Chapter 22
Nanobioremediation and Its Application for Sustainable Environment

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Abstract People in the twenty-first century are struggling for proper remediation and management of huge amounts of contamination which is generated daily from various sources, and cause environmental degradation and posing a challenge to the survival of the global biological community. Nanomaterials deliver amazing properties, are economically viable and eco-friendly and they can therefore be used effectively in the bioremediation of environmental contaminates. The technique of nano-bioremediation is a hybrid method, which can be used for the detoxification or remediation of pollutants through the use of nanotechnology. The nanoparticles (NPs) used in the method of bioremediation of pollutants can be synthesized biologically from various plant extracts, bacteria, algae, enzymes and fungi. The application of these synthesized biogenic NPs exhibits high performance in the remediation of contaminates from our ecosystem, offering a sustainable and highly promising approach for the cleaning up of the environment. The technique of nano-bioremediation is an excellent sustainable advanced technology for the remediation of pollutants from the ecosystem through the application of biologically produced NPs. There are several metallic NPs, such as Zn, Fe, Ag, Cu and Au, that can be used in the remediation of contaminants, but these are toxic to many essential soil microorganisms. The use of NPs synthesized biologically by using various plant extracts, yeasts, algae, bacteria and fungi is eco-friendly and sustainable, proving highly effective for the detoxification of some specific pollutants from the environment. Hence, the combination of remediation and biosynthesis by using nanotechnology results in sustainable development and, eventually, a sustained environment.

Keywords Biosynthesis · Nanobioremediation · Sustainability · Eco-friendly · Detoxification · environmental clean-up

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22.1 Introduction

The complete removal, or even the decrease, of organic and inorganic contaminates, from the environment of polluted sites through the use of nanomaterials (NMs) or nanoparticles (NPs) produced by algae, bacteria and fungi assisted by nanotechnology is termed nanobioremediation. In the present day, environmental contamination is considered a major issue throughout the world and a threat to the biotic community. The development of excessive industrial complexes over the past two centuries is the cause of the addition of a large amount of toxic contaminates or unused waste materials to the air, soil and water and the cause of health hazards among both human beings and animals (Sherry Davis et al. 2017; Yadav et al. 2021). Sustainability towards the environment is defined as responsible collaboration with the environment to prevent the degradation or depletion of natural resources and permit the maintenance of environmental quality on a long-term basis. However, the worldwide definition of sustainability is simply sustainable development which also leads to environmental degradation, and the programs of sustainability now comprise the restoration and protection of the natural resources of the environment. One of the vital strategies for the restoration of natural resources is bioremediation, which is carried out by using microbes. The term "remediate" is used to remove the contaminates, whereas the term "bio-remediate" means the removal of contaminates from the environment by using biological organisms. The technique of bioremediation is highly beneficial to the traditional process of remediation because it is highly capable and economical, the optimization of biological and chemical sludge (with no need for any supplementary nutrient), selectivity towards specific metals and the possibility of recovery of metals and restoration of biosorbent. However, this method of remediation is not practicable for the sites polluted with some specific toxic materials, especially aromatic and chlorinated compounds, which are hazardous to most of the microbial community. The NPs possess a high capacity for remediating such kinds of hazardous pollutants and produce a healthy substrate, which facilitates microbial activity and enhances the level of environmental clean-up. Although NPs are synthesized by a physicochemical process, the synthesis by biological route is more sustainable and beneficial (Pandey 2018; Gothandam et al. 2020). In the process of nanobioremediation, the NPs used may be either non-metallic or metallic and of different dimensions. The metallic NPs are of various kinds, including single metal NPs, carbon-based NPs, modified NPs, bimetallic NPs, etc. The NPs of metals are applied in various fields, including drug delivery, the synthesis of nanocomposites, electronics, medical imaging, sensors, non-linear optics, antimicrobial agents, biolabelling and hyperthermia of tumours. The microorganisms such as algae, bacteria, protozoans, fungi, etc. are stimulated during the growth process by adjusting or modifying the environmental condition. If the level of the contaminates is extremely high, then there is a possibility that the microorganisms might be destroyed; hence, in order to solve this problem the biological process of nanotechnology associated with physiochemical approaches is commonly termed "nanobioremediation" (Samson et al. 2021; Patra Shahi et al. 2021).

22.2 Nanobioremediation

The rapid establishment of industrial complexes, deforestation, population growth and the development of technology have led to the addition of excessive amounts of contaminants into the environment. The vital contaminants such as toxic inorganic, organic materials, heavy metals, chlorinated compounds and other complex materials are hazardous not only to human society but also to the entire biological world and environment. Over the past two decades, NPs have been used effectively for the treatment materials, owing to their eco-friendly nature, high efficiency and cost-effectiveness. The Fe-NPs are regarded as the first NP used for the remediation of contaminates from the environment. The process of nanobioremediation is a promising method of using the combined form of biological and physicochemical technology. This process used NPs to degrade or break down the pollutants to the concentration up to the favourable level of biodegradation and results in the remediation of pollutants. The technology of nanobioremediation is highly effective in cleaning up the toxic pollutants from soil and water by using NPs, which are synthesized biologically from microorganisms or phytoextracts. The zerovalent Fe-NPs are highly effective in the treatment of acidic water containing a high concentration of heavy metals (HMs) because the surface of the NPs is able to adsorb the HMs at its surface. The extreme chemical, thermal stability, excellent affinity and adsorption properties of CNTs proved themselves as a beautiful candidate material for remediation of pollutants from the environment (Rajput et al. 2022; Pete et al. 2021). It is a perfect replacement for activated carbon for cleaning up inorganic and organic contaminates along with heavy metals such as Cr (VI), Pb, Zn, Hg, etc. The Zn NP is a photocatalyst, having semiconducting characteristics, and is capable of the full degradation of several toxic substances from dyes and pharmaceutical drugs. Again, the NPs of Au, Cu and Ag have different applications in a diversified field and are found to be mainly effective against the remediation of organic dyes from wastewater. The technique of nanobioremediation is a multi-technology method of remediation of contaminates because of its sustainability, efficiency, non-toxicity, time duration and availability of resources. The NPs of TiO_2, metallo-porphyrinogens, dendrimers, CNTs and swellable organically-modified silica (SOMS) are potentially effective in the remediation of contaminates in both in-situ and ex-situ methods. The NPs of TiO_2 offer high performance in the remediation of a wide variety of chemical fertilizers, pesticides, insecticides and herbicides by the method of photocatalysis from the resources of infected groundwater (Kumar and Gopinath 2016; Fang et al. 2011). NPs such as Fe, Ti, Cu synthesized biologically in combination with the NPs of metal catalysts such as Au, Pt, Ni, Pd increases the rate of redox reaction. The NPs of Pd possess the capability of catalyzing the method of reduction of $C_2H\ Cl_3$ to C_2H_4 without the production of any vinyl chloride as a by-product. The NPs of silica stimulate the remediation of Pb, the NPs of Zn remediate CS_2 from air and hydroxyapatite in nanocrystalline form is effective for removal of Cd and Pb. NMs such as fullerenes, zerovalent nano-Fe, ZnO, TiO_2 NPs and CNTs are highly effective in the remediation of the highly toxic pollutants such as DDT, carbamates and heavy metals such as As, Cd, Cr and Pd from the soil. The Fe-NPs synthesized biologically can be widely applied in the remediation of 2, 3, 7, 8-tetrachlorodibenzo-p dioxin, Lindane, PCBs, dyes, pesticides and hydrocarbons by using bacterial metabolism (Yadav and Ahmaruzzaman 2021).

