Chapter 18
Nano-Bioremediation Using Biologically Synthesized Intelligent Nanomaterials

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18.1 Introduction

The total landmass present in the world accounts for about 13,003 million hectares. 37.6% of the total landmass is classified as an "agriculture area" by FAO (Marklund and Batello 2008). The use of synthetic fertilizer and pesticides in agriculture contaminate the soil affecting its health and fertility. For instance, urbanization and industrialization in China lead to the contamination of 19% agricultural soil (Zhao et al. 2014). Toxic elements like cadmium (Cd), copper (Cu), nickel (Ni), Zinc (Zn), etc. contaminate the soils, sediments, and groundwaters, posing a high threat to the

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environment and human health (Antoniadis et al. 2017; Sarkar et al. 2017; Niazi et al. 2018). The contaminants enter the soil system through various anthropogenic activities like spillages of pesticides and herbicides, industrial discharges, and discharges from service industries (solvent use, cleaning, and paint removal). Moreover, an organic compound such as trichloroethane (TCA), trichloroethylene (TCE), perchloroethane (PCA), etc.

According to WHO, survey data of 2015 reports about 494,550 deaths and 9.3 disability life due to long-term exposure to Pb. Even many young children's deaths have occurred when exposed to Pb-contaminated soil in countries like Nigeria, Senegal, and other countries (WHO 2018). Similarly, 35–77 million people got poisoned in Bangladesh due to soil contamination (Smith et al. 2000). These incidents show the importance and severity of the impact of soil contamination.

The focus on remediation of soil is the severity of risk based on different soil and human health contaminants. Remediation is done to preserve the limiting source (soil) for the future generation. Depending on the country, region, state, and local (community), the cleanup strategy must be employed. Soil contamination can also occur in nature, depending on the geochemical properties of source rocks, weathering process, volcanic eruption, etc. (Cui et al. 2018). Anthropogenic activities like agricultural practices, industrial production, military practices, mining, smelting operation, etc. add up toxic element concentration in soil. The toxic elements are collectively called as potential toxic element (PTE) (Hou and Li 2017).

The conventional methods of soil remediation could be categorized into physical and chemical methods. Physical remediation methods include excavation and removal, barrier system that prevents entry of contaminants to the soil, etc. Chemical methods include stabilization and solidification using chemical reaction agents. Similarly, biological remediation includes employing microbes for degradation or converting toxic elements to non-toxic ones Prasad and Aranda (2018). However, physical and chemical methods are not feasible and produces toxic residues like toxic sludge.

On the other hand, biological treatment takes its own time of action (Khan et al. 2018). To overcome these limitations, an urge for new sustainable technology is required. Nanotechnology is a promising field of science at the nanoscale level. It provides a sustainable technology for removing contamination of soil, thereby enhancing its health and maintaining soil fertility (Prasad et al. 2014, 2017). Nanomaterials are highly reactive, have high surface-to-volume ratio, and are smaller in size. These characteristics made these materials useful in situ remediations of soil compared to other traditional methods (Panpatte et al. 2016). The remediation mechanism is based on sorption, reduction, or chemical oxidation (Guerra et al. 2018). The remediation is of two types in situ and ex situ. The former treats the soil in the contaminated site, whereas the latter removes soil from the contaminated site and treats it externally outside its environment. Out of which in situ remediation was found to be feasible and effective.

18.2 Conventional Technology of Soil Remediation

18.2.1 Physical Methods

It includes soil washing, vitrification, encapsulation, electrokinesis, and permeable barrier system. We will see in brief about each technique.

18.2.1.1 Vitrification

Vitrification is a process of converting materials into a glass or glass-like substances. It could be applied as both in situ and ex situ methods. It employs heat to destroy organic compounds through pyrolysis or combustion and fusing inorganic metals into glass-like materials. These glass structures will be composed of oxides of silicon, boron, and alkaline earth metals. There are three heat treatment stages called first, second, and third heat generation (Reddi and Inyang 2000).

