
**MICROBIAL NANOTECHNOLOGY'S ROLE IN TOXIC WASTE CLEANUP: THE
POWER OF NANOPARTICLES**

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Abstract

Pesticides, antibiotics, steroids, azo dyes, and carcinogenic chemicals are just some of the pollutants that have caused problems in the environment. Toxic control from industrial waste is a serious obstacle for industries. These contaminants are extremely hazardous to the environment. Through the production of environment friendly nanomaterials (NMs), nanotechnology can lower the expenditure by industries to mitigate these pollutants. Because of their improved physical, chemical, and mechanical qualities, NMs are gaining popularity. The use of microorganisms in the synthesis of nanoparticles (NPs) gives green biotechnology an even more massive push as an emerging sector of nanotechnology for sustainable manufacturing and cost savings. The purpose of this quick summary is to discuss the various elements of industrial wastewater bioremediation using microbial nanotechnology (NT) interaction. The usage of microbial enzymes in combination with nanotechnology has resulted in increased enzyme activity and reusability.

Keywords: Nanoparticles, Bioremediation, Microorganism, Microbial nanotechnology, Green technology, Industrial effluents.

1.0. Introduction

Bioremediation is emerging as a substitute method for preventing the loss of biodiversity in response to the rising issue of environmental pollution. Several technical and managerial advancement tactics have been tried, however nanobiotechnology stands out as a viable solution for pollution removal. At the moment, hydrocarbons, heavy metals, pharmaceuticals, pesticides, and explosives are among the contaminants of concern. These toxins may be harmful towards both health and environment. Long term co-infection may promote to the emergence of toxins and carcinogenic, which degrade gradually and remain in the ecosystem for a very long period. A serious issue now facing the world is hazardous material contamination of the soil, groundwater, and air, especially petroleum. [1].

Even though many standard physical-chemical techniques, including adsorption, electrochemical treatment, precipitation, and electrocoagulation, are currently in use, there is still a pressing need for the creation of new techniques that are efficient, eco-friendly, and economical for the removal of environmental contaminants. Utilizing low-tech, low-cost methods, microorganisms are utilised in bioremediation technology to remove toxins. It is predicated on the presence of specific microorganisms and a medley of advantageous environmental elements. This method is highly potential for treatment toxic compounds and media susceptible of breaking components because it depends on spontaneous microbial activity regulated by various consortia of microbial strains. Any approach that utilizes fungus, green plants, microbes, or their enzymes to restore the contaminated natural environment might be considered [1]

The effectiveness of the degradation of organic pollutants has lately been improved by the development of techniques. Among them, bioremediation techniques have been demonstrated to be a state-of-the-art and successful means to eliminate toxins in a number different environments, as well as a reasonably flexible management choice that can be used on a wide scale [2]. Both bioaugmentation and biostimulation have been demonstrated to be effective techniques to speed up the cleaning of a polluted site with little harm to the ecological system [3]. Bioaugmentation engenders non-native oil-degrading bacteria while biostimulation encourages the growth of native microorganisms.

Although bioremediation is an effective and flexible method for recovering from a range of pollutants, it is inefficient when dealing with high contaminants, xenobiotics, or compounds that are heat-resistant, leading to significant treatments effectiveness and recovery times. Numerous investigations have been made to assess the beneficial effects of NMs and biological treatment methods and to clarify the physically, chemically, and biologically interactions that occur in soil and groundwater [6].

This systemic review is aim to understand the microbial NT through which the removal of toxic waste pollutants and the use of various microorganism, green nanotechnology to remove and valorize the toxic waste material.

2.0. Fate of Soil Contaminants

Solid, liquid, and gaseous phases can all be used to describe the pollutants in soil. Numerous variables, including soil characteristics like pH, clay content, and organic matter concentration as well as the properties of chemical compounds, allow pollutants to move into the soil. Diffuse pollution and point source pollution are the major ways that pollutants in soil are created [167–168]. The occurrence of natural occurrences that interfere with agricultural activities and the discharge of pollutants from wastewater treatment plants are typical examples of diffuse sources of contaminants [169]. These events cause pollutants to settle out in the soil and enter surface waters. Point sources, such as factories, landfills, and industrial operations, are the activities that create and release pollutants into the soil [169]. The three main processes for introducing contaminants into the soil are volatilization, leaching, and suspension [169]. The contaminants that are emitted will travel through the soil, penetrate the pore space, and remain on the surface of organic or mineral substances. Additionally, the contaminants will seep into damp soil or evaporate into the sky. Heavy metals, which also include persistent organic pollutants and inorganic pollutants, are the most harmful contaminants in soil because they are very difficult to eliminate or decompose.

For a variety of contaminants, notably heavy metals that can linger in soil for several decades, soil is thought to be the best place to store them. Contaminants that were carried into the soil system will change into more stable solid phases and be maintained in the soil's organic phase. This vehicle is undergoing a permanent process termed as ageing. Because ageing will decrease the permeability of soil, the process of ageing has shown to degrade soil qualities [170]. The ageing process will cause the pollutants in soil to be sequestered, and the amount of adsorption and diffusion between the contaminants and soil will be restricted. The amount and behaviour of soil organic matter and black carbon, as well as the soil's inorganic components and structure, are the key elements that contribute to ageing [170]. The pH of the soil, the presence of clay minerals, the concentration of organic matter, and other potential parameters are all strongly correlated with the sedimentation of heavy metals in the soil.

One of the elements influencing how heavy metal pollution are transported into the soil environment is the mineral clay. The capacity of clay minerals to absorb metal ions from the soil is connected to both the specific adsorption and the exchange of ions [167]. The removal of the proton from the metal ions at the clay minerals' sites or the adsorption of hydroxyl ions from the metal ions completed the process of metal ion adsorption through clay minerals. Since each form of clay mineral has a unique capacity for absorbing substances at the mineral edges, kaolinite has a stronger capacity for holding heavy metals than other types of clay minerals [171].

When it comes to kaolinite, the surface edges contain a higher concentration of weak acid, which increases the mineral's ability to adsorb heavy metals onto its surfaces. Additionally, clay minerals that may expand, like vermiculite, have a larger potential for adsorption than kaolinite. This is a result of the adsorption process that took place in the vermiculite mineral's interlayer gaps. Compared to silty soil, the clay mineral has a larger potential for adsorption [172]. By increasing or lowering the quantity of organic matter present, the soil's organic matter content can also have an impact on the presence of heavy metals in the soil. For instance, the formation of metal-organic complexes in soil with a high organic matter content might reduce the amount of metal in the soil and plants [173].

Although there would be less adsorption of heavy metals in soil due to the reduced concentration of organic matter, ions of heavy metals will still be present [174]. However, because heavy metal pollution are often bound to the moist compounds in soil, the amount of organic matter has a significant influence on the mobility of heavy metals [175]. The quantity of heavy metals in soil solutions will rise as a result of complexes forming in organic matter. Additionally, the adsorption capability of organic matter will be impacted by the functional group in metal ions [167]. Negatively charged heavy metals have a higher propensity to bind to organic materials and become more stable at high pH levels [167].

3.0. Method to Remove Waste Pollutants in Soil

Technologies for removing waste from the environment should adhere to a number of fundamental technical standards, such as robustness, the absence of other adverse environmental effects, the capacity to sustain water supply systems over an extended period of time, and compliance with the quality standards of physical, chemical, and microbiological approaches. There are several techniques for removing trash from soil at the moment, which may be categorised into three groups: physical, chemical, and biological methods (Figure 1).

