combustion (Krantzberg et al. 2010).

The contaminants are mostly found in water, air and soil. The toxicity of contaminants is defined as toxicity level and measured in ppm (parts per million) or ppb (parts per billion). The toxicity level for mercury in water is 0.002 ppm and that for arsenic in soil is 10 ppm. The contaminants are present in the environment in mixtures as well as in very low concentration. Therefore, it is necessary to develop some technique that could detect the contaminants present even in low concentrations. The answer to this alarming question is nanotechnology. "Nano" is derived from a Greek word meaning dwarf. One billionth of a meter (10^{-9}) represented by length of 10 "H" atoms lined up in a row makes a nanometer. Naturally, nanotechnology had emerged a billion of years ago from the point where the molecules began to arrange themselves in form of a complex structure. Various tools for measuring nanotechnology are scanning tunneling microscope (STM), atomic force microscope (AFM), molecular beam epitaxy (MBE) and scanning probe microscopes (SPMs) (Roco et al. 1999). Nanotechnology has an ability to control the matter at nanoscale and thus creates some materials with specific properties and functions. Nanotechnology is the advanced technology which uses materials with dimensions between 1 and 100 nm and produces the devices using these nanomaterials (Guzmán et al. 2006). The small size and larger surface area to volume ratio of nanoparticles help in developing sensitive, accurate and miniature devices (nanosensors) for the monitoring of pollution levels in the environment (Formoso et al. 2016). Moreover, using nanotechnology, the harmful pollutants could be degraded into the less toxic form and also reduce the amount of pollutants by minimizing the quantity of material used in the manufacturing processes. Therefore, nanotechnology not only helps in the detection of pollutants but also in their treatment.

Nanotechnology helps in lowering down the pollutant generation by applying industrial processes and material technology. Therefore, it has three major applications in the field of environment:

- Pollution detection (sensing and detection)
- Prevention of pollution
- Purification and remediation of contamination

9.2 Detection of Contaminants Using Nanotechnology

For the efficient treatment of pollutants, it is very necessary to develop the detection methods which will help in the fast and precise detection. The sensors need to be portable and remote so that detection could be carried over large field areas. Sensor is a device that produces a digital electronic signal upon interaction with the compound (biological or chemical) that has to be detected. Using the conventional sensors, the pollutants in biological samples, soil, water, air, chemical substances and industrial products can be detected in low levels up to ppm and ppb. These detection levels could be improved using nanoparticles for the development of sensors. The developed sensors using nanoparticles are highly selective and accurate. They help in the detection of heavy metals, microbial pathogens, organic compounds etc. even at very low concentration (Formoso et al. 2016). With the increased surface area to volume ratio, the reactivity increases and thus its sensitivity. Moreover, the small size also increases the number of reactive sites on the sensor which help in the detection of multiple compounds (multiplex sensors).

Nanosensors in the form of nanowires and nanotubes have been developed for environmental monitoring. Single-walled carbon nanotubes (SWCNTs) have been used for the detection of NH_3 and NO_2 which prove to give faster response as compared to solid-state sensors (Kong et al. 2000). Moreover, the SWCNTs can be operated at room temperature, whereas solid-state sensors are operated at 200–600 °C. This enhanced reactivity is based on the fact that gaseous atoms bind directly to the SWCNTs resulting in increase or decrease of electrically generated signal. In addition to SWCNTs, boron-doped silicon nanowires have been used for the detection of glucose in water (Shao et al. 2005), calcium, antibodies and proteins (Cui et al. 2001; Patolsky and Lieber 2005). The real-time sensing using nanowires is used for the detection of pathogens and biological and chemical agents in food, water, and air.

9.3 Treating Pollutants Using Nanotechnology

The contamination of places in the vicinity of manufacturing plants such as abandoned mines, lakes, rivers, underground storage leakages and landfills is a great matter of concern. The contaminants in these areas could be organic compounds such as creosote, chlorinated solvents, benzene etc. and heavy metals like arsenic, lead, mercury and cadmium. The conventional methods used for the waste treatment are expensive, time-consuming and laborious. Therefore, nanotechnology can be used to develop cost-effective and specific methods. The treatment technologies involve the pretreatment and removal of contaminated site, i.e., pump and treat method. This method disturbs the ecosystem as contaminants are removed from the site and carried to a different site for the treatment purposes (Filipponi and Sutherland 2007). This problem could also be solved using nanotechnology as it can help in the development of in situ treatment technologies which are specific and efficient for a particular pollutant. The organic dyes (indigo carmine and methylene blue) can also be removed from the wastewater using nanocomposites made from surface-functionalized TiO_2 nanoparticles, CNT (carbon nanotubes), and PAN (polyacrylonitrile) (Mohamed et al. 2016).

