Nanobioremediation: Ecofriendly Application of Nanomaterials

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Mohammad Rizwan and Minhaz Uddin Ahmed

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Abstract

Nanoparticles (NPs) or nanomaterials (NMs) or nanostructure materials (NSMs) or nanoclusters (NCs) or nanocomposites (NCMPs) exhibit unique physical properties, chemical properties, and biochemical properties; and hence it has received much attention from scientists and researchers in different fields of sciences, engineering, and technology. Applications of NPs or NMs or NSMs or NCs or (NCMPs) have also increased in different areas of environmental sciences including bioremediation. Bioremediation provides a good cleanup strategy for some types of waste such as effluent, agriculture, and domestic waste; but as it is expected, it is not effective for all. Therefore, NPs or NMs or NSMs or NCs or NCMPs may be applied for rapid, effective, and efficient bioremediation, which

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will not only have less toxic effect on microorganism; it will also improve the microbial efficiency and activity for the rapid degradations of specific organic waste and to reduce the toxic and hazardous effect of heavy metals. The use of NPs or NMs or NSMs or NCs or NCMPs will be rapid, efficient, effective, and economic. In this chapter, we have summarized the major type of NPs or NMs or NSMs or NCs that have been currently used for bioremediation of waste, wastewater, and toxic materials.

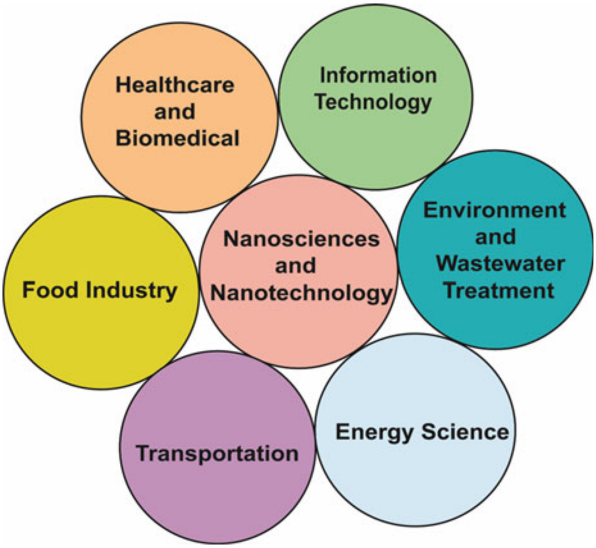
Keywords
Nanoscience · Nanotechnology · Nanoparticles · Nanomaterials · Nanostructure materials · Nanoclusters · Nanocomposites · Bioremediation · Environmental sciences · Waste and wastewater · Heavy metals · Toxic materials · Nanobioremediation · Microorganism · Ecofriendly · Economical

Introduction

The current decade has seen tremendous development in nanosciences and nanotechnology (NS and NT) in all areas of sciences, engineering, and technology [1]. The design, characterization, production, and application of structures, devices, and systems by controlled manipulation of size and shape on the nanometer scale (atomic, molecular, and macromolecular scale) that produces structures, devices, and systems with at least one novel/superior characteristic or property is known as nanotechnology [2]. According to definition, NS and NT is involved with objects on the nanoscale or materials, measuring between 1 and 100 nm [3]. NS and NT have gained much importance and uses in biomedical sciences [4], food industry [5], catalysis [6], optics [7], energy science [8], and environment [9], specifically in bioremediation [10]. Nanoparticles (NPs) or nanomaterials (NMs) or nanostructure materials (NSMs) or nanoclusters (NCs) or nanocomposites (NCMPs) have unique physical properties, chemical properties, and biochemical properties [11–13]; these properties are having immense importance for the application in bioremediation which enhance the biocatalytic activity and efficiency of the microorganism [14]. Application of NS and NT has revolutionized many technology and industry sectors like information technology, energy, environmental science, medicine, homeland security, food safety, and transportation as illustrated in Fig. 1. There are various eco-friendly applications of nanotechnology as far as environmental science is concern such as materials that provide clean water from polluted water sources in both large scale and portable application and one that detect and clean up environmental contaminants (waste and toxic material), i.e., remediation [10, 14].

"Remediate" means to solve a problem, and "bioremediate" means to use biological organisms such as bacteria, fungi, protests, and other microorganisms or their enzyme to solve an environmental problem such as contaminated soil or groundwater [10, 14–18]. The use of plants to clean up the environment is known as phytoremediation, and it is also considered as a type of bioremediation [19, 20].