The remediation of different kinds of pollutants, the use of nanomaterials (NMs), and their method of synthesis were represented in Table 22.1.

The nanobioremediation is highly popular for the following two reasons:

- The first one is the presence of NPs, which promotes the increase in the surface area, leading to the increase in the rate of reactivity.
- It is the cause of the requirement of less activation energy, for which the reaction can proceed easily and effectively.

The technique of surface plasmon resonance (SPR) is another technique, which is used for the detection of toxic heavy metals by using NPs. Finally, we can conclude that nanobioremediation is highly effective for the remediation of groundwater, solid wastes, soil, surface water, wastewater and especially effective for the removal of heavy metals and uranium (Patel et al. 2020).

Table 22.1 Kinds of NMs, their method of synthesis and pollutants remediated (Rizwan et al. 2014)

Kinds of NMs	Methods of synthesis	Pollutants remediated
Nanoparticles (NPs) of metals	Photochemical Electrochemical Thermochemical Biochemical	Pt, Ni, Rh, Cu, Pd, Au, Ir, Ag, Co, FeNi, CdTe, Cu_3Au, ZnS, CoNi, CdSe
Carbon NMs	Arc-discharge Chemical vapour deposition Laser ablation	MWNT, SWNT, fullerenes
Nanocomposite	Innovative techniques	Nanocomposite of polyethylene oxide and polyethyleneimine; conjugated polymer composites, CNT epoxy composites include hydrocarbon polymer composites, fluoropolymers, polyethylene glycol, CNTs with polycarbonates, polyester polyamides, and so forth
NPs of metal oxide	Hydrothermal Reverse micelles method Solvothermal Electrochemical deposition Sol-gel technique	ZnO, MgO, $BaSO_4$, Fe_2O_3, Fe_3O_4, TiO_2 $BaCO_3$
Bionanomaterials	Biological	Viruses, protein NPs and plasmids
Polymer NMs	Electrochemical method of polymerization	Nanowire of polypyrrole, poly(3,4-ethylenedioxythiophane) dendrimers (PAMAM), polyaniline

22.2.1 Challenges of NPs in Nanobioremedaition

The use of nanotechnologies for the remediation of pollutants is, at present, only confined to the laboratory scale and its industrialization for application in practical purposes is still a challenge. Although NPs show promising outcomes for the remediation of pollutants, there are some disadvantages related to their application in polluted sites, such as decreases in reactivity over time, and the impact on microorganisms and transportation.

Example The NPs of some metals gradually decreases their reactivity after the use of a particular period of remediation owing to their restriction of movement through obstructing the effectiveness of soil. Therefore, to overcome these difficulties suitable stabilizers such as lactate are added in order to enhance the ionic mobility of the Fe-NP within the soil.

Another vital problem of using NPs in the process of nanobioremediation is the limited information about the impact of NPs related to the growth of microbes. Some NPs show a toxic effect on the microbial community. Although several experimental studies were carried out to learn about the impact of NPs or nanotechnology on the microbial community in a controlled and regulatory manner, the results are still contradictory. Some of the experimental studies show inhibitory impact on microorganisms such as *Escherichia coli* and *Staphylococcus aureus* have been observed, whereas in a few cases the stimulatory effect of NPs is found because of electron donation to microorganisms such as methanogens and bacteria. The existence of soil microorganisms in the environment is highly essential and is considered a vital part of the natural cycle of nutrients in our ecosystem, playing a key role in the remediation of inorganic and organic pollutants and the immobilization of heavy metals from nature. The substantial decrease in the population of soil microorganisms is the cause of weakening the resistance power of soil towards the remediation of contaminants. Several different mechanism pathways have been suggested to explain the toxicity of NPs leading to the death of microorganisms, which includes the disruption of the cell membrane by generating reactive oxygen and the interruption of the absorption of nutrients by the cell membrane, resulting in the decrease in growth of microbes. In the case of the growth of the fungal colonies, no impact of NPs is observed. Again, some specific microorganisms are capable of secreting particular polysaccharides and enzymes to protect themselves from the toxicity of the NPs (Zhou et al. 2022; Ali et al. 2016). This problem of NP toxicity can be prevented by coating the NPs with some polymeric materials. The various use of NMs are given in Fig. 22.1.