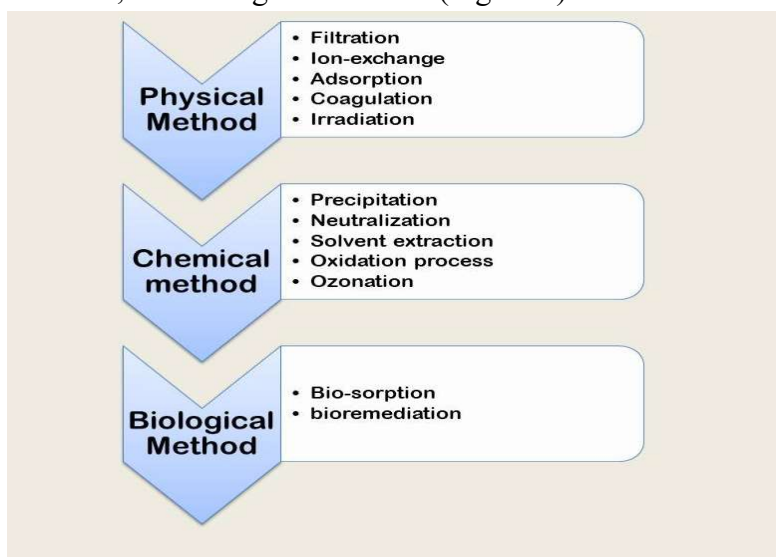


Figure 1: Different Method to Remove Waste Pollutants in Soil

3.1. Physical Treatment

Technologies that remove the pollutants from the soil solids are a part of physical soil remediation. The separation process is a volume reduction procedure that moves the contaminant to another medium, such as air or water, and gathers it in a concentrated form. The new contaminated media may need further treatment, depending on their amount and concentration. This further treatment might either eliminate the pollutant or concentrate it for recovery/reuse or eventual disposal. As a result, the requirement for a treatment train to finish the process is commonly caused by physical separation therapy. Either in situ or ex situ physical therapy is carried out employing separation technologies (soil is excavated). The fundamental benefit of in situ treatment is that it enables soil remediation without the need for excavation or transportation. It also gets around limits on the redeposition of treated soil when disposing of land. Treatment periods for in-situ cleanup are often longer. It is also more challenging to guarantee treatment homogeneity because of the subsurface's variability [62].

By encouraging the pollutants to leave the area of contaminated soil, in situ treatment must also be concerned with preventing the spread of contamination. There are 3 kinds of in-situ physical remediation for organically polluted soil:

- 1) Vadose zone soil vapour extraction and several techniques to improve pollutant removal by vaporisation; for the saturated zone, 2) air sparging (pressurising groundwater with air to volatilize VOCs); and 3) Soil flushing, which entails using chemicals like surfactants to improve the removal efficiency of water moving through contaminated soil as well as the flushing action of groundwater in pump-and-treat systems [62].

3.2. Chemical Treatment

Chemical soil remediation techniques include those that eliminate or change organic pollutants chemically. Utilizing chemical oxidants like hydrogen peroxide, the chemical destruction process includes oxidation to carbon dioxide. Chemical or ultraviolet (UV) reduction and dechlorination using alkaline reagents are two transformation processes. Chemical treatment methods also include the stabilisation of contaminated soil, in which chemical pollutants are immobilised and rendered more inert in the environment in a matrix generated by chemical processes. Chemical therapies can also be used in situ or ex situ, much as physical treatments [62].

3.3 Biological Treatment

Biological treatment of industrial wastewater, municipal waste, chemical waste or other waste is a process whereby organic substances are used as food by bacteria and other microorganisms. Almost any organic substance can be used as food by one or more species of bacteria, fungi, ciliates, rotifers, or other microorganisms (Figure 2).



Figure 2: Biological Treatment of Waste Material

4.0 Bioremediation

Remediation means to get rid of an issue and if it is associated with taking care of an ecological issue like soil and groundwater contamination is called bio-remediation. Bioremediation is a mechanism which utilizes the living microorganisms to reduce natural contaminations or to anticipate contamination [176]. It is an evolution towards elimination of toxins from the climate in this way reestablishing the first characteristic environmental factors and forestalling further contamination. Bioremediation also can be a permanent in situ solution for contamination instead of simply translocating the problem. Remediation of heavy metals, metalloids, or other inorganic pollutants from soil or water can be done by this technique [177]. It is a cost-effective, efficient, novel, eco-friendly, and solar-driven technology with good public acceptance as compared with other engineering techniques (Figure 3).

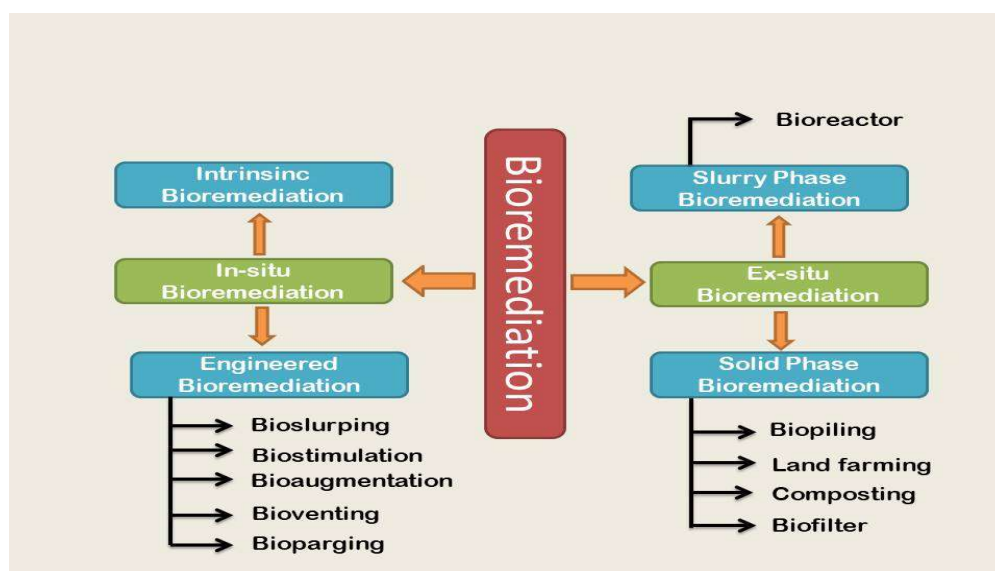


Figure 3: Different methods in Bioremediation

A. Based on applied strategies: bioremediation techniques applied on the basis of strategies can be classified in two categories.

- Ex-situ bioremediation.
- In-situ bioremediation

4.1 Ex-situ bioremediation

Ex-situ as name suggests its mean to remove contamination mat to a remote treatment location. This classification is not much popular because it involves the big task of excavating polluted soil and transports it to offsite. The basic principal of ex situ remediation is to introducing the correct soil oxygen, moisture and nutrient conditions on offsite [178]. However, Ex situ bioremediation process poses a hazard to spreading contamination or risking an accidental spill during transport [179].

4.2 In-situ bioremediation

Bioremediation process is done at the contamination site defines the in-situ method. In situ is the preferred bioremediation method, as it requires less mechanical efforts to eliminates spreading contaminants and prevent the spread of pollutant through transportation or pumping away to other treatment locations In situ bioremediation are biological processes which include microorganisms metabolize organic contaminants to inorganic material, such as carbon dioxide, methane, water and inorganic salts. This process can be achieved either in natural or engineered conditions [180].