Fig. 1 Schematic illustration of nanosciences and nanotechnology application



Bioremediation allows natural processes to clean up harmful, toxic hazardous, heavy metals, chemicals, and waste from the environment. Microscopic "bugs" or microbes that live in soil and groundwater like to eat certain harmful chemicals, such as those found in gasoline and oil spills [21, 22]. When microbes completely digest these chemicals, they change them into water and harmless gases such as carbon dioxide. Bioremediation of a contaminated site typically works in one of two ways. In first case various substances such as the right temperature, nutrients (fertilizers), and amount of oxygen (depending upon aerobic or anaerobic microorganism) are used to enhance the growth (population) of whatever pollution-eating microbes (indigenous microorganisms) might already be living at the contaminated site [23]. In the second, less common case, specialized microbes (exogenous microorganisms) are added to degrade the contaminants [24]. However, in each case once harmful, toxic, and hazardous chemicals and wastes are cleaned up and microbes have eaten their available "food," the microbes die.

Bioremediation applications fall into two broad categories: in situ or ex situ. In situ bioremediation treats the toxic material in the location in which it was found so it is less expensive, minimum release of contaminants to the environment, and large volume or area can be treated. However, it is slower and some time may be difficult to manage. Ex situ bioremediation processes require excavation of contaminated material or toxic substance before they can be treated. Ex situ techniques can be faster, easier to control, and used to treat a wider range of contaminants and soil types than in situ techniques [25]. Some examples of bioremediation technologies are phytoremediation, bioventing, bioslurping, bioleaching, land farming, bioreactor, biosparging, windrows, bioabsorption, composting, bioaugmentation, rhizofiltration, mycoremediation, bioplies, and biostimulation (illustrated in Fig. 2) [26].

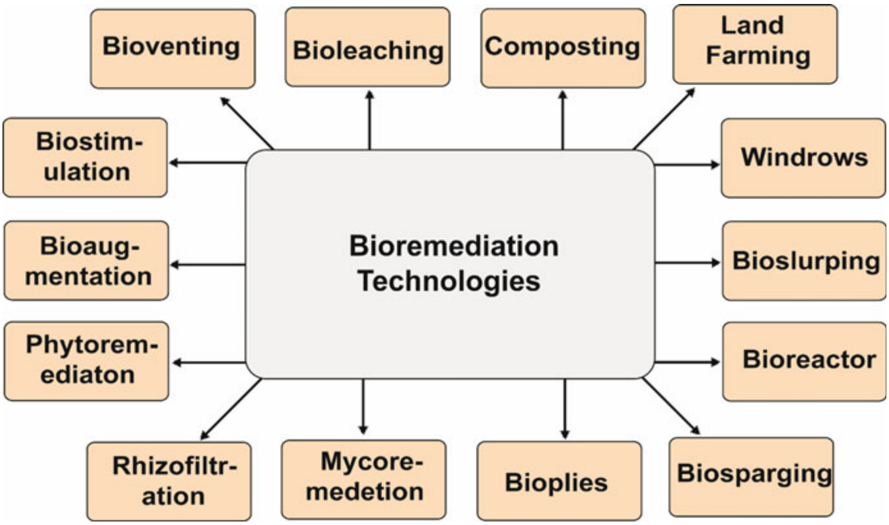


Fig. 2 Schematic illustration showing types of bioremediation technologies

The Science of Bioremediation with Nanomaterial: Nanobioremediation

There are various reasons for different nanoparticles (NPs) or nanomaterials (NMs) or nanostructure materials (NSMs) or nanoclusters (NCs) or nanocomposites (NCMPs) to be used in bioremediation, as illustrated below with various examples reported in literatures [14, 27, 28]. Several studies have utilized NPs or bimetallic NPs or NMs or NSMs or NCs or NCMPs as an effective oxidant instead of granular zero-valency metal in the cleanup of environmental contaminants, mainly because (i) NPs or NMs or NSMs or NCs or NCMPs can diffuse or penetrate into a contamination zone where microparticles cannot reach and (ii) higher reactivity to redox-amenable contaminants than that of microsized particles can be obtained. It is observed that oxide-coated FeO can form weak and outer-sphere complexes with contaminants such as carbon tetrachloride (CT) which can be broken down into methane, carbon monoxide, or formate through electron transfer, whereas, benzoquinone, bytrichloroethene, and other chlorinated aliphatic hydrocarbons can be decomposed to chemical compounds having minimum harmful effect [29]. TiO_2 nanotubes have been used for the photocatalytic degradation of the pentachlorophenol (PCP) [30]. NPs can also be used as biocatalysts for reductive dichlorination, for example, when palladium Pd (0) NPs are deposited on the cell wall and inside the cytoplasm of *Shewanella oneidensis* and charged with H* radicals by adding different substrates such as hydrogen, acetate, and formate as electron donors in a bioreductive assay containing Pd (II). When these charged Pd (0)-deposited *Shewanella oneidensis* cells are brought in contact with chlorinated compounds