18.2.1.2 Electrokinetic Technique

This technique is suitable for an adequate grain soil system and effective in situ solutions. Electrodes are placed into the contaminated site, and a direct electrical current is applied that induces the movement of ions present in the soil towards the electrodes. Three principles are applied simultaneously: electro-osmosis, electromigration, and electrophoresis (Czurda et al. 2002). It can be used to remove organic as well as inorganic contaminants.

18.2.1.3 Permeable Barrier System

Usually, it is called pump-and-treat technology wherein groundwater is taken out of the aquifer, treating it in a water treatment plant, then back to the aquifer, or discharging it into the ground. This method was found inefficient with organic pollutants in groundwater. So, as an alternative method, the permeable wall was developed. Lower-density nonaqueous liquids will float on the water surface, and nonaqueous dense particles will settle down at the aquifer (Starr and Cherry 1994).

18.2.1.4 Encapsulation

It is a preventive measure taken to avoid further spreading of contaminants from the actual site of occurrence. For instance, bentonite is usually used as supporting slurry walls for the trench. Moreover, thin walls are a cost-effective way of encapsulation. A heavy steel beam is placed into the ground, which is vibrated with a high-pressure jet. Similar advancements in techniques include sheet pile walls, bored pile walls, injection walls, artificial ground freezing, etc. (Philip 2001).

18.2.1.5 Soil Washing

It is a widely utilized technique for removing heavy metals and organic contaminants from the soil system. The main principle is selective categorizing fine contaminants, followed by solid/liquid phase separation of the remaining suspension. It does not directly remove contaminants but separates soil fraction containing high pollutants from low pollutant soil. The separation could be done using magnetic separation. The two primary steps are wet liberation and classification unit (Wilichowski 2001).

18.2.2 Chemical Methods

The chemical method includes precipitation, ion exchange, and membrane filter process.

18.2.2.1 Precipitation

In this technique, metal ions are dissolved with precipitant resulting in the formation of insoluble compounds. Further, these solid sediments could be removed using solid or liquid filtration techniques. Several materials are used as precipitating agents includes digested sludge, iron salts, calcium hydroxide, and aluminum iodide salts. It was found very effective against metal oxides (Bradl and Xenidis 2005).

18.2.2.2 Ion Exchange

It is a ubiquitous method for the removal of heavy metals. The basic principle behind this technique is an ion exchanger matrix with dissociable counter ions. The most common materials employ as matrices are polystyrene or polyacrylate, whereas condensation resins were made up of phenol and formaldehyde (Hahn 1987).

18.2.2.3 Flocculation

This method transforms the suspended colloidal particle into an easily separating form. Further, it can be removed using any mechanical means from supernatant or using flocculant. The main inorganic flocculation chemicals are ferric and ferrous salts, aluminum iodide salts, and calcium hydroxide (Lagaly 1986).

18.2.2.4 Stabilization

This is very effective in situ application, and it immobilizes or stabilizes, thereby reducing the mobility of contaminants. It is done by chemical/physical means. The stabilizing agents are directly injected into the contaminated site. These agents convert the toxic substance into less soluble, immobile, and less toxic (US EPA 1989).

18.2.3 Biological Methods

The most common biological approach is microbial remediation and phytoremediation of heavy metals contaminants in soil. However, the only limitation is that it takes its course of time to come into effect.

18.2.3.1 Microbial Degradation

Microbes like bacteria, fungi, actinomycetes, etc. In one way, the rhizosphere bacterial community has a close relationship with the root system, thereby forming a sheath, thus preventing toxic heavy metals (Inamuddin et al. 2021). Similarly, vesicular-arbuscular mycorrhizal (VAM) limits outside contaminants' uptake by plants (Paul and Clark 1996).

18.2.3.2 Phytoremediation

Plants have several mechanisms to sequester or stabilize the elements and prevent translocation into sensitive terrestrial portion. The plant takes up non-essential elements such as As, Cd, Na, Se, and Pb. Plants uptake of water and transpiration is an essential process (Ensley 2000). Simultaneously, photovolatilization of a volatile organic compound and certain metalloids is achieved through translocation and transpiration (Fig. 18.1).