22.2.2 The Principle of Nanobioremediation

The method of nanobioremediation possesses the capability of decreasing the average cost of remediating large-scale contaminates in a shorter space of time. The basic principle of nanobioremediation may be defined as the degradation of waste

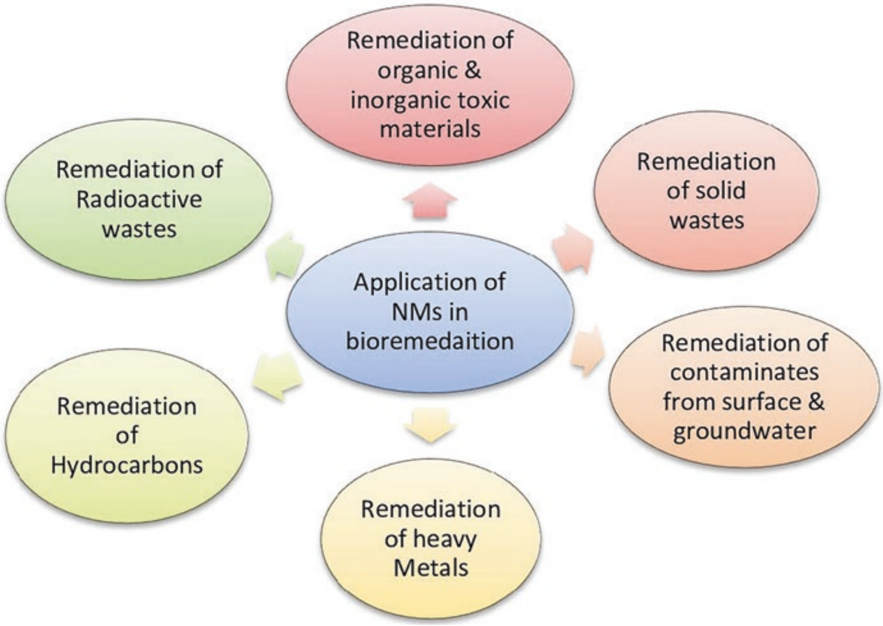

Fig. 22.1 Different application of NMs in the process of bioremediation

materials (contaminates) by using a catalyst in the nanoscale as a medium, which permits these to enter deep inside the toxic contaminants and remediate these wastes safely through different microorganisms without degrading the surrounding environment. These microbial communities exist worldwide and are competing with each other for their existence and growth. These microbes provide many benefits to the environment such as remediating heavy metals (HMs) into a non-toxic state through the mineralization of waste organic pollutants as end products (H_2O, CO_2) may be converted into different metabolic intermediate products, which can be utilized as metabolites for the growth of these microbes. The use of these toxic materials causes defence of their cell walls due to the formation of degradative enzymes, which make these suitable for fighting with different HMs and also consumed by the microbial community. For successful and effective nanobioremediation, now that modified microorganisms are being used, which may be able to control and regulate the activity of microbes, and also the mechanism of their growth activity in the polluted sites is easily recognized. The response of these microorganisms concerning changes in climatic conditions can be easily monitored. After the absorption of the pollutants by the microorganisms, special kinds of membranes are created around these microbes, which support them in protecting them from the access of foreign materials into the cells. The vital fact in which the technique of nanobioremediation defines is the dimension of the NPs, because the NPs are extremely small particles, being generally bacterial or fungal, which can easily be inserted within the contaminates with the microorganisms and are able to degrade the pollutant matter. The NPs show improved activity than microparticles because NPs penetrate easily into the sites of pollutants and facilitate the clean-up process than the usual bioremediation technology. The substances of nanoscale dimension used for the remediation of the contaminated sites include NMs, nanoclusters, nanostructured materials, etc. The added NPs are also used for the further immobilization of the cells of the microorganisms, which may be used for recovering some particular chemicals (Parthipan et al. 2021; Dzionek et al. 2016).

22.2.3 Challenges of Nanobioremediation

As mentioned earlier, the use of nanotechnologies for the remediation of contaminates from the environment is now restricted just to the laboratory scale and its industrialization and commercialization in the application of practical field is still a challenge for researchers. Although the use of NPs in the method of nanobioremediation provides amazing results for the removal of pollutants, there are still some limitations related to their application such as transportation, the influence of microorganisms and the loss of reactivity over time.

Example Some NPs of metals become inactive after their reactivity of some specific period during the remediation of pollutants from the contaminated sites owing to the limitation of passing fluids because of the blocking impact of soil. Hence, to solve these problems stabilizers such as lactate can be used to improve the rate of mobility of Fe-NPs in soil.

The toxicity of NPs with regard to microorganisms is a major challenge towards nanobioremediation, which results in the death of some kind of microorganisms due to damage to the cell membrane by generating reactive oxygen, a decrease in the absorption of nutrients through the cell membrane through retarding the rate of growth. The influence of the filter is generally carried out at the ultimate phase of deposition, which is the cause of clogging or blocking the pores of the soil and prevents the passage of any particles inside the soil. Therefore, the process of filtration is a vital limitation and challenge for the application of nZVI remediation because it restricts the NPs to reach the bottom layer. Again the NPs have more density than water, which is the cause of settling the NPs in a fluid medium and contributes, in part, to the clogging effect. Hence, to increase the mobility, reactivity and stability of the NPs various kinds of improved surface coatings materials have to be developed. The use of inert polymeric material for coating is an effective process of stabilizing NPs with the help of sodium carboxymethyl cellulose (CMC), lactate and guar gum as additive materials (Azubuike et al. 2016; Vázquez-Núñez et al. 2020).

22.2.4 Interaction of NPs with Microbes and Soil

The detailed explanation of the interactions of the NPs with the native microbial community and soil particles is a highly challenging job owing to a lower number og monitoring points and few periods of monitoring. The major parameters monitored and controlled at the time of application for the remediation of the contaminates are the oxidation-reduction potential exhibited by nano-zerovalent iron (nZVI) over time, electrical conductivity, the concentration of Fe, pH, dissolved oxygen in case of groundwater, etc. After the insertion of nZVI, the redox potential decreased to a substantial level at the subsurface, a finding which is confirmed by the production of H_2 gas. Although the addition of nZVI suspension made the system alkaline, no appreciable change in pH at the subsurface is observed because of buffering through the groundwater. The existence of micro-biota in the soil normally depends on the properties and level of contamination of the sites and creates some indigenous species, which possess the ability to to degrade or remediate the waste contaminant of the soil. The addition of nZVI stabilizes with the polymeric materials and functions as a promoter for growth by offering massive biodegradation or bioremediation of toxic organic materials and facilitates decontamination in the polluted sites. The formation of complex compounds with Fe^{3+} and Fe^{2+} after the addition of a suspension of nanoferro materials can cause chemical changes on the surfaces of NPs under a normal ambient environment. These compounds formed influence directly to the native flora and might interfere with the long-term immobilization of toxic inorganic or metallic contaminates such as uranium (IV) and chromium (VI) (Cao et al. 2019; Perea Vélez et al. 2021).