5.0 Types of remediation

Remediation is the procedure used to treat and lessen environmental damage or contamination brought on by pollutants, toxic materials, or other dangerous agents. Different remediation techniques exist, each of which is intended to solve a particular class of environmental issues (Figure 4). Here are a few typical remedial methods:

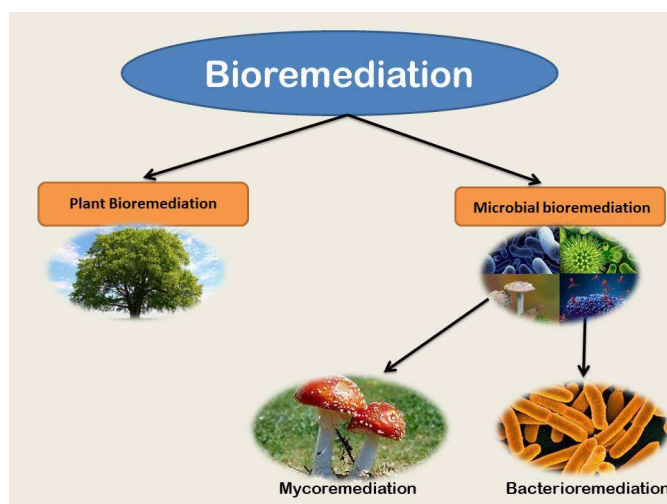


Figure 4: Bioremediation perform by plant and microbial bioremediation

5.1 Plant bioremediation

Hazardous substances that are present in the soil's natural environment are what cause soil contamination. The main sources of contaminated soil are mining, manufacturing, landfill sites, particularly those that are accepting industrial wastes (e.g., paint residues, batteries, electrical wastes, etc.), municipal or industrial sludge, and heavy metals, which can naturally occur in soil but rarely at toxic levels [66].

A wide variety of amendment agents have been used to manipulate the bioavailability of heavy metals and to obstruct their diffusion in soil by inducing various sorption processes, including adsorption to mineral surfaces, formation of stable complexes with organic ligands, surface precipitation, and ion exchange [67]. This is because the activity of heavy metals in soil is controlled by sorption-desorption reactions with other soil constituents. There are two different kinds of amendment agents: mobilising agents, which increase the bioavailability and mobility of heavy metals and improve their removal through plant ingestion and soil washing (i.e., the phytoextraction process), and immobilising amendment agents, which lessen the bioavailability and mobility of heavy metals and lessen their transfer to the food chain by preventing their leaching to groundwater (i.e., phytostabilization). The phytoremediation method used to control polluted soils includes both phytoextraction and phytostabilization processes [70].

5.2 Microbial Bioremediation

In order to remove environmental contaminants, microbial bioremediation uses microorganisms and/or their byproducts (enzymes or used biomass) [71, 72, and 73]. It is crucial to remember that microorganisms are ubiquitous, and as a result, contaminants in various environmental compartments constantly come into touch with microorganisms [74, 75]. Pollutants are broken down or transformed by microbes using their natural metabolic processes, with or without modest route changes to direct the pollutant into the usual microbial metabolic pathway for breakdown and biotransformation. The majority of synthetic substances, such as hydrocarbons (such as oil), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), radionuclides, and metals, can be degraded, transformed, or accumulated using applied bioremediation processes [76, 77, 78, 79]. The range of chemical contaminants that are degraded or detoxified is increased by the occurrence of a broad diversity of microbial species in nature. As a natural process, microbial bioremediation has the benefit of being widely accepted [79]. In most circumstances, compared to other techniques for cleaning up hazardous waste, it is a low-cost technology [75]. Instead of contaminants being transmitted from one form or one medium to another, it is feasible to completely destroy the target organic pollutants in situ and ex situ [79].

5.1.1. Factors for Effective Microbial Bioremediation

A potent and environmentally acceptable method for removing pollutants from the environment, such as heavy metals, organic compounds, oil spills, and more, is microbial bioremediation.

Several important elements need to be taken into account to ensure the efficacy of microbial bioremediation (Figure 5):

- **Microbial Population:** The right sorts of microbes may biodegrade all kinds of pollutants.
- **Characteristics of the pollutants:** It is crucial to comprehend the chemical and physical characteristics of the pollutants. The kind of pollutant, its concentration, solubility, and toxicity can have an impact on the microbial strains selected as well as the bioremediation strategy.
- **Oxygen:** There should be enough oxygen to facilitate aerobic biodegradation (0.4 mg/liter in soil or water or around 2% oxygen in the gas phase).
- **Water:** The soil's moisture content should range from 50 to 70 percent of its water-holding capability (if bioremediation of contaminated soil is taken as an example).
- **Nutrients:** To maintain healthy microbial development, nutrients such as nitrogen, phosphorus, and sulphur are necessary.
- **Temperature:** Microbial development requires temperatures between 0 and 40°C.
- **pH:** In order to promote healthy microbial development and prompt biodegradation, the ideal pH range should be between 6.5 and 7.5. [80]

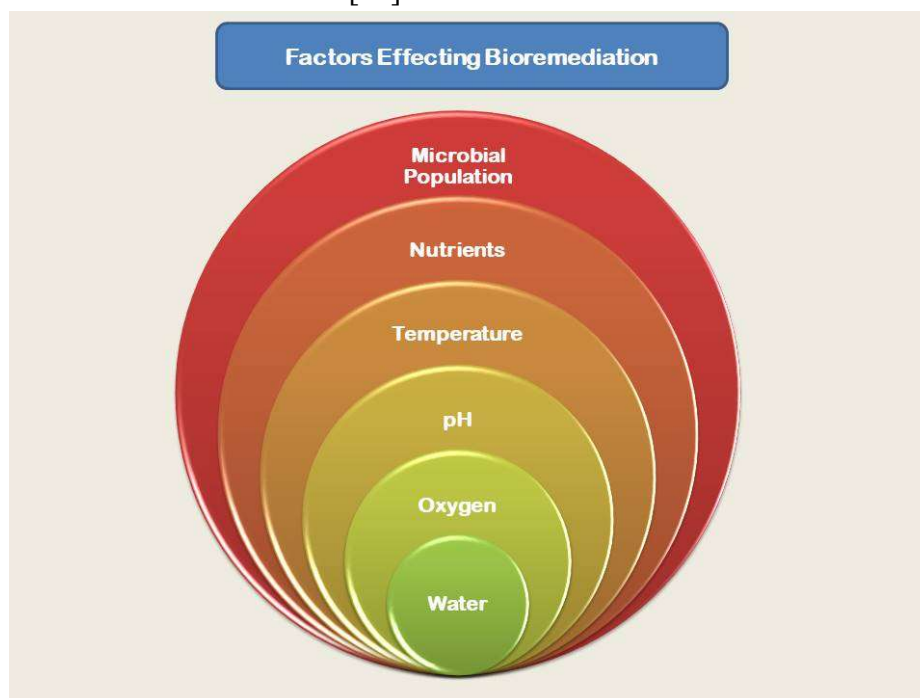


Figure 5: Factors which Effect Microbial Bioremediation

5.2. Advantages of Bioremediation

Cleanup of polluted locations and environmental protection can be accomplished through the use of bioremediation. In comparison to conventional cleanup techniques, it has a number of benefits. The following are some of the main benefits of bioremediation (Figure 6):

1. Natural Process: The public accepts bioremediation as a natural technique for treating waste from polluted materials like soil. Microbes multiply, break down the pollutant, and release

harmless byproducts. Typically, the products left behind after treatment are safe substances including carbon dioxide, water, and cell biomass.

2. Complete Destruction: A number of toxins can be completely destroyed via bioremediation. Many dangerous substances can be changed into safe goods. As a result, there is a lower possibility of future responsibility related to the handling and disposal of contaminated material.

3. On-Site Treatment: Without significantly interfering with daily operations, bioremediation may be done right at the contaminated site. This eliminates the requirement to carry massive amounts of garbage off-site, minimising the risk that doing so will have on the environment and human health.

4. Cost-Effective Process: Bioremediation is less expensive compared to other methods that are used for the removal of hazardous waste [80]

5. Environmental friendliness: To dissolve or change toxins, bioremediation uses natural processes and microorganisms. When compared to chemical or mechanical processes, it frequently creates less toxic byproducts, making it more ecologically benign.