(PCP), the H* radical on the Pd (0) can catalytically react with PCP, resulting in the removal of the chlorine molecule from the chlorinated compounds (PCP) [31]. NPs can be further used to immobilize microbial cells that can degrade or biorecover specific chemicals. On the other hand, unlike conventional cell immobilization on micron-sized media or a fixed surface, microorganism can be immobilized on the magnetic NPs or NMs or NSMs or NCs or NCMPs which can be further separated from the bulk solution and can be reused for the treatment of the same substrate. For example, Shan et al. used ammonium oleate functionalized magnetic NPs (Fe_3O_4) and coated it on the surface of *Pseudomonas delafieldii*, by applying an external magnetic field to these microbial cells coated with magnetic nanoparticles concentrated at a specific location on the reactor wall, separated from the bulk solution, and recycled for the treatment of the same substrate. These microbial cells were added into a bioreactor at a high biomass concentration and were demonstrated to desulfurize organic sulfur from fossil fuel (that is dibenzothiophene) as effectively as non-NP-coated cells [32]. Therefore, the specific NPs or NMs or NSMs or NCs or NCMPs will be discussed hereafter focusing on remediation of various types of waste. These include applications for solid waste, soil, groundwater and wastewater, petroleum and petroleum products (hydrocarbon), soil remediation, uranium remediation, heavy metal pollution, and electronic waste. The ability of NMs or NSMs or NCs or NCMPs to abate pollution production is in progress and could potentially catalyze the most revolutionary changes in the environmental field in the coming decades. Figure 3 illustrates recent application of the NPs or NMs or NSMs or NCs or NCMPs being used for bioremediation.

Nanoiron and Its Derivatives in Bioremediation

Remediation has grown and evolved; and adopting new technologies improved remediation process. Among various technologies, one of the most established systems is that termed as “pump-and-treat.” Pump-and-treat systems operate on the basis of removing contaminated groundwater from the ground, downstream of the contaminated site, and then treating it before returning it to the ground. This technology takes a long time to achieve cleanup goals, and it is also expensive to operate and maintain. Therefore, reducing capabilities of metallic substances, such as zero-valent iron (ZVI), were examined for their ability to treat a wide range of contaminants in hazardous wastewater [14]. Kim and Carraway reported that the disappearance of pentachlorophenol (PCP) from aqueous solutions in contact with zero-valent metals (ZVMs) may be due to dechlorination reactions or sorption to ZVM-related surfaces [33]. Whereas, nanoscale iron particles and their derivatives offer more alternatives to many remediation technologies, the small particle size of the nano iron (1–100 nm) facilitates a high level of remedial versatility due to large surface area provided by nanomaterials compared to macroscopic materials [10]. This allows a much greater diversity in applications of nanoscale iron particles and their derivatives as compared to the traditional ZVI. Nanoscale zero-valent iron (nZVI) and reactive nanoscale iron product (RNIP) are the most basic form of the