22.2.5 Advantages of Nanobioremediation

The major advantages or benefits of applying NPs in coupling with bioremediation are as follows:

- The increase in the rate of removal of contaminates because of the comparatively greater surface area of the NPs
- More reactivity towards the contaminants
- NPs can easily penetrate or diffuse inside the zone of contamination, which the microorganisms are unable to reach.
- Much enhanced reactivity to redox-amenable pollutants
- Very much quicker rate of degradation than normal microbial degradation
- The production or manufacturing cost is comparatively less
- The NPs added can immobilize microbial cells
- Suitable NPs and microbes must be chosen according to the environmental conditions for the degradation of toxic waste materials.
- It is a completely sustainable and natural process with minimal or almost no side effects

- It can be applied in both ex-situ and in-situ conditions of the contaminated sites for improving the environmental condition.
- The rate of reversal is very quick and satisfactory; the water and soil can also be again reutilized for other different purposes
- In this technique, the toxic organic materials are effectively degraded into simple non-toxic substances and cannot be moved to other areas.
- In nanobioremediation, a sensor can be used for environmental variability
- Among the various NPs the nZVI and its derivatives are found to be more important in nanoremediation
- Because of the improved efficiency, the low cost of treatment and sustainability and its use at a large scale the in-situ method of remediation is more preferable and feasible (Singh et al. 2020; Koul and Taak 2018).

22.2.6 The Science of Nanobioremediation

Presently, a huge number of NMs have been used successfully in the treatment of wastewater, air and soil. The removal of toxic contaminates by using nanobioremediation is effective because of some of the amazing properties of the NMs, which include a large surface area, an extremely high capacity of reactivity, the quick rate of dissolution and the higher ability of sorption. These unique properties play a vital role in cleaning up the contaminants from the environment. Several approaches based on nanotechnology were found to be successful or effective only on a laboratory scale, and apparently very few of them can be used in commercial settings. However, there are some sings that among these processes some, such as nanoadsorbents, nanotech-based membranes and nano-photocatalysts, have proved popular and also commercialized. The various properties possessed by different NMs are highly advantageous in using bioremediation to clean up the ecosystem (Abatenh et al. 2017).

Example The NMs applied for nanobioremediation have normally more volume of contact for interaction with the pollutants causing an increase in its reactivity (Jeevanandam et al. 2018).

Furthermore, NMs possess a quantum effect, which is the cause of decreasing the necessary activation energy and making feasible the chemical reactions associated with the bioremediation. Another fact exhibited by the NPs is surface plasmon resonance, which can be effectively utilized for the identification of the toxicity level of the affected regions. According to the dimension, a number of non-metallic and metallic NMs have been used for bioremediation of contaminates and the cleaning up of the environment. This is because the NPs possess the capability to infiltrate or diffuse into the zone of contamination, where the micro-particles are incapable of entering and the reactivity of the NPs towards redox-sensitive contaminates is considerably higher. Experimentally, it was found that the Fe^0 in the nanoscale form on coating with oxide possesses the capability to produce weak

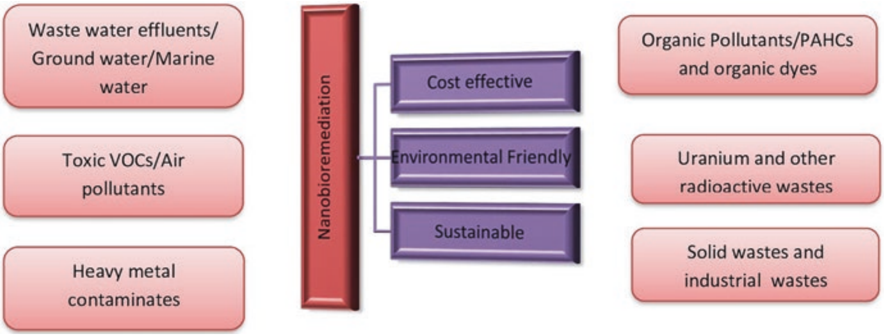

Fig. 22.2 Schematic diagram representing the different contaminate targets and the three most significant attributes of nanobioremediation

complexes on combination with CCl_4 and pollutants of a similar category, leading to the increase in its reactivity. Usually, CCl_4 undergoes reaction through electron transfer and is transformed into either CO_2, or CH_4, formate, but in the field assessment and batch experiments halogenated aliphatic hydrocarbons, trichloroethene and benzoquinone can be degraded into some simple by-product materials of comparatively much less toxicity (Rahman and Singh 2020). Figure 22.2 represents different contaminate targets and the three most significant attributes of nanobioremediation.

Moreover, the destruction of pentachlorophenol (PCP) is also carried out in the laboratory by using TiO_2 nanotubes via photoelectrocatalytic reaction and single-metal NPs can also be applied as biocatalysts for the reduction and removal of chlorine (Shen et al. 2009).

Again, an assessment of bioreductive was carried out, in which it was detected that Pd(0) NPs were successfully deposited inside the cytoplasm and cell wall of *Shewanella oneidensis*. The addition of some electron donors, including H_2, formate and acetate, is the cause of charging Pd(0) along with the formation of H* radicals. When a chlorinated toxic pollutant like PCP comes into contact with Pd(0)-coated, charged *S. oneidensis*, the H* radicals reacts on the Pd (0) and the cause of the successful removal of chlorine. The microbial cells possess the ability of biorecovering or degrading some particular chemicals on immobilization with the added NPs. The magnetic Fe_3O_4 NPs on modification by the addition of ammonium oleate were on coating with the cell surface the microorganism *Pseudomonas delafieldii* exhibits magnificent results. By the use of an external magnetic field, the cell walls were detached from the bulk solution and subsequently recycled for remediation or treatment. The NPs coated with the microbial cells can able to desulfurize the organic sulfur present in the fossil fuel in a system of bioreactors (Baragaño et al. 2020; Kumari and Singh 2016).