6. Minimal Environmental Impact: Because bioremediation does not need the excavation and transfer of contaminated materials, it often leaves a smaller ecological imprint than other remediation methods. This lessens carbon emissions, habitat damage, and soil erosion.

7. Sustainability: Microbial populations may adapt and continue to break down toxins over time after they've been formed, offering long-term, sustainable cleaning options. This may lessen the requirement for continuous maintenance and supervision.

8. Site Preservation: Bioremediation minimises impact to local flora and animals while preserving the site's natural characteristics and ecosystems. Particularly in ecologically delicate places, this is crucial.

9. Lower Energy Consumption: Bioremediation procedures often require less energy than energy-intensive techniques like thermal treatment or incineration, which helps to lower greenhouse gas emissions.

10. Minimal Secondary Waste: Chemical remediation techniques frequently generate secondary waste streams that need to be disposed of. Due to the fact that microorganisms metabolise pollutants into less dangerous compounds, bioremediation frequently produces less secondary wastes.

11. Flexibility: A variety of pollutants, such as hydrocarbons, heavy metals, pesticides, solvents, and more, can be remediated via bioremediation. To specific pollutants and site circumstances, different microbial species and tactics might be used.

12. Lower Health concerns: Compared to chemical-intensive cleanup techniques, bioremediation procedures often provide less health and safety concerns to employees and the surrounding populations.

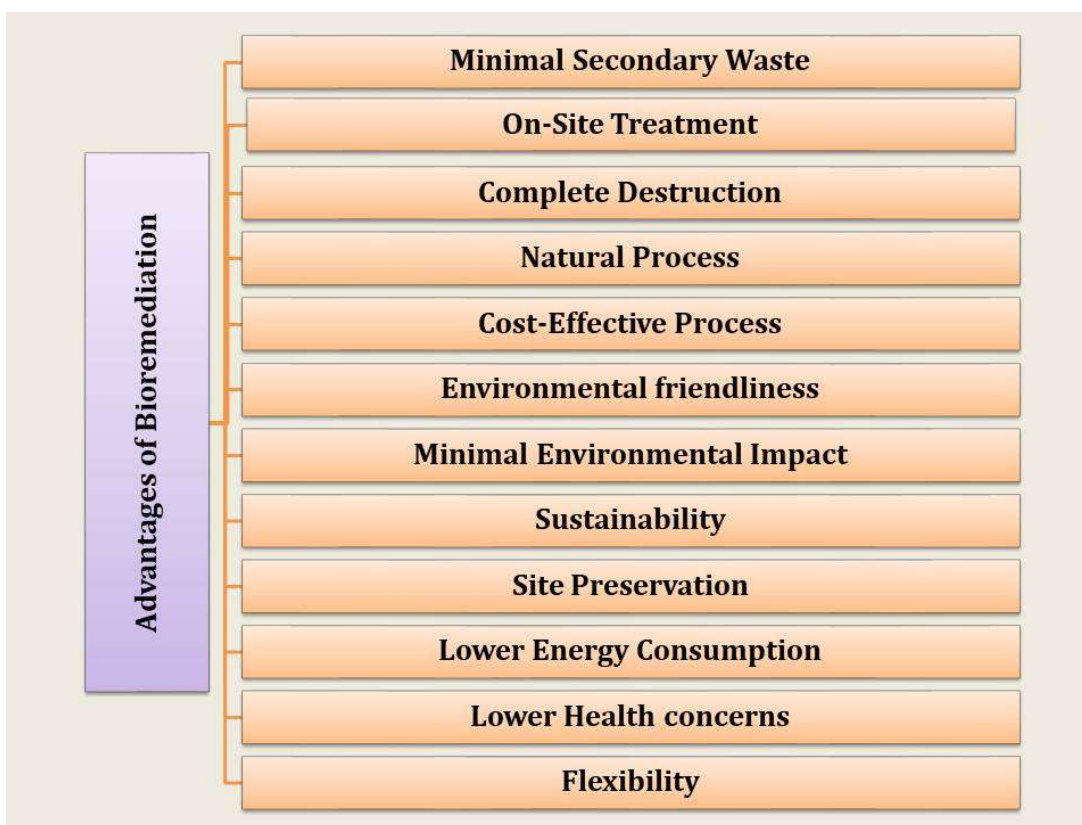


Figure 6: Advantages of Bioremediation

5.3. Limitation of Bioremediation

Limited to biodegradable compounds-Bioremediation is only possible with biodegradable substances. This process is prone to quick and total deterioration. The byproducts of biodegradation may be more hazardous or persistent than the original substance (Figure 7).

1. Specificity

The biological procedures are quite specific. The presence of metabolically active competent microbial populations, adequate environment growth conditions, and optimal amounts of nutrients and contaminants are all critical site criteria for success.

2. Technological Advancement

Bioremediation methods that are suitable for places with complex mixtures of contaminants that are not evenly distributed in the ecosystem must be designed and engineered via study. It could be present as gases, liquids, or solids.

3. Time Taking Process

In comparison to alternative treatment techniques like excavation and pollutant removal from the site, bioremediation takes more time.

4. Regulatory Uncertainty

Since there isn't a consensus on what constitutes "clean," we can't state with certainty that remediation has been completely finished. As a result, it is challenging to assess the effectiveness of bioremediation, and there is no suitable endpoint [80].

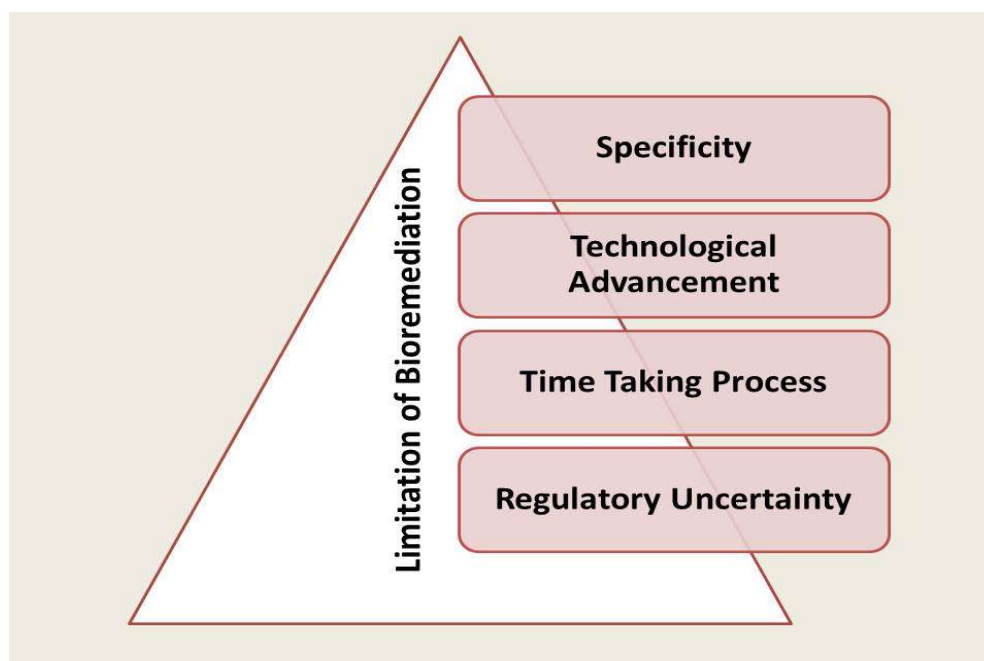


Figure 7: Limitation of Bioremediation

6.0. Importance of NT in bio-remediation

The industry releases around 10 million metric tonnes of harmful chemical substances annually. Following their release, these molecules may combine to produce substances like polychlorinated dibenzo-p-dioxins or polychlorinated dibenzofurans, which are byproducts of numerous chlorine-based chemical processes [7–10]. The pathogenicity of these active substances, along with its numerous combinations with biotic or abiotic environmental factors such as microbes, plant, animal, waters, mineral, organic material, air, and others, has hampered successful remediation techniques [11-13]. When NMs and NPs are utilised in combination with biotechnologies, remediation capacities can be considerably increased, eliminating process intermediates and speeding breakdown [14, 15].