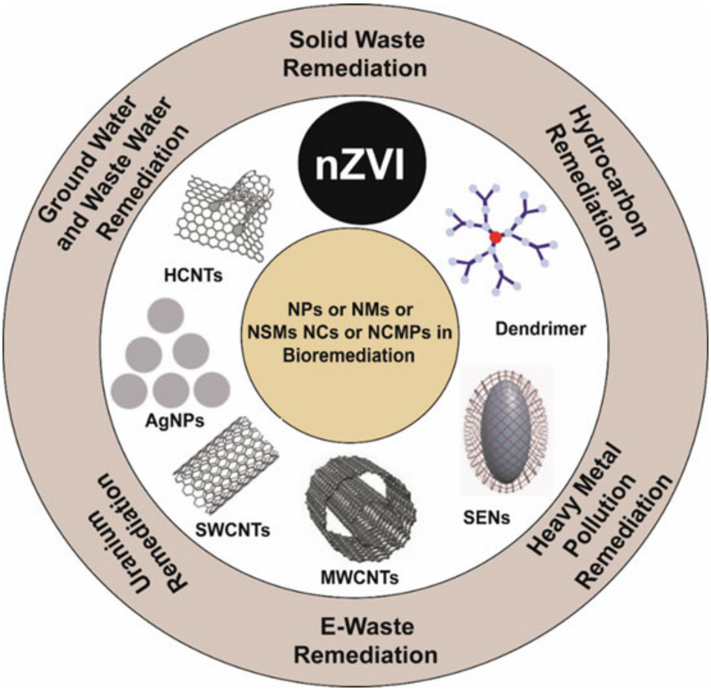


Fig. 3 Schematic illustration of the use of nanoparticles (NPs) or nanomaterials (NMs) or nano-structure materials (NSMs) or nanoclusters (NCs) or nanocomposites (NCMPs) in bioremediation

nano iron technology [34]. Kanel et al. synthesized nZVI and tested for the removal of As (III), which is a highly toxic, mobile, and predominant arsenic species in anoxic groundwater [35]. On the other hand, Kanel et al. also removed As (V) from groundwater using nZVI as a colloidal reactive barrier material [36]. Ponder et al. reported that supported zero-valent iron NPs ("Ferragels") rapidly separate and immobilize Cr (VI) and Pb (II) from aqueous solution, reducing the Cr (V) to Cr (III) and the Pb (II) to Pb (0) while oxidizing the Fe to goethite (α-FeOOH) [37]. In another report Schrick et al. used high surface area of bimetallic nickel-iron NPs (1:3 Ni: Fe) as a reagent for the dehalogenation of trichloroethylene (TCE) [38]. Iron can also be used to construct a reactive wall in the path of a contaminated groundwater plume to degrade halogenated organic compounds [39].

Dendrimers in Bioremediation

A dendrimer (from Greek dendra for tree) is an artificially manufactured or synthesized nano-sized radially symmetric molecule built up from branch units called monomers [40]. Such processes involve working on the scale of nanometers (a nanometer is 10^{-9} or a billionth of a meter or a millionth of a millimeter).

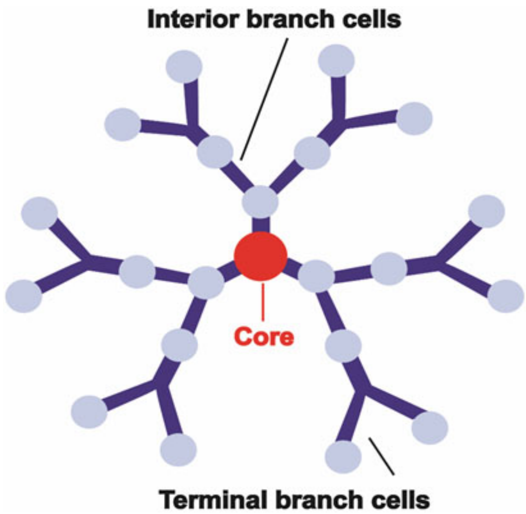


Fig. 4 Schematic illustration of the component of the dendrimer

Technically a dendrimer is a polymer, which is a large molecule comprised of many smaller ones linked together and typically consisting of three components: a core, interior branch cells, and terminal branch cells as illustrated in Fig. 4.

Dendrimers have some proven applications and numerous potential applications. Dendrimers are of interest to researchers in medical technology, where they might help carry and deliver drugs in the body or serve as replacements for plasma components [41]. Recently, researcher has proposed dendrimer application in clean water recovery unit. Among various types of dendrimers, PAMAM dendrimer has attracted special attention due to its unique structure, efficiency, and innoxious properties and has been used in water treatment. The researcher is also using dendrimer/titania nanohybrid for the removal of the organic or phenolic contaminant from wastewater, to develop simple filtration unit with hybrid organic/inorganic filter modules of high mechanical strength and high surface area for the removal of organic pollutants by utilizing TiO_2 porous ceramic filters. Alkylated poly(propylene imine) dendrimer, poly(ethylene imine) hyperbranched polymer, or β-cyclodextrin are being impregnated in the pore resulting in hybrid organic/inorganic filter modules of high mechanical strength and high surface area [42, 43].