22.3 Various NPs Used in Nanobioremediation

The different NPs used in the process of nanobioremediation are as follows:

22.3.1 Nano-Fe and Its Related Derivatives Applied in Bioremediation

The nanosize of zero-valent iron (nZVI) can be suitably synthesized and effectively applied for the removal of As(III), which is normally recognized in groundwater, mobile and extremely dangerous for human health. Through the application of nZVI, the toxic contaminate As (IV) can be effectively eliminated from groundwater because arsenic is converted into a colloidal state and serves as a reactive barrier material. The NPs of nZVI supported by ferragels are able to immobilize and separate Cr (VI) and Pb (II) at a rapid rate from the aqueous solution by reducing Cr (VI) to Cr (III) and Pb to Pb (0), but Fe is oxidized to goethite (α-FeOOH). The NPs of (Fe/PAA) of nZVI supported by poly (acrylic acid) were identified to be extremely effective for the separation of chlorinated hydrocarbons from soil and groundwater. The nano-Fe serves as a reactive wall in the path of contaminated groundwater plumes for the bioremediation of the toxic halogenated organic materials. NPs of Fe and Ni in the ratio of 3:1 show very good performance in the separation of halogen from trichloroethylene. The toxic substance, such as PCP, can be removed from the aqueous solution through the application of zero-valent metals (ZVMs). This is due to the dechlorination or sorption at the surface associated with ZVM. Recently, it is shown that DDT can be decontaminated by eliminating Cl_2 and its associated compounds, which is extremely effective by the application of fine nanopowdered zero-valent Fe. This zero-valent Fe in nanopowder form in buffered aqueous solution without or with Triton X-114 (non-ionic surfactant) can be highly effective in the elimination of DDT, DDE [2,2-bi's(p-chlorophenyl)-1 and DDD [1,1-dichloro-2,2-bis(pchlorophenyl)ethane]. Specifically, we can say that Fe possesses the capability of elimination of DDT, DDE and DDD effectively (Bhalerao 2014; Betancur-Corredor et al. 2015). Table 22.2 represents the remediation of different pollutants significantly by using nano-iron technology.

22.3.2 Use of Dendrimers in Bioremediation

The term "dendrimers" is a Greek word, combining the two words "dendri", which means the branch of a tree, and "meros", which means part of a tree. Dendrimers are usually monodisperse and highly branch macromolecular compounds, which are recently recognized in the field of polymers. The compound dendrimer is a polymeric material, which is a giant molecule comprisingseveral small molecules

Table 22.2 Remediation of different pollutants through nano-iron technology (Rizwan et al. 2014)

Carbon tetrachloride (CCl_4)	Chrysoidine	Cis-dichloroethene
Trichlorobenzene $C_6H_3Cl_3$	Cadmium (Cd)	NDMA
Chloroform ($CHCl_3$)	Tropaeolin	Trans-dichloroethene
Chloromethane (CH_3Cl)	Acid red	Vinyl chloride
Dichloromethane (CH_2Cl_2)	Acid orange	1,1-Dichloroethan
Orange II	Trichloroethane ($C_2H_3Cl_3$)	Nitrate (NO^{3-})
Hexachlorobenzene	Mercury (Hg)	PCBs
Lindane	Tetrachloroethene($C_2H_2Cl_4$)	Perchlorate
Pentachlorobenzene ($C_2H\ Cl_5$)	Nickel (Ni)	Dioxins
DDT	Arsenic (As)	Dibromochloromethane
Dichlorobenzene	Bromoform($CHBr_3$)	TNT
Chlorobenzene (CH_5Cl)	Dibromochloromethane	Dichromate

(monomers) by covalent bonds. Dendrimers have some specific important applications and also some potential applications. Dendrimers are highly branched and monodispersed giant molecules having controlled or regular design and composition containing three components:

- A central core
- Radial symmetry or interior branch cells
- A peripheral group or design containing three components

Since dendrimers contain many voids on their surface, it is easier for them to interact with other materials. Hence, NPs composite associated with dendrimers can be applied for increasing the catalytic properties in many chemical reactions. This kind of modern composite material can be efficiently used for the treatment of water, wastewater and dyes because of their greater surface area, lower toxicity and high reactivity. The composite PAMAM/dendrimers are specifically used for the treatment of water, since they are a non-toxic and effective agent for water treatment. A new simple filtration unit is now developed for of organic contaminants by using TiO_2 porous ceramic filters, where the pores present in its surfaces were saturated with a dendrimer of alkylated poly(propylene imine), a β-cyclodextrin or poly(ethyleneimine) hyperbranched polymer producing a hybrid model of inorganic/organic filter modules which has a greater surface area and high mechanical strength (Najafi et al. 2021; Sudhakar et al. 2020).

22.3.3 Carbon Nanotubes (CNTs) and Nanocrystals Used in Bioremediation

CNTs are now treated as a new modified adsorbent used for the removal of different toxic heavy metals such as Cd, Cr(VI), Pb, Ni, Cu, Hg Zn, As and Co. Hence, CNTs are considered an interesting adsorbent material for the remediation of heavy metals and its ions from aqueous solutions. Now, CNT(s) and cyclodextrins (CD) are effectively used as suitable less cost materials for the treatment of water and wastewater (Mubarak et al. 2013).

Example FeO/multiwall CNTs on modification by cyclodextrin (FeO/MWCNTs/CD) were synthesized by adding 1,6-diisocyanatohexane as the cross-linking agent, which is found to be an interesting material for remediation of organic contaminates (Hu et al. 2010).