Microbial treatments have gained popularity over physical, chemical, and biological cleanup techniques because of their affordability and versatility [16]. Bioremediation procedures include bioaccumulation, bioaccumulation, biotransformation, and biological stabilisation [17, 18]. Plants and microorganisms including such bacteria and fungus, as well as mixtures of the two, are used in these technologies. Biological systems and NMs have been combined in recent years to enhance and hasten the elimination of hazardous substances from the environment [19].

The term "nano-bioremediation" describes techniques for removing pollutants that make use of nanoparticles, bacteria, or plants [20]. These methods are based on the characteristics of the organisms that remove contaminants. They named the processes nanoremediation, microbiological nanoremediation, and phyto-nanoremediation as a consequence [21]. A healthy interaction between nanoparticles (NPs) and life forms is critical since bioremediation relies on living organisms to clean up contaminated environments. In this case, a few factors are crucial. Nanotoxicity, NP size, and nanonutrition, in particular, are known to have an influence on living organisms, and hence the entire bioremediation process may be affected [22].

Numerous variables, such as the NMs size and shape, their surface coating, the chemical makeup of the NMs and contaminants, the kind of organism, the media, pH, and temperature, among others, had an impact on the physiochemical interactions between the NMs, biota, and pollutants figure 1. These occurrences become more difficult as the number of potential parameters influencing such interactions grows. For the proper growth of living things, increasing the temperature and pH of the medium is essential. These traits may, in turn, affect the stability of NMs and contaminants [23].

For instance, Au NPs were stable in MilliO water with a buffer but became unstable at pH 4, 7, and 8 [24]. The thermal stability of Cu NPs was also demonstrated to be influenced by various production methods. As far as we are aware, there hasn't been anything written about how the parameters mentioned above affect the nanobioremediation of pollutants. For example, proper experimental methods should be used to investigate how temperature and pH impact the synergic activity of NMs and live microorganisms for pollutant cleanup [25].

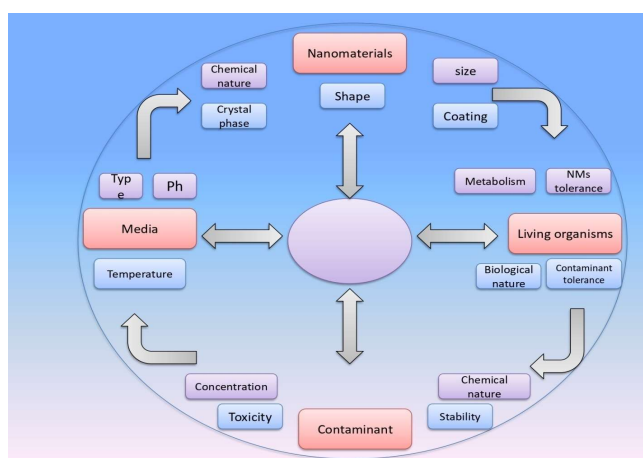


Figure 8: Several variables impact the interface of NMs and living organisms with contaminants. Two-way arrows are used to represent interactions.

Figure 9 shows the NMs, contaminants, and biota's physicochemical interactions. Numerous processes, including dissolution, adsorption, and biotransformation, can take place when NPs and biota interact [26]. Each of the mentioned occurrences might have an impact on how the pollutants deteriorate. In this case, metabolism is also involved. NPs can have a biocidal or biostimulant effect on living things, which can change how well the organisms involved in remediation perform. Utilizing both NPs and live animals may have a beneficial synergistic effect.

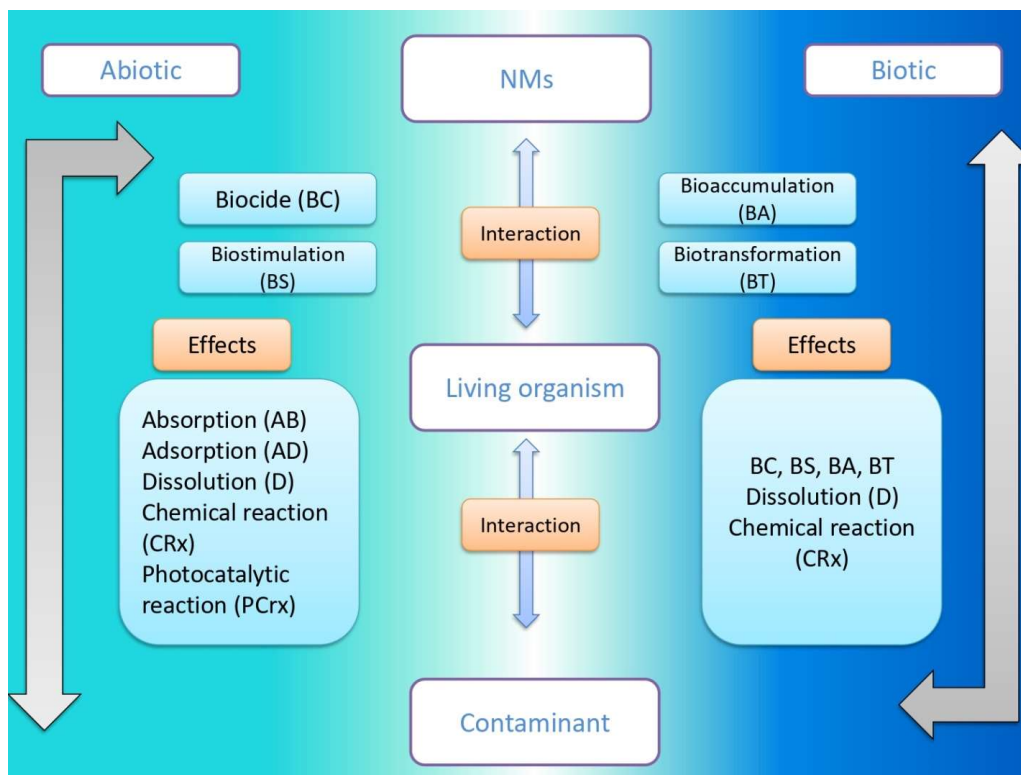


Figure 9: Various occurrences occur as a result of the physical, chemical, and biological interactions between NMs, live organisms, and pollutants during nanobioremediation processes.

Mechanisms of adsorption are essential in nanobioremediation. Swelling is a result of both sorption and absorption. The initial link between the pollutant and the sorbent occurs near the surface. However, in the second scenario, the pollutant reaches deeper sorbent layers and dissolves them to produce a solution. Additionally, a distinction can be seen. Because the former requires a chemical reaction while the latter just uses physical forces, chemisorption and physisorption may be distinguished from one another. Pollutants can be immobilised, sequestered, and concentrated by sorption in every circumstance [27].

Much research has been conducted to better understand the nature of NM-based adsorption processes [28-30]. Mechanistic, thermodynamic, and kinetic studies are therefore needed to explain how the nanomaterial behaves when it interacts with contaminants. Numerous models that

characterise the behaviour of involving the biological matrix in remediation processes are given by various authors [31–34]. These models include the Freundlich and Temkin isotherms, the Langmuir and Dubinin-Radushkevich models, among others. Depending on the kind of NMs, photocatalytic approaches may be utilized to break down pollutants. Further by biotransforming the resultant molecules, biotic systems can reduce the levels of pollutants in the environment. In addition, a number of enzymes secreted by living things have the capacity to break down a variety of contaminants [35].