18.3 Knowledge of Nanotechnological Application in Soil Remediation

18.3.1 Nanomaterials Used in Soil Remediation

Several types of nanomaterials could be employed in the remediation of soil. They are nanoscale: zeolite, zero-valent iron, iron oxide, phosphate, iron sulfide, carbon nanotubes, etc. Zeolite is employed as an adsorbent and catalyst for different

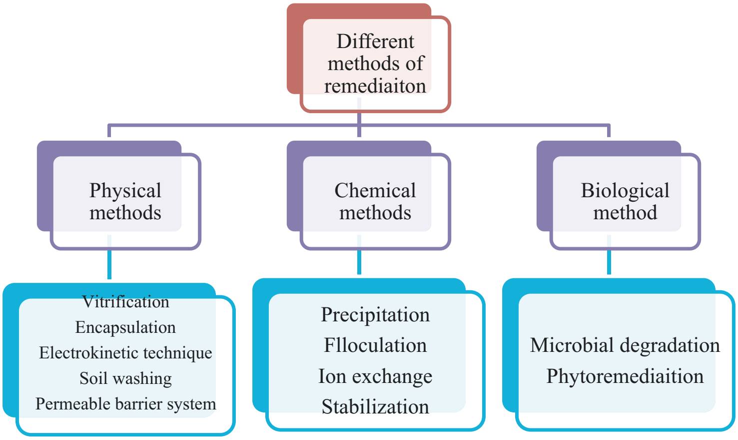

Fig. 18.1 Various methods employed in soil remediation

pollutants. These materials have a porous structure containing many cations making it readily exchangeable to other solutions. Zeolite application has provided a reduction in Hg uptake by some plants (Haidouti 1997). Then nanoiron oxide and nano-zero-valent iron oxide provides effective remediation while not having any secondary contamination. Since iron is already present in the soil, it is cost-effective and very effective against stabilizing heavy metals. This is due to their very high adsorbing capacity, which is being studied in a different context (Hua et al. 2012). Phosphate-based nanoparticles have a similar effect on pollutants and produce highly insoluble phosphorous compounds for absorbing heavy metal pollution. These particles were utilized in the soil amendment. Figure 18.2 depicts the various nanomaterials used in soil remediation.

18.3.2 Nano-Bioremediation of Organic Pollutants

Bioremediation is a practical, eco-friendly method of soil remediation using biological organisms as a tool for remediation (Kumar et al. 2021). It will be of double benefit when nanotechnology could be coupled with bioremediation. Nano remediation was utilized for chemical decontamination over the last two decades. However, integration in bioremediation is a new development, still at its infantry stage. Singh et al. studied the effect of stabilized Pb/Fe bimetallic nanoparticles on lindane contamination in soil followed by treatment using *Sphingomonas* sp. strain. It showed better efficacy in combining both techniques (Singh et al. 2013).

Nanomaterials enhance the availability of organic contaminants to biological agents. Similarly, altered membrane selectivity phytotoxic nanomaterials increases organic pollutants (Gong et al. 2018). Moreover, Le et al. 2015 studied the efficacy of bimetallic Pb/nFe on chemical oxidation of hexachlorinated biphenyls; further, it was degraded using *Burkholderia xenovorans* (Le et al. 2015). Similarly, De la