The efficiency of the removal of p-nitrophenol from water by using the NMs of these composite is around 70%. Again another study identified that the NMs of FeO/MWCNTs/CD possess the outstanding capability of regeneration and are a promoter of excellent low-cost material in the treatment of water and wastewater. Therefore, some specific exceptional properties of carbon-based NMs, including CNTs, nanocrystals facilitate advanced technologies to recognize and solve a wide range of environmental problems and can be applied as sorbents, technologies for renewable energy, membranes of high-flux, antimicrobial agents, environmental sensors, or as depth filters which help in the strategies for pollution prevention. The NMs, such as multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs) and also hybrid carbon nanotubes (HCNTs), show excellent performance for the removal of toxic C_6H_5 (C_2H_5) from contaminated water. The SWCNTs show a better capability of sorption for ethylbenzene than MWCNTs and HCNTs and serve as an excellent material to maintain good water quality. Hence, SWCNTs can be applied to remediate the environment to avoid diseases caused by ethylbenzene. Now, CNTs and CDs, both in combination, can be used for the monitoring and treatment of water pollution. Recently, another NM composite (CD-co-hexamethylene/toluene-di-isocyanate polyurethanes modified by CNTs) has been developed, which can be effectively applied for the removal of organic pollutants from wastewater up to a very low level of concentration. The polymer nanocomposites associated with CNT, thiacalixarenes and calixarenes are observed to be an appropriate material for the removal of organic pollutants such as p-nitrophenol and some metal pollutants such as Cd^{2+} and Pb^{2+} from contaminated wastewater. The NM CNTs calcium alginate (CA) possesses the excellent property of adsorption of copper and possesses almost 69.9% copper removal efficiency, even at a pH as low as 2.1. The NMs of magnetic-MWCNT composite can be successfully used for the removal of cationic dye from contaminated water and MWCNTs can be used effectively for the removal of Ni^{2+} ions from industrial effluents (Zhang et al. 2019; Sivashankar et al. 2014; Bina et al. 2012).

22.3.4 Enzyme NPs Used in Bioremediation

Proteins and enzymes are found to be highly precise and effective, which serves as a biocatalyst for the bioremediation of many contaminates. Figure 22.3 shows different approaches of enzymatic bioremediation.

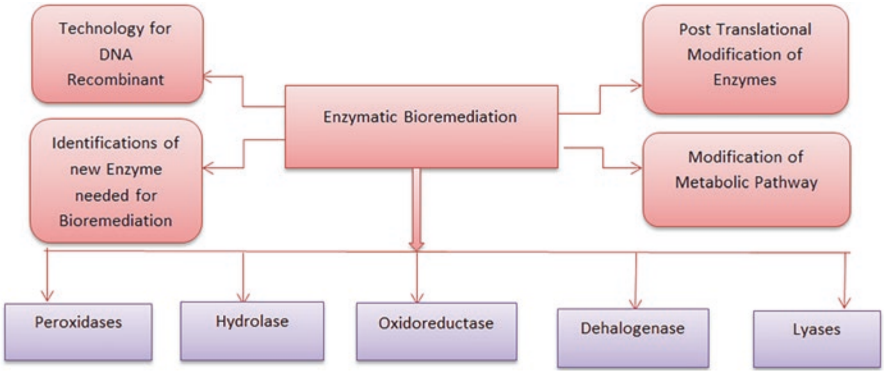

Fig. 22.3 Approaches of enzymatic bioremediation

The remediation of the pollutants through the use of various microbes is usually a slow process, which sometimes retards the possibility of bioremediation. Therefore, microbial enzymes obtained from their cells can be used more successfully for bioremediation than total microorganisms, in order to overcome this problem. Again, enzymes are biological macromolecules having complex structure and catalyzes various biochemical reactions associated with the path of degredation of contaminates. The use of enzymes is the cause of decreasing the energy of activation of the reactant molecules or species, and therefore sdincreases the reaction rate of sbioremediation. The bioremediation associated with the purified and partly purified enzyme never depend upon the growth and reproduction capability of the specified microorganism in the contaminated atmosphere, whereas it can depend upon the function of the enzyme as a catalyst concealed by the microbial community. In a soil which has a lower concentration of nutrients, bioremediation can be achieved successfully by the use of purified enzymes. The toxic materials generated during the microbial biotransformation are never formed by the use of enzymatic biotransformation, which maintains a clean, safe and sustainable environment. The enzymes are more mobile and specific towards the substrate in the environment as compared to the microbial community. However, the inadequate level of stability and comparatively less catalytic lifetimes of the used enzymes present a problem in their being used as a suitable profitable alternatives as catalysts. The activity of enzymes decreases because of oxidation, which is the cause of their shorter lifetime and the reduction in stability, thereby interpreting these as less efficient in catalytic activity. Again, there is another pathway of stabilizing and reusing the enzyme NPs for a longer period due to the addition of magnetic Fe NPs to it. If the Fe-NPs are strongly attached to enzymes, then enzymes can be easily eliminated from products or reactants through the application of a magnetic field (Sharma et al. 2018; Kumar and Bharadvaja 2019).

22.3.4.1 Single-Enzyme NPs Used in Bioremediation

Enzymes are usually structural proteins and are effective in specific reactions as biocatalysts for the remediation of pollutants from nature. However, their lower stability and their comparatively shorter life cycles restricts their applicability as potential catalysts when compared with synthetic catalytic material. Since enzymes easily undergo oxidation, they can rapidly lose their activity and becoming less effective. The attachment of NPs to enzymes forms a new substance, which is an effective pathway of enhancing their stability, success, reusability and longevity. The magnetic Fe-NPs are more suitable, because they can be separated easily after use through the application of a magnetic field. The two most potential catabolic enzymes used for this purpose are peroxides and trypsin; they form uniform core-shell magnetic nanoparticles (MNPs). The activity and lifetime of the enzymes used enhance histrionically from hours to weeks and the conjugation of enzyme and MNPs are highly stable, economical and show excellent performance. The MNPs can shield the enzymes leading to the prevention of oxidation during the time of bioremediation and increasing the lifetime of the added enzymes. Enzymes usually acted as magnificent biocatalysts, which are used in various potential applications, such as chemical conversions, bioremediation and biosensing; otherwise, if it is conjugated with NPs, then its performance increases exponentially. Recently, nano-porous silica on conjugation with enzymes shows a high surface-to-volume ratio and exhibits magnificent performance in the bioremediation of the contaminates present in nature (Kim et al. 2006; Rizwan and Ahmed 2019).