NPs can reach contaminated locations that other objects cannot due of their size. As a result, nanobioremediation technology may be used in innovative ways [36]. This feature sets it apart from other corrective methods. Other concerns, however, such as the standardisation of techniques to assess the toxicity of NPs and NMs in water and soil, a description of how they engage with biotic and abiotic components, and the proper regulatory system in which these materials may be used, are required [37].

7.0. NT is an important factor for environment and human health

Global environmental problems are escalating, and we must behave as though the Earth is in peril. We must adopt a new attitude and approach disasters with new perspectives and methods, as well as with clarity and determination. It takes millennia to clean up environmental pollution in the soil, water, and air. The main sources of pollution in the environment are industrial and car exhaust emissions [38]. Human toxicity is a common trait of POPs like dioxins and PAHs [39]. When exhaled in significant quantities, carbon monoxide (CO) can become acutely poisonous. Depending on the amount of exposure, heavy metals like Pb can harm a living thing in a short period of time or over time [40].

Cancer, heart difficulties, CNS malfunction, and skin diseases are only a few of the ailments caused by dangerous compounds [41]. Condensation, flocculation, froth floatation, sand filtration, and AC adsorption have all been widely used for many years. They do have several limitations, though, including ineffective metal ion scarping, high energy requirements, and nonrecyclable chemical production. These problems seem to have a viable answer in nanotechnology [42].

The development of healthier, green energy with significant advantages for the environment and human health has a great deal of promise to be facilitated by NT [43]. NT methods are being researched for their potential to offer solutions for pollution management and mitigation as well as to boost the effectiveness of current environmental cleanup techniques [44]. By reducing the energy needed for manufacturing and processing, enabling post-use recycling of products, and developing and using environmentally friendly materials, nanotechnology may help the environment [45]. Currently, nanotechnology offers a lot of potential for addressing sustainability issues, but we also need to take into account the threats to the environment and public health [46].

NT has the potential to make a significant contribution to the development of cleaner, greener technologies with significant advantages for the environment and human health [43]. NT methods are being researched for their potential to offer solutions for pollution management and mitigation as well as to boost the effectiveness of current environmental cleanup techniques [44]. By reducing the energy needed for manufacturing and processing, enabling post-use recycling of products, and developing and using environmentally friendly materials, NT may help the environment [45]. Currently, NT offers a lot of promise for addressing sustainability-related issues, but we also need to take into account the threats to the environment and public health [46].

8.0. Using NMs to aid in soil Bioremediation

Soil contamination and degradation remain key environmental concerns, and remediation has become a worldwide problem. Agricultural productivity and food safety are significantly impacted by soil reservoir degradation, which calls for immediate attention. Heavy metals, pesticides, and POPs (persistent organic pollutants) damage soil, exacerbating the situation. Polluted soil raises the danger of food chain poisoning due to biomagnification. Agriculture production is significantly impacted by the need to feed more people as well as the challenges of preventing additional land degradation [47].

Immobilisation, often known as adsorption, is a common therapeutic procedure. For removing metal pollutants from soils, this sort of remediation technology offers a number of noteworthy benefits, including efficacy, affordability, and environmental friendliness [48]. Carbon nanotubes, metal oxides (ferric oxide and titanium oxide), and other nanocomposites have been utilised to immobilise soil pollutants [49]. For instance, ferric oxide nanoparticles have an extraordinary capacity to absorb and immobilise heavy metals, such as cadmium and arsenic, from a range of medium samples [50].

Sea life in the vicinity suffers from oily waste, which is a problem [51]. Iron NPs efficiently remove total petroleum hydrocarbons (TPHs) from water with an enhanced efficiency of 88.34 percent [52]. Therefore, NT-based treatments can produce high-performance treated water with fewer contaminants and harmful substances, as well as heavy metal removal. NT can be utilised in concert with biological treatments to lessen the hazards of environmental toxins. Organic dyes may be successfully removed from surfaces using industrial methods supplemented by nanoparticles [53]. Gold and silver NPs are excellent dye degrading catalysts that work in two steps: electron accumulation on the particle surface followed by dye transportation for a reduction process [54].

Magnetic NPs offer a wide variety of uses in adsorption and catalysis for environmental cleanup [55]. Polyacrylamide-modified magnetite NPs can be used because they offer soil erosion and arsenate leaching [56]. Pollutant immobilisation on-site has received a lot of attention as a practical and economical method of cleaning up polluted soils. Various NM-based whole form alterations have been researched in order to find a material that combines low cost, high efficiency, increased stability, low environmental effect, and maximum reusability. Nanohydroxyapatite particles

successfully immobilise metal concentrations in pore water by reducing the exchangeable percentage of metals in polluted sediments and soils [57].

According to this investigation, they were able to remove 80% of soil-bound Cr using nZVI stabilised with sodium carboxymethyl cellulose (VI). Abiotic reductive reactions in soil, either alone or in conjunction with immobilisation methods, can be utilised to treat redox-sensitive elements as pollutants, impacting their mobility and toxicity directly. When nZVI was given to pyrene-affected soil, for example, it provided strong reducing conditions, allowing pyrene to be reduced. NMs are also used in advanced oxidation processes (AOPs), which break down organic contaminants in polluted soil by using a variety of oxidants [58].

Utilize soluble Fe and hydrogen peroxide or persulfate to effectively degrade organic contaminants by oxidation (II). However, acidic pH (which is necessary to avoid Fe (II) precipitation) and accompanying drawbacks, such as the cost of early acidification and negative impacts on soil quality and microorganisms, limit these activities. As a result, solid iron phases have been suggested as an alternative to soluble Fe (II) in order to enable chemical oxidation without changing pH. Iron particles enhance the procedure when used in conjunction with chelating ligands [59].

Green NPs have a lot of potential for cleaning up enclosed spaces that have been contaminated with dangerous metal ions. These resources can be utilised to restore and clean up contaminated areas. Ferrous NP may be used to clean heavy metal-contaminated water and soil, as well as being a superb eco-friendly fertiliser. These nanofertilizers aid synchronise plant nutrient uptake while reducing groundwater contamination since they are immobilised and won't change into permanent chemical or gaseous forms that are out of reach for the developing plant [60]. Optical coatings for solar energy applications have been made from magnetite (Fe_3O_4) and greigite (Fe_3S_4) with siliceous material produced by bacteria [61].

9.0 Synthesis of NPs by Microbes

Because it has a clean, safe, non-toxic impact, and uses a method that is kind to the environment, green technology is widely regarded as a bioremediation technique [81]. Microbes use a bottom-up approach to produce NPs, and the majority of the processes involve reduction and oxidation. The conversion of toxic pollutants into less harmful chemicals is the fundamental idea behind bioremediation. The toxicity, solubility, and mobility of contaminants can be reduced by microbe-produced nanoparticles [82]. In compared to metallic NPs created using chemical processes, biologically produced metallic nanoparticles are more stable at ambient temperature over extended periods of time [83].

The biosynthetic processes are stabilised by the microbial proteins that cover the metallic nanoparticle surface. By using the right techniques, the cost of producing nanoparticles may be reduced to $1/100^{\text{th}}$ of what it would be using chemical synthesis approaches. Fewer biogenic nanoparticles can effectively remove large amounts of pollutants. The biogenic nanoparticles have strong catalytic activity and a huge surface area, but they cannot combine because of capping agents produced by microorganisms. Microbes may produce NPs either intracellularly or

extracellularly [81], with extracellular biosynthesis being more common due to its low cost as it does not require downstream processing. Microbes can create the corresponding NPs by absorbing precursor metal ions and employing the detoxification process [84].