Carbon Nanomaterials in Bioremediation

A variety of carbon NMs (MWCNTs, SWCNTs, and HCNTs) each possessing unique functionalities are in various stages of research and development that are potentially applicable to the remediation of industrial effluents, groundwater, surface water, and chemical and biological contaminants from water and drinking water [44, 45]. The removal of ethylbenzene from aqueous solution by multi-walled-, single-walled- and hybrid-carbon nanotubes (MWCNTs, SWCNTs, and HCNTs) have been evaluated; the equilibrium of amount of ethylbenzene removed by SWCNTs was higher than by MWCNTs, and the SWCNTs performed better for ethylbenzene sorption than the HCNTs and MWCNTs. Carbon nanotubes, specially SWCNTs, are efficient and rapid adsorbents for ethylbenzene which possess good potential applications to maintain high-quality water. Therefore, carbon NMs especially SWCNTs may have potential application in removing the chemical and biological waste from the environment [46]. Li et al. developed an environmental friendly adsorbent by immobilizing CNTs with calcium alginate (CNTs/CA). CNTs/CA was further evaluated for the copper adsorption properties via equilibrium studies. Experimental results demonstrated that even at a lower pH of 2.1, CNTs/CA copper removal efficiency was high and reaches up to 69.9% [47]. On the other hand, Kandah and Meunier demonstrated the application of MWCNTs to remove nickel ions from water [48], and in a similar study, Gong et al. use magnetic multi-wall carbon nanotube nanocomposite to remove cationic dye from aqueous solution [49].

Single-Enzyme NPs (SENs) in Bioremediation

Enzymes are specific proteins which act as biocatalysts in bioremediation [50]. However, compare to the synthetic catalysts, lack of longer stability and relatively short catalytic lifetimes of biocatalyst makes it less economical with minimum usefulness. Stability and longer lifetime of the enzymes depended on its ability to resistant to the oxidation. More enzymes are resistant to the oxidation making it more economical, efficient, and useful. There are various methods of increasing the stability, longevity, and reusability of the enzymes [51, 52]. Attachment of the magnetic iron NPs is another effective way to increase the stability, longevity, and reusability of the enzymes [50, 53]. When enzymes are attached to the magnetic iron NPs, then enzymes can easily separate from reactants or products by applying a magnetic field. With this purpose Qiang et al. used two different catabolic enzymes, trypsin and peroxides, to attach with uniform core-shell magnetic nanoparticles (MNPs). The study further demonstrated that conjugation of MNPs to the trypsin and peroxide enzymes dramatically increased the stability, efficiency, and lifetime as well as enhanced the activity of the enzymes. MNP-enzyme conjugates were resistant to oxidation due to shielding of the enzymes by MNPs which enhance the lifetime of the enzymes from few hours to weeks. Due to attachment of the enzymes with MNPs of high magnetization, MNP-enzyme conjugates can be magnetically separated efficiently, making enzymes more productive and economic [50].

Engineered Polymeric NPs for Bioremediation

Hydrophobic contaminants such as polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals, persistent in the environment and considered as a significant environmental problem. Therefore, Tungittiplakorn et al. studied the potential application of poly (ethylene) glycol-modified urethane acrylate (PMUA) nanoparticles for improved bioremediation of PAHs, as the solubility and mobility of the PAHs has been shown to be limited by the sorption. Further, bioavailability of the PAHs decreases due to sequestration of PAHs by sorption to soil and by partitioning in nonaqueous phase liquids (NAPLs). To overcome this problem, it has been demonstrated that the polymer nano-network particles increase the "effective" solubility of hydrophobic organic contaminant phenanthrene (PHEN) and from contaminated aquifer material enhance the release of PHEN. For enhancing the bioavailability of PHEN, PMUA precursor chain was developed. It was demonstrated that, PMUA NPs increased the mineralization rate of PHEN crystal in water, PHEN sorbed on aquifer material, and in the presence of aquifer media PHEN dissolved in a model NAPL (hexadecane). Further study shows that PMUA particles enhance both the release of sorbed and NAPL-sequestered PHEN as well as increased its mineralization rate. It was also studied that the accessibility of contaminants in PMUA particles to bacteria could be an effective method for enhanced in situ biodegradation rate in remediation through natural attenuation of contaminants. Further, bioreactors could be used to recycle extracted NPs from soil washing or pump-and-treat remediation schemes. The properties of PMUA NPs were found quite stable in the presence of a heterogeneous active bacterial population. Therefore, PMUA particles can be further reused after the PHEN bound to the particles has been degraded by bacteria [54]. In a further study, Tungittiplakorn et al. prepared amphiphilic polyurethane NPs for their use in remediation of soil contaminated with PAHs [55].