22.3.5 Engineered Polymer-Based NPs for Bioremediation of Contaminants

Those toxic organic contaminates having hydrophobic properties, mainly polycyclic aromatic hydrocarbons (PAHs) present in the soil, exhibit less solubility and mobility and strongly undergo sorption by the soil. Furthermore, the sequestration of sorption into the soil in the nonaqueous phase liquids (NAPLs) is the cause of decreasing bioavailability. The NP of amphiphilic polyurethane (APU) is developed for the remediation of PAHs present in the contaminated soil. The NPs are normally synthesized from poly(ethylene glycol) or polyurethane acrylate anionomer (UAA) or urethane acrylate (PMUA) with effective modification, undergo cross-linking and emulsion with water and cause the remediation of PAHs. The APU particles possess the capability of increasing transport and desorption in the similar way to surfactant micelles, but whereas this is similar to the components of surface-active micelles, the individual cross-linked forerunner chains in APU particles do not freely undergo sorption at the surface of the soil. The APU particles can able to attain desired properties, which are stable and their concentration is unchanged in the aqueous medium. The NPs of APU are designed in such a way that their interior regions possess a higher affinity towards phenanthrene (PHEN) and its hydrophilic surfaces stimulate the mobility of the particles in the soil. The attraction of the APU particles towards pollutants such as PHEN can be regulated by altering the dimension of the hydrophobic segment utilized in the synthesis of the chain. The rate of mobility of the colloidal particles of APU present in the soil can be regulated through the change in dimension of the sagging water-soluble chains, which are attached at the surface of the particle or charge density. The capability to regulate the properties of the particles provides great potential for synthesizing various kinds of NPs, which are able to optimize the ousvariety of pollutants and their kinds along with soil conditions. The addition of NPs based on polymeric materials enhances the solubility of the organic pollutant, PHEN, and also accelerates the rate of release of PHEN from the polluted aquifer substances. The NPs synthesized from poly (ethylene) glycol with modified urethane acrylate (PMUA) are the cause of accelerating the rate of bioavailability of PHEN. The NPs of PMUA also exhibit the rate of mineralization of PHEN crystal in an aqueous medium with sorption of PHEN on the aquifer substances and are able to dissolve hexadecane. The approachability of pollutants towards the PMUA particles via bacteria indicates the use of particles, which is highly effective in accelerating the rate of in-situ biodegradation for the bioremediation of contaminates via natural attenuation. The nature of the PMUA NPs is usually stable in the heterogeneous population of microbes; this leads to the reusability of these after the PHEN bonded with NPs, which are degraded through bacteria. Now, researchers made attention to the remediation of biogenic uraninite by using NPs because of the tiny particles and its biological occurrence (Dhillon et al. 2012; Tungittiplakorn et al. 2004; Mazarji et al. 2021).

22.3.6 Use of Biogenic Uraninite NPs for Remediation of Uranium

The reduction of U(VI) through the use of a microbial community has been represented to be catalyzed a number of microorganisms, among which most of these are sulphate or metal-reducing bacteria. The reduction of microbial U(VI) is preferably an unexpected method through which the microbial enzyme transfer occurs at a high concentration of electrons to U(VI). The initial step is the synthesis of biogenic uraninite and reduction of U(VI) to U(IV). The transfer of electrons is supposed to be mediated by cytochromes of c-type, which are localized either on the outer part of the membrane or in the periplasm. However, the mechanism through which cytochromes transfer requisite electrons to U(VI) is unidentified. Since U(V) is comparatively less stable as an aqueous complex, it is possible therefore to proceed with an enzymatic reduction from U(VI) to U(V) with simultaneous disproportionation to U(IV) and U(VI). Following the reduction of U(VI) to U(IV), in the second stage, the synthesis of biogenic uraninite involves the precipitation of mineral products. Now researchers are focussing on the synthesis and application of biogenic uraninite because of its significance in the strategies of bioremediation owing to its natural biological origin and its small dimensions. It was finally concluded that these significant NMs are highly effective in the bioremediation of subsurface U(VI) pollution (Banala et al. 2020; Vogt et al. 2011).

22.3.7 The Phytoremediation of Heavy Metals by Using NPs of Noaea Mucronata

The contamination of soil and water by toxic heavy metals has been a increasing global problem. for a few years. Researchers have been working continuously to remediate the contaminated sources of water and land. Experimentally, it was found that six important plant species, *Gundelia tournefortii, Noaea Mucronata, Centaurea virgata, Angustifolia, Reseda lutea, Eleagnum and Scariola Orientalis*, possess the capability of accumulating heavy metals such as Cu, Ni, Zn, Pb and its ions from water and soil. The plant species *Chenopodiaceae* is found to be the best accumulator of Pb and also a very good accumulator for the the heavy metals Zn, Ni, and Cu. In the case of Fe, the plant species *Reseda lutea* serves as the best accumulator. The NPs synthesized from *N. mucronata* possess the excellent capability of bioaccumulation. It was found that the concentration of HMs decrease drastically during the successful bioremediation of three days. Hence, the plant species *N. mucronata* is a highly efficient accumulator and the NPs of these particles exhibit high performance for bioremediation and detoxification in a critical situation (Mohsenzadeh and Chehregani Rad 2012; Chehregani et al. 2009).

22.3.8 Microbial Nano-biomolecules for the Remediation of Contaminants

The non-glucan exopolysaccharide is symbolized as EPS-605 self-assembled, which forms NPs of the spherical size of almost 176 nm radius. It consists of mannose, galactose and glucose, modified many times such as acylation, carboxylation, phosphorylation and sulfation, and possesses a higher negative charge. The NPs of EPS-605 exhibit a higher ability of biosorption for the heavy metal ions Pb^{2+}, Cd^{2+}, Cu^{2+}, and methylene blue as compared to nanosorbents and biosorbents. The capability of adsorption of EPS-605 is influenced by various environmental factors, such as temperature, pH and the initial concentration of the adsorbate, time of contact and the existence of circumstantial electrolytes. However, EPS-605 acts as an outstanding reductant for the formation of monodispersed silver and gold NPs (AgNPs and AuNPs). The nanoparticulate immobilized *laccase* possesses the capability to decolourize the toxic Congo red dye by the direct attachment of enzyme NPs on the glass bead surface in order to measure the activity of decolourization of the non-immobilized and immobilized *laccase* (Mandeep and Shukla 2020; Kalia and Singh 2020).