Since microbe application is a low-cost procedure [86], microorganisms don't need a lot of energy [85] or capping or stabilising agents. Under typical circumstances, creating fine, homogenous, and useful NPs is difficult [87]. The biogenic sources offer a secure, economical, and ecologically friendly way to create metal NPs [88]. Scientists have found it profitable to use biological resources as nanofactories because of benefits including well-defined morphologies, simplicity in manufacturing, scalability, and improved biocompatibility [89]. According to what is stated below and listed in Table 1, microorganisms including fungi, actinomycetes, and bacteria are frequently utilised to produce NPs containing metals like lead, cadmium, nickel, iron, and silicon (Figure 10).

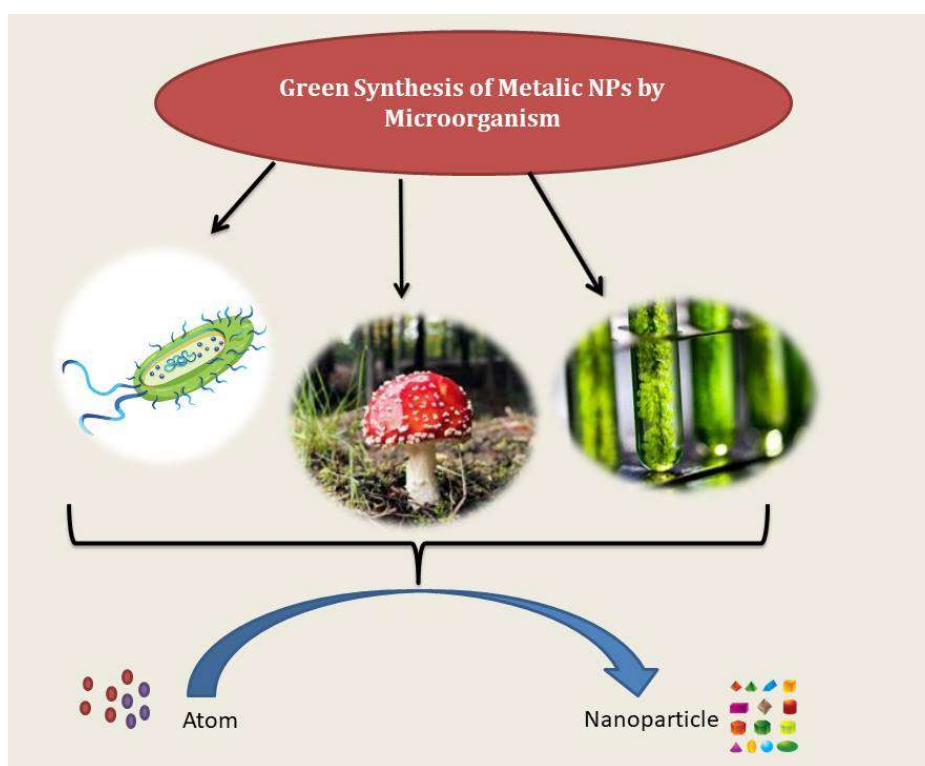


Figure 10: Green synthesis of metallic NPs by Microorganism

9.1. NPs synthesis by bacteria

The bacteria are considered as prospective bio-resources for producing nanoparticles including, gold, silver, platinum, magnetite cadmium sulphide, titanium, TiO_2 , and others that are listed in Table 1. Due to their capacity for environmental adaptation, bacteria are crucial microorganisms for the production of NPs [90]. The ability of certain bacteria to convert or precipitate hazardous inorganic ions into harmless, insoluble metal nanoparticles has been reported [91]. Bacteria may create metal and metalloid NPs both intracellularly or extracellularly depending on a variety of physico-chemical factors, including exposure time, pH, temperature, bacterial concentration, and

metal salts. Extracellular mechanisms involving media-found proteins or cell wall constituents can decrease metal ions [92].

But during the internal process, functional groups on the cell wall draw metals and metalloids, and metals interact with proteins within the cells to generate NPs through ionic attraction [92]. Dead bacteria may be employed for the manufacture of NPs in the same way as live bacteria since extraction is simple, and extracellular reduction appears to be preferable to intracellular reduction. Because they serve as a biological platform for mineralization, bacteria can be used as biocatalysts [93]. The bacteria have the ability to decrease or precipitate metal ions as well as mobilise or immobilise metals. Because of their enzymes, bacteria may create inorganic nanoparticles and catalyse a variety of processes. The extracellular release of bacterial enzymes allows for the large-scale production of pristine NPs (100-200 nm size). The S-layer and bacterial cells' ability to bind metals makes them suitable for use in bioremediation. Metals may permeate through the bacterial cell wall into the cytoplasm and then be transported back to the wall for extracellular secretion, which is a highly important role for the cell wall. Chemical reactions that change positive charge into negative charge for certain groups, including amines and carboxyl groups, might modify the cell wall with metal binding sites. Since no costly or hazardous chemicals are needed for the synthesis or stabilisation processes, using bacteria to produce nanoparticles is a profitable technique [94] (Table 1).

9.2. NPs synthesis by Actinomycetes

The actinomycetes, which have characteristics of both fungus and bacteria, are essential in the synthesis of metal NPs. Under difficult environmental circumstances like high temperature and alkaline temperatures, *Thermomonospora* species created gold ions. Gold NPs between 5 and 15 nm in size were produced by *Rhodococcus* species alkali-tolerant actinomycetes [95]. It has been noted that the cell wall has a higher concentration of NPs than the cell membrane. Since there was no impact on cell development following the creation of NPs, the metal ions were not hazardous to the cells. Due to their vast surface area and ability to secrete secondary metabolites, actinomycetes are suitable sources for the creation of NPs. Metallic NPs can be produced by actinomycetes both within and outside of cells [96]. *Streptomyces hygrosopicus*, *Rhodococcus* sp., *Thermoactinomyces* sp., *Nocardia farcinica*, *Streptomyces viridogens*, and *Thermomonospora* sp. have all produced gold NPs [97]. *Streptomyces* species were also used to create copper, zinc, manganese, and silver NPs [98]. The creation of NPs by actinomycetes is highlighted in Table 2.

9.3. NPs synthesis by Fungi

A possible source for the creation of NPs is filamentous fungus. The mycelium of fungus has a large surface area and secretes a large quantity of proteins that can directly contribute to the creation of nanoparticles [99]. Filamentous fungi are considered to be more successful at producing nanoparticles due to their capacity to produce proteins, enzymes, and metabolites, ease of increasing and downstream processing, commercial feasibility, formation of large attributed to the prevalence of mycelia, and low-cost manufacturing method needs [100, 101]. Numerous

filamentous fungus species have very rapid growth rates and are simple to maintain in lab settings [102] (Table 3).

In comparison to those produced by bacteria, fungus exhibit more monodispersity when producing nanoparticles of nanoscale dimensions *Fusarium oxysporum* produces gold nanoparticles when AuCl_4 ions are present in an aqueous solution by releasing reducing agents into the mixture. This process is catalysed by the NADH enzyme. Due to their ability to attach to proteins via the coupling of cysteine and lysine residues, the produced NPs exhibit long-term stability [103]. The filamentous fungus have a great capacity for regeneration and environmentally safe production for the considerable synthesis of metal NPs with economic viability [104].

The following organisms absorbed heavy metals from polluted sites and were used to produce nanoparticles: *Rhizopus arrhizus*, *Trametes versicolor*, *Ganoderma lucidum*, *Cladosporium resinae*, *Aspergillus niger*, *Funalia trogii*, *Penicillium* sp. and *Aureobasidium pullulans* [105, 106]. Reports of copper NP production and uptake of copper (II) by dead biomass from *Hypocrea lixii*. NiO NPs could be produced both extracellularly and intracellularly by the same microorganism [107].