Biogenic Uraninite NPs in Bioremediation

Biogenic uraninite is a biogeological, natural nanoscale material. Recent research has demonstrated the chemical and structural complexities of these important natural NMs. Geoscientist has great interest in biogenic uraninite due to its immense potential in bioremediation strategies, nano-size range, and biological origin. In spite of its tiny size, the molecular-scale structure, and energetics, hydrated biogenic uraninite appears to be similar to those of coarser particle, abiotic, stoichiometric UO_2. These physicochemical properties of biogenic uraninite have immense importance as a moderator for the bioremediation of subsurface U (VI) contamination [56].

Bioremediation of Electronic Waste

Electronic waste, also known as "e-waste," is obtained from integrated circuits (ICs) of obsolete and discarded electronic goods including radios, mobile phones, laptops, computers, printers, iPods, as well as batteries. Most of the components (~90%) of the ICs can be recycled and reused. Heavy metals such as Si, As, Fe, Cu, Al, Pb, Zn, Cr, Cd, Hg, and Ba are worthy and economical for recycling. Physical and chemical treatments of the e-waste for the recycling using strong acids and reagents are hazardous and noneconomical and put extra burden on the environment. The use of biological method of synthesis of the nanoparticles using microorganisms and plant extracts can be an alternative, economical, green approach for the recycling of the metals from the e-waste. Using this approach Majumder uses leaf extracts of the weed (*Lantana camara*) and microorganisms (Fusarium and Pseudomonas) for extracting copper as NPs from ICs e-waste. This work also demonstrates the application of biological method in recycling of metals from the e-waste for the bioremediation, which is both eco-friendly and economical [28].

Bioremediation (Phytoremediation) of Heavy Metal

Across the globe many countries are facing environmental pollution with heavy metal. To decrease the burden of the environmental pollution in the last two decades, various strategies have been made to remediate the polluted soil and water resources. Recently, the use of plants in metal extraction (phytoremediation) has appeared as economical and eco-friendly alternative in the removal of heavy metal excess from soil and water [57]. Using phytoremediation strategies Mohsenzadeh and Rad conducted a field study in a dried waste pool of a lead mine with the native accumulator plants. The experimental result demonstrated that six dominant vegetations, namely, *Gundelia tournefortii*, *Centaurea virgata*, *Reseda lutea*, *Scariola orientalis*, *Elaeagnus angustifolia*, and *Noaea Mucronata*, accumulated heavy metals. Further, *Noaea mucronata* was evaluated for its ability for the bioaccumulation ability of NPs from experimental water containers. The study shows that amount of heavy metals decreases many fold in water during 3 days bioremediation [58]. In other study Fernandes et al. used salt marsh plant, *Phragmites australis*, for the medium contaminated with Ag and AgNPs and demonstrated the importance of plants in phytoremediation [59].

Conclusions and Prospects

In this chapter we have presented an overview of emerging field of NS and NT in twenty-first century and their tremendous applications in various fields with a special emphasis on environmental applications. To minimize the increasing burden of the waste, waste in water and soil, toxic and hazardous materials, and heavy metals in drinking water and soil, application of the NS and NT in bioremediation has immense importance [35, 43, 49, 50, 55, 59]. Application of NPs or NMs or NSMs or NCs or NCMPs in bioremediation of waste, wastewater, and toxic materials is both economic and eco-friendly. NMs or NSMs or NCs or NCMPs not only catalyze degradation of waste and toxic materials, which is toxic to microorganism, but it also helps and enhance the efficiency of microorganisms in degradation of waste and toxic materials. Further phytoremediation can be applied in the removal of heavy toxic metal from contaminated soil [60]. Due to its immense potential, it is expected that their application will increase with a great leap in the near future, and it will play a critical role in sustainable development.

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