22.3.9 *Engineered Polymeric NPs Used in the Remediation of Soil*

The toxic organic pollutants polynuclear aromatic hydrocarbons (PAHs) are hydrophobic in nature and are a common contaminant present in the groundwater, which is strongly sorbed to soil, making their removal highly problematic. Another NP, amphiphilic polyurethane (APU), is highly effective in the bioremediation of PAHs from contaminated soil. The use of NPs of poly (ethylene glycol), polyurethane acrylate anionomer (UAA) and modified polyurethane acrylate (PMUA) is the cause of cross-linking and emulsification in water. The particles of APU possess the capability of increase in transport and desorption in the pathway similar to that of other surfactant micelles;however, it differs from the surface-active constituents of micelles. The different cross-linked predecessor chains in the APU particles freely sorb to the surface of the soil. The engineered APU particles have independent concentration, are stable in an aqueous medium and exhibit a greater affinity towards phenanthrene. Their surface exhibits hydrophilic properties, which stimulate the mobility of the particle in soil. The interaction of APU particles towards the pollutants can be regulated by the alternation of the hydrophobic segment that can be applied in the synthesis of chains. The mobility of the colloidal form of APU in the soil is regulated based on the size of the sagging water-soluble chains or charge density that can be found on the surface of the particle (Guerra et al. 2018; Thomé et al. 2015).

22.4 The Science Regarding Bioremediation by Using NM

There are several reasons for using various kinds of NMs in bioremediation to clean up the environment.

- The surface area of the NMs is much larger than that of any other materials; therefore, more quantities of the NM particles come into contact with the surrounding toxic materials, therefore tremendously increasing the reactivity.
- Since NMs exhibit a quantum effect, which is the cause of the requirement ofa lesser amount of activation energy to feasible the chemical reactions for bioremediation.
- There is another property, known as surface plasmon resonance, which is provided by NPs, and causes the identification of toxic contaminated materials.
- Because of the tiny size of different non-metallic and metallic NPs such as single metal NPs, carbon base NMs and bimetallic NPs, etc., they can be highly

effective for cleaning of the environment (Rahman et al. 2020). The science behind this is as follows.

1. NPs possess the capacity to penetrate or diffuse inside the zone of contamination, whereas microparticles or any other particles cannot be penetrated.
2. NPs show higher reactivity towards the redox reaction of the contaminants. It was found that the oxide-coated zero-valent Fe develops feeble complexes in the outer sphere of the contaminants such as tetrachloride (CT). The oxide coating accelerates the reactivity via electron transfer. CT undergoes cleavage and produces CH_4, formate and CO_2. Again the toxic compound benzoquinone is broken and converted into C_2HCl_3 and other hazardous chlorinated compounds are broken down into comparative molecules of less toxicity.
3. TiO_2 nanotubes possess the potential to degrade or break down pentachlorophenol (PCP) into non-toxic simple products via photoelectrocatalytic reaction. The single metal NPs shows good performance as biocatalysts in case of reductive dechlorination.
4. The NPs of Pd(0) are gathered inside the cytoplasm and cell wall of *Shewanella oneidensis*, which is charged by the radicals due to the incorporation of various substrate molecules such as hydrogen, formate and acetate and act as electron donors in the bioreductive analyze comprising Pd (II). At the time of deposition of charged Pd (0), *S. oneidensis* cells come into contact with the chlorinated compounds, where the radicals of Pd (0) react catalytically with PCP and cause of elimination of Cl_2 molecules from toxic chlorinated materials (Cecchin et al. 2017; Zhang and Hu 2018).
5. NPs also used effectively for the immobilization of microbial cells, which can undergo degradation or biorecovery of some specific chemical compounds. Like usual cell immobilization on an immovable surface or micron-sized media, the magnetic NPs (specifically Fe_3O_4) undergo functionalization with ammonium oleate with a coating over the *Pseudomonas delafieldii* surface. By the application of an external magnetic field to the microbial cells, the cells coated with magnetic NP are deposited at a particular location on the surface of the reactor wall, which is detached from the bulk solution and then recycled to make it suitable for the treatment of the substrate.
6. The addition of microbial cells in a bioreactor having a high level of biomass concentration leads to the removal of sulfur from the fossil fuel (dibenzothiophene) similar to non-NP-coated cells (Liu et al. 2009).

22.5 Conclusion

The science of nanotechnology is an advanced field, which can be used potentially in the environmental sector such as with the treatment of water and wastewater, green synthesis, sensor design and the remediation of pollutants. The toxic contaminates and organic substances can be effectively removed from the polluted area by using NMs of the appropriate kind. The NMs produced biologically are playing a key role in cleaning the polluted area or regions. The microbial cells, such as compartments of cytoplasmic vesicular and periplasmic space, control the size and shape of NMs, which is necessary for suitable application. The field of nanotechnology potentially influences the interaction between environment and energy. Since NMs are toxic towards the environment and undergo bioaccumulation, therefore we have to adopt the green synthesis process of destroying contaminants without any kind of toxic effect on the biota and environment. More emphasis is given to the formation of smart NMs for the effective remediation of the environment and maintaining sustainability. The application of NMs not only reduces the cost of detoxification of waste materials but also catalyzes the remediation reaction and increases the effectiveness of the microorganisms. Although, the approach of nanobioremediation plays a vital role in maintaining a sustainable environment, so far as a safety factor is concerned the use of NMs is the cause of health risk impacts considering the relation between use and synthesis. The NPs synthesized biologically are more suitable to inhabit the toxic effect on the microbes and maintain a sustainable environment.

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