9.3.1 Nano-traps (Nanofilters and Nanomembranes)

For the treatment of wastewater and waste air, nanomaterials such as nanomembranes, nano-adsorbents, and nanofilters have also been developed (Filipponi and Sutherland 2007). Like nanoparticles, these nanomaterials have properties such as large surface area, high surface-volume ratio and specificity. These are also known as nano-traps. One such membrane was developed by Rice's CBEN (Center for Biological and Environmental Nanotechnology) for the treatment of wastewater, i.e., ferroxane membrane (iron oxide ceramic membrane) (Cortalezzi et al. 2003, 2005). Researchers from the University of Tennessee have been trying to develop a nano-trap that will not only specifically detect the contaminant but also convert it into nontoxic form upon reaction with it. One other advancement in the use of nanomembranes is developed by UCLA (University of California, Los Angeles) which is a reverse osmosis (RO) membrane and is used for the treatment of wastewater and desalinization of seawater. The membrane allows the inward movement of water molecules and the repulsion of contaminants (organic matter and bacteria). This semipermeable property of the membrane is due to the design of engineered nanoparticles and cross-linked matrix of polymers. This design results in the formation of nano-sized holes which act as tunnels for the entry of water. These membranes also serve the advantage of increased shelf life as these are not prone to clogging as in conventional RO membranes (Shon et al. 2013). Heavy metals such as Cu (II), Ni (II) and Pb (II) could be easily adsorbed on the surface of carbonaceous nanofibers (CNFs) with Pb (II) showing the highest affinity for CNFs (Ding et al. 2016). Similarly radionuclides [Eu (III) and U (VI)] could also be removed from the environment using CNFs. The advantage of CNFs is that they are readily available and cheap source (Sun et al. 2016).

9.3.2 Nanoparticles

9.3.2.1 Iron Nanoparticles

The most suited example of the treatment of the environment using nanotechnology is the use of iron nanoparticles (Fe^0) for the remediation of soil and groundwater (Zhang 2003). Iron is the nontoxic compound present in soil, rocks and water; therefore, it is used by many industries as "iron powders" for the treatment of their fresh industrial wastes. But this iron powder cannot be used for the treatment of waste that has been previously dumped into the soil or water. In addition, the reduction using iron powders is partial, i.e., TCE (trichloroethylene) and PCE (perchloroethylene) are partially reduced to DCE (dichloroethylene). The products of partial reduction are much toxic than the parent compounds. Further, the iron powders could be used only for a limited period of time due to the formation of passivation layers on their surfaces. Therefore, the technology has shifted from the use of iron powders to iron nanoparticles. The nanoparticles (1–100 nm) are 10–1000 times effective as compared to iron powders. They are easily transported with the groundwater as they have small size and larger surface area. Further, the nanoparticles serve the advantage that they do not change with the change in nutrient availability, pH, or temperature of soil. Thus, they remain in suspension creating an in situ treatment zone. Both the *in vitro* and in vivo studies show that the iron nanoparticles are able to degrade completely a number of contaminants such as PCBs, organochlorine pesticides and chlorinated organic solvents. When compared with the iron powders, the nanoparticles were able to degrade the contaminants completely without the formation of toxic by-products due to higher stability and reactivity of iron nanoparticles (Wang and Zhang 1997). The nanoparticle suspension is prepared and injected to the contaminated site. The concentration of nanoparticles at the injection site remains for 6–8 weeks and then slowly gets eliminated into the groundwater, whereas the concentration of contaminants is nearly eliminated within few days (Zhang 2003).

In addition to the zerovalent iron nanoparticles, the bivalent iron nanoparticles (Fe-Pd) have also been used for the bioremediation (Elliott and Zhang 2001). They have proved to be much efficient than zerovalent iron nanoparticles as they could be used for the ex situ wastewater treatment by immobilizing them on silica or activated carbon.

"Pump and Treat" system has been commonly used in the remediation of water (Tratnyek and Johnson 2006). In this system the water is pumped from the soil to the surface, is treated and then injected back to the ground. This method was applicable till 1999. And then another way called permeable reactive barrier (PRB) was devised which was used to clean subsurface groundwater without bringing it to the surface. It can be used to clean pesticides, polychlorinated biphenyls (PCBs), hydrocarbons, aromatic nitro compounds and chromate compounds. In order to overcome the cost of this method, zerovalent iron (ZVI) has been employed. ZVI is of two types:

- Nanoscale ZVI (nZVI)
- Reactive nanoscale iron product (RNIP)

nZVI has 100–200 nm of diameter composed of iron of valency zero, whereas RNIP has 50/50 weight of Fe and Fe_3O_4. ZVI has a higher reactivity toward Cu^{2+}, No^{3-}, chlorinated hydrocarbons and Cr_2^{2-}. The nano-iron is also used directly in soil, solid waste, and sediments, or the nanoparticles are directly attached to the solid matrix like activated carbon for use. Other metals like zinc, palladium, cobalt, copper and gold can also be used in place of iron to reduce the contaminants. Two alloys of iron, i.e., nickel-copper, have also been used to degrade and remove trichloroethane and trichloroethylene (O'Carroll et al. 2013).