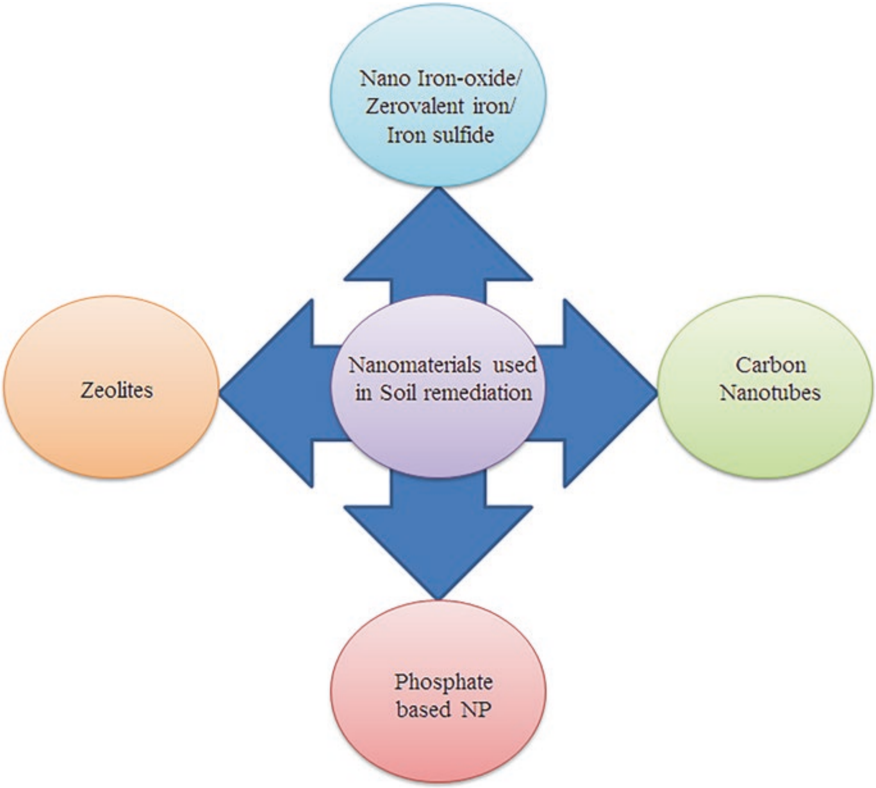

Fig. 18.2 Different nanomaterials utilized in soil remediation

Torre-Roche et al. also investigated DDT's accumulation by fullerene nanoparticles has increased the uptake of DDE significantly (De la Torre-Roche et al. 2012). Wu et al. also investigated the reduction of toxicity and translocation of polybrominated diphenyl ethers to Chinese cabbage by the application of Ni/Fe bimetallic nanoparticles. On the other hand, materials like carbon nanotubes harm *Chlorella vulgaris* grown in diuron-contaminated soil. Much work must be established to use this potential technique effectively.

18.3.3 Nano-Bioremediation of Inorganic Pollutants

Remediation of inorganic pollutants like heavy metals could be achieved by nano-bioremediation. Liang et al. showed a significant impact by nano-hydroxyapatite and nano- carbon black on lead phytoextraction by ryegrass (*Lolium temulentum*) (Liang et al. 2017). Hu et al. suggested that the accumulation of heavy metals in plants nanomaterials brings about a change in cell wall permeability (Hu et al. 2015). Different nanomaterials respond differently to various heavy metals and uptake of the same in plants (Gong et al. 2018).

18.3.4 The Fate of Nanoparticles Used in Soil System

Reports related to the fate of nanoparticles in water systems are more, whereas much work has not been done in the soil system. Nanomaterials deployed in the soil for various purposes interact first with soil components (organic or inorganic), and then depending on their nature, it undergoes physical, chemical, or biological changes (Darlington et al. 2009; Ben-Moshe et al. 2010). The most common physical changes in aggregation with the same type nanomaterials (homoaggregation) or aggregation with other soil constituents or pollutants (heteroaggregation). As a result, it reduces nanoparticles' mobility and behavior (Lowry et al. 2012; Batley et al. 2013). Soil organic matter also plays a vital role in behavior and the fate of nanomaterials by adsorption and stabilization. Even at a low concentration of 0.05 mg, L-1 of HS revoked the toxicity of nC60 (Lei et al. 2018). It also has an impact on the solubility and stability of NMs.