The pollution of textile industries due to the release of inorganic salts and water-soluble dyes is also a major problem. nZVI can be used for the degradation of textile dyes and have proven to be much efficient due to their nontoxicity, low cost and higher reactivity toward the contaminant. Moreover their stability could also be increased using various supports such as bentonite, nickel, nickel-montmorillonite, kaolin, rectorite, cellulose and graphene (Raman and Kanmani 2016).

9.3.2.2 Titanium and Zinc Nanoparticles

The ZnO and TiO_2 are the semiconductors and are widely used for the remediation purposes as they are cheap and readily available. When these are used in the nano-size form, the results of the remediation are far more effective as the surface area for the interaction is larger. The main purpose of using ZnO and TiO_2 nanoparticles is the construction of solar photocatalysis remediation systems. In these the contaminants such as chlorinated benzene are converted into benign products by solar radiation. These semiconductors can degrade a number of toxic compounds (Oyama et al. 2002), but still there is a need to increase their efficiency as they absorb only ultraviolet (UV) light which is only 5% of the total solar spectrum. This could be overcome by coating the nanoparticles using inorganic or organic dyes which will shift the absorbance from UV region to visible region (Subramanian et al. 2001). The efficiency of TiO_2 can be enhanced by conjugating them with gold nanoparticles. The ZnO nanoparticles are known to act on the principle of "sense and shoot" as they can detect the chlorinated phenols and also help in their treatment (Kamat et al. 2002). ZnO nanoparticles doped with vanadium could be used for the removal of malachite green dye (Khezami et al. 2016). The bacterial enzymes could also be used for the biosynthesis of TiO_2 nanoparticles and then used for the treatment processes. In one study amylase from *Bacillus amyloliquefaciens* was used for the biosynthesis of TiO_2 nanoparticles and then used for the removal of reactive red 31 (RR31) dye from the contaminated sites (Khan and Fulekar 2016).

9.3.2.3 Magnetic Nanoparticles

The magnetic nanoparticles are the nanoparticles of rust, and they help in purification of water by the removal of arsenic under magnetic effect (Yavuz et al. 2006). The nanoparticles of rust have larger surface area and 10 nm diameter and act as small magnets. This helps in the attachment of arsenic to the nanoparticles which can then be removed with the help of magnets. Thus, the water is treated and becomes arsenic-free. As compared to the conventional techniques (filtration and centrifugation), the use of magnetic nanoparticles serves the advantage of being simple, requires less amount of sample, improves efficiency and requires no electricity (Gu et al. 2003). The arsenic-contaminated water is mostly present in remote areas where power is a major problem. In these areas the best method of treating wastewater is the use of magnetic nanoparticles (Gu et al. 2006). FS@IDA magnetic solid chelator powder composed of Fe_3O_4@SiO_2 nanoparticles coated with iminodiacetic acid can be used for the removal of Cd (84.9%) and Pb (72.2%). The advantage of the use of FS@IDA is easy removal of heavy metals through efficient chelation and simple magnetic separation (Fan et al. 2016).

9.3.2.4 Ferritin Nanoparticles

Ferritin is an iron-containing 24 polypeptide cage-like protein that controls the formation and functioning of mineralized structures and also stores iron in animals and plants (Theil 1987). Ferritin remediates chlorocarbon and toxic metals under the effect of solar radiations and visible light (Moretz 2004). The stability of ferritin and its nonreactiveness under photoreductive conditions have proved to be advantageous over other ferrous catalysts. An important application of ferritin is that it changes Cr(VI) which is a carcinogenic pollutant to Cr(III) which is less poisonous and insoluble in water (Watlington 2005). Alcohols present in the water could be oxidized using hybrid formed by Pd in nanometallic form and ferrtin isolated from *Pyrococcus furiosus* (Kanbak-Aksu et al. 2012).

9.3.2.5 Polymeric Nanoparticles

Polymeric nanoparticles have been used in the treatment of water. These behave as amphiphilic molecules which have both hydrophobic and hydrophilic character. In the availability of water, a polymer cell with a diameter of several nanometers is formed with hydrophilic part inside and surrounded by the hydrophobic part. In order to stabilize these nanoparticles, cross-linking is done before aggregation. Amphiphilic polyurethane (APU) nanoparticles are used as a remediation agent. The traces of TNT (trinitrotoluene) were detected using electrochemical sensor developed on poly(styrene-co-acrylic acid) PSA/SiO_2/Fe_3O_4/AuNPs/lignin (L-MMS)-modified GCE (glassy carbon electrode). TNT was preconcentrated on the surface of electrode due to the presence of Fe_3O_4/AuNPs and lignin film which resulted into fast response time (3 sec). The electrode serves the advantage of being used repeatedly for five adsorption/desorption cycles (Mahmoud et al. 2015).

9.3.2.6 Bioactive Nanoparticles

Germfree and germ reduction in water or environment is provided by nanotechnology. But the increasing population and pollution has made the situation worse. So, an alternative which is offered is antimicrobial nanotechnology. Strong antimicrobial activity has been shown by various nanomaterials via different mechanisms (Dizaj et al. 2014). Some of which are listed below:

- Fullerol, ZnO, and TiO_2 are used in the production of reactive oxygen species (ROS) by photocatalysis and thus damage the viruses and cells.
- Silver and aqueous fullerene nanoparticles interrupt the energy transduction in the cell.
- Chitosan inhibits enzyme activity and synthesis of DNA.
- Peptides, chitosan, carbon nanotubes, ZnO, carboxy-fyllerene and fullerol interfere with bacterial envelope and disrupt it.

  For the prevention and control of fungal diseases in agriculture, various fungicides such as TBZ (tebuconazole) and carbendazim MBC (methyl-2-benzimidazole carbamate) are used. These can cause harm to the environment and human on leakage. They can be removed from the contaminated sites by the use of polymeric nanocapsules and solid lipid nanoparticles as the fungicides are encapsulated in these nanoparticles with >99% association efficiency (Campos et al. 2015).

9.4 Dendrimers

Dendrimers have nanoscale dimensions, controlled composition, and highly branched polymers used for the removal of metal contaminants (Diallo et al. 2005). They can bind to the appropriate surface and are soluble in nature as they form the cages to trap the zerovalent metals and metal ions. The research is under process to use the dendrimers in ultrafiltration systems as the nano-chelating agents.

9.5 Nanocatalysts

The compound that increases the speed of a reaction without being utilized in the reaction is called catalyst. The reactivity of a catalyst depends on its active site at which the reaction occurs. As the size of the compound decreases to nano level, the reaction surface area increases due to which its efficiency is enhanced (Gemming and Seifert 2007). Nanocatalysts are used for the generation of sulfur-free fuels. During the refining processes of fuels, sulfur remains in the fuel which upon combustion produces sulfuric acid. This could be reduced by treating the fuels with nanocatalysts (nano-sized cerium oxide). The organic dyes such as anionic monoazo dye, cationic phenothiazine dye and cationic fluorescent dye can be degraded efficiently in the presence of gold and silver nanoparticles synthesized using the juice of *Punica granatum* (Kumari and Philip 2015).

9.6 Problems to Be Solved

With the advancements in technology, a number of sensors have been developed for the continuous monitoring of environment. The microorganisms have been used for the development of sensors for environmental monitoring since the past, but their genomic analysis for better understanding has recently come to be known (Feldman and Harris 2000). The microbes could be studied and identified at their genetic levels to develop the efficient sensors for environmental monitoring and treatment. This could be only possible with the help of new advancements in nanotechnology. Further there is little knowledge about the nature, transformation process and chemical composition of the nanoparticles. In addition, it is difficult to identify the nanoparticles in soil, air and water. The conventional methods used for the detection of nanoparticles are nonquantitative, slow and not precise for the data collection. Therefore, the detection methods should be improved so that the nanoparticles can be detected easily and efficiently. Thus, the refinement of the recently used nanotechniques is required for an efficient detection and treatment of environmental contaminants.

9.7 Conclusion

With the globalization, pollution levels are increasing at alarming rates. A number of techniques such as filtration, centrifugation, and chromatography have been used for the monitoring and treatment of pollution levels, but these techniques have many loop holes. Nanotechnology can overcome these gaps and develop new and efficient means of detecting and treating pollution levels. Nanoparticles, nanocatalysts and nanocomposites have been the boons of nanotechnology for healing of the environment. Various nanoparticles such as iron, magnetic, TiO2, ZnO, ferritin and polymeric and bioactive nanoparticles give rapid response and also help in eradication of the pollutants. Some of the gaps such as study and use of microbes at genetic levels for the remediation of environmental resources need to be overcome to get the best results from nanotechnology in the environment.

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