Since nanoparticles size is the minimal range, it can enter plants through osmotic pressure, cell wall pores, and capillary force. In most cases, the application of NMs over plants shows a positive result, but some plants also show a phytotoxic effect against NMs (Mazaheri-Tirani and Dayani 2020). The toxic effects of NPs could be observed in germination, biomass, and root elongation (Lin and Xing 2007; Racuciu and Creanga 2007; Lee et al. 2010). Similarly, it has a toxic effect on soil microbes too. Wu et al. (2020) showed carbon nanotubes' effect on functional genes and pathways of soil microbial communities, especially on carbon and nitrogen cycles. The toxicity of NMs is based on the concentration, nature, and synthesis process (Chen et al. 2019).

18.4 Green Synthesis of Nanoparticle

The very first essential step in nanotechnology is the synthesis of desired nanoparticles according to its target function. Nanoparticles could be synthesized through physical, chemical, and biological methods. There are numerous reports on the techniques of synthesizing nanoparticles. The most used physical approach includes evaporation-condensation, thermal decomposition, sputtering and sonication, etc. In comparison, chemical approaches include the sol-gel method, colloidal method, and chemical reducing technique using reducing agents.

These synthesis techniques could be categorized into the top-down method and bottom up methods. The former approach is made by etching nanoparticle from a substrate i.e., scaling down a bulk material to nanoparticles. In contrast, the other method is based on engraving particles onto a substrate, i.e., atoms are stacked to get a crystal plane, which is further arranged to get nanostructures since these methods use inorganic reagents that make them toxic to the environment and human health.

Therefore, an alternative method using bio-organism (plants extract, microbes, algae, secondary by-products like protein, lipids, etc.) was adopted for NP synthesis

(Prasad et al. 2016, 2018; Srivastava et al. 2021; Sarma et al. 2021). Green synthesis of nanoparticles makes use of eco-friendly, non-toxic, cost-effective reagents. So, the biological method of synthesis undergoes a bottom-up approach using reducing and stabilizing agents (Singh et al. 2011; Aziz et al. 2014, 2015, 2016, 2019; Joshi et al. 2018). Synthesis of NPs by using agro-waste should be employed to reduce the cost (Sangeetha et al. 2017). The feasibility of scaling it up to mass production will lead to waste utilization and reducing the production cost.

18.5 Intelligent Nano-Biosensors for Soil Remediation: An Innovative Approach

A biosensor is an analytical device that senses the biological changes and provides data into readable form. It comprises three crucial components, namely, detector, transducer, and bioreceptor (Dhole and Pitambara 2019; Singh et al. 2020). A biosensor at the nanoscale is called a nano-biosensor.

For the detection of heavy metals in the soil system, microbial cells can react to an available fraction of heavy metal ions, developed like luminescent bacterial sensors (Ivask et al. 2004). The application of intelligent nano-biosensors for environmental remediation is at the infantry stage. The concept behind intelligent nano-biosensors is they analyze the contaminated site with their biosensor capability and procure data, analyze it, and provide an apt solution to be employed in the site. For such a high-end device, more research must be taken to understand the soil system's pollutants. Then pollutant mediated changes in soil composition must be determined—similarly, nanomaterials' effect in various soil systems, its effect on soil microbes, and associated plants.

18.6 Conclusion and Future Perspective

Despite the promising potential of nanomaterials in application over environment and soil remediation, extensive research has been done in the development of new innovative technology for soil remediation. The limitation present in the current technology of remediation stresses nanotechnology shows higher results than conventional techniques. Since different nanomaterials react differently to pollutants, more research has to be done in understanding such effect at the same time to know about the fate of nanomaterials in the soil system. Extensive research should be done in understanding the fate of nanomaterials in the soil system and its toxic effects. Similarly, government bodies should implement regulations and guidelines for nanomaterials used in soil remediation. The effect of different nanomaterials in different soil systems should also be analyzed. So, green synthesized nanomaterials can be employed as non-toxic to the environment and a sustainable one. Combining nanotechnology strategies with bioremediation and biosensor in soil remediation is beneficial and could be used for future remediation. Nanotechnology will provide effective remediation of toxic pollutants in a cost-effective, sustainable, and without much disturbance in ecosystem balance.

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