Table 1: NPs synthesize by Bacteria

| S.no | Bacteria | Type of NPs | Synthesis methods | Characterizations | Morphology | Size (nm) | References |
|------|--------------------------------|-------------|-------------------|-------------------|-------------|-----------|------------------------------------|
| 1. | <i>Lactobacillus</i> species | Titanium | Cell culture | XRD, TEM | Spherical | 40–60 | Prasad et al. (2007) [108] |
| 2. | <i>Pseudomonas Putida</i> | Silver | Extracellular | FTIR, SEM | Spherical | 70 | Thamilselvi and Radha (2013) [109] |
| 3. | <i>Serratia nematodiphila</i> | Silver | Extracellular | TEM, XRD | Crystalline | 10-31 | Malarkodiet al. (2013) [110] |
| 4. | <i>Escherichia coli</i> (DH5a) | Silver | Extracellular | TEM | Spherical | 10-100 | Ghorbani (2013) [111] |
| 5. | <i>Bacillus</i> strain CS11 | Silver | Extracellular | TEM | Globular | 42-92 | Das et al. (2014) [112] |

| | | | | | | | |
|-----|---------------------------------------|------------------|---------------|---------------------|-----------------------|-------|-------------------------------|
| 6. | <i>Bacillus methylotrophicus</i> | Silver | Extracellular | TEM, EDX | Spherical | 10-30 | Wang et al. (2016) [113] |
| 7. | <i>Novosphingobium</i> species | Silver | Extracellular | XRD, TEM | Spherical Crystalline | 8-25 | Du et al. (2016) [114] |
| 8. | <i>Pseudomonas fluorescens</i> CA 417 | Silver | Extracellular | FTIR, XRD, EDS, TEM | Cubic Spherical Oval | 10-60 | Syed et al. (2016) [115] |
| 9. | <i>Bacillus</i> sp. | Titanium dioxide | Cell culture | FTIR, XRD, TEM | Spherical | 22-97 | Khan and Fulekar (2016) [116] |
| 10. | <i>Brevibacillus formosus</i> | Gold | Cell culture | FTIR, DLS, TEM | Spherical | 5-12 | Srinath et al. (2017) [117] |
| 11. | <i>Pseudomonas</i> sp. efl | Silver | Cell culture | SEM, TEM, EDS | Spherical | 50 | John et al. (2020) [118] |

Table 2: NPs synthesis by Actinomycetes

| S.no | Actinomycetes | Type of NPs | Synthesis methods | Characterizations | Morphology | Size (nm) | References |
|------|---------------------------------------------|-------------|-------------------|-------------------|------------|-----------|----------------------------------|
| 1. | <i>Streptomyces hygroscopicus</i> | Gold | Intracellular | TEM | Spherical | 10–20 | Waghmare et al. (2014) [119] |
| 2. | <i>Streptomyces kasugaensis</i> NH28 strain | Silver | Cell filtrate | TEM, FTIR | Rounded | 4.2–65 | Składanowski et al. (2016) [120] |
| 3. | <i>Streptomyces capillispiralis</i> | Copper | Extracellular | TEM, XRD | Spherical | 3.6–59 | Hassan et al. (2018) [121] |
| 4. | <i>Streptomyces</i> species | Silver | Extracellular | TEM, FTIR | Spherical | 2.3–85 | El-Gamal et al. (2018) [122] |

Table 3: NPs synthesis by Fungi

| S. no. | Fungi | Type of NPs | Synthesis methods | Characterizations | Morphology | Size (nm) | References |
|--------|----------------------------------|-------------|--------------------------------|-------------------|------------|-----------|------------------------------------|
| 1. | <i>Aspergillus niger</i> | Silver | Extracellular | TEM, ESI | Spherical | 20 | Gade et al. (2008) [123] |
| 2. | <i>Fusarium solani</i> | Silver | Extracellular | TEM, FTIR | Spherical | 5–35 | Ingle et al. (2009) [124] |
| 3. | <i>Pleurotus sajor-caju</i> | Silver | Extracellular | SEM | Spherical | 5–50 | Nithya and Ragunathan (2009) [125] |
| 4. | <i>Coriolus versicolor</i> | Silver | Extracellular Intracellular | FTIR, TEM, XRD | Spherical | 25–75 | Sanghi and Verma (2009)[126] |
| 5. | <i>Penicillium fellutanum</i> | Silver | Extracellular | TEM | Globular | 5–25 | Kathiresan et al. (2009) [127] |
| 6. | <i>Trichoderma viride</i> | Silver | Extracellular | FTIR, TEM | Spherical | 5-40 | Fayaz et al. (2010) [128] |
| 7. | <i>Epicoccum nigrum</i> | Silver | Extracellular | XRD, TEM | Spherical | 1-22 | Qian et al. (2013) [129] |
| 8. | <i>Guignardia mangiferae</i> | Silver | Extracellular | HR-TEM, SAED, XRD | Spherical | 5-30 | Balakumaran et al. (2015) [130] |
| 9. | <i>Fusarium oxysporum</i> | Silver | Extracellular | FTIR, TEM | Spherical | 5-13 | Husseiny et al. (2015) [131] |
| 10. | <i>Arthroderma fulvum</i> | Silver | Cell filtrate | XRD, TEM | Spherical | 15.5 | Xue et al. (2016) [132] |
| 11. | <i>Colletotrichum</i> sp. ALF2-6 | Silver | Cell free extract | FTIR, XRD, TEM | Myriad | 5-60 | Azmath et al. (2016) [133] |

| | | | | | | | |
|-----|-----------------------------------------|--------|--------------------|--------------------|----------------|--------|---------------------------------|
| 12. | <i>Duddingtonia flagans</i> | Silver | Extracellular | DLS, TEM | Quasispherical | 30-409 | Costa Silva et al. (2017) [134] |
| 13. | <i>Fusarium oxysporum</i> | Silver | Cell-free filtrate | DLS, SEM | Spherical | 24 | Hamedi et al. (2017) [135] |
| 14. | <i>Aspergillus oryzae</i> MTCC no. 1846 | Silver | Cell filtrate | XRD, TEM, FTIR | Spherical | 7-27 | Phanjom and Ahmed (2017) [136] |
| 15. | <i>Fusarium keratoplasticum</i> | Silver | Culture filtrate | XRD, FTIR | Spherical | 6-36 | Mohmed et al. (2017) [137] |
| 16. | <i>Rhizopus stolonifera</i> | Gold | Culture filtrate | XRD, TEM, FTIR | Spherical | 9.47 | AbdelRahim et al. (2017) [138] |
| 17. | <i>Trichoderma longibrachaitum</i> | Silver | Culture filtrate | FTIR, TEM | Spherical | 10 | Elamawi et al. (2018) [139] |
| 18. | <i>Penicillium oxalicum</i> GRS-1 | Silver | Extracellular | XRD, FESEM | Spherical | 10-40 | Rose et al. (2019) [140] |
| 19. | <i>Aspergillus fumigatus</i> BTCB10 | Silver | Cell-free filtrate | ATR-FTIR, XRD, SEM | Spherical | 322.8 | Shahzad et al. (2019) [141] |

10.0 Ancient Pollution Removal Techniques and Their Consequences

Before the discovery of NT, conventional techniques such as coagulation, adsorption, and improved oxidation processes mixed with electrochemical and biological processes (Table 4) were utilised. Traditional approaches to treating contaminated water include flocculation and coagulation. They are employed as a biological treatment's pretreatment, enhancing the waste's capacity to degrade naturally and eliminating macro contaminants [155].

Table 4: Different pollutant removal method and its side effects

| Pollutant removal method | Side effect | Ref. |
|--------------------------|---------------------------------------------------------------------------|-------|
| Biological processes | Cannot treat toxic or refractory organic pollutants and have limitations. | [156] |

| | | |
|----------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Zeolite adsorption | They might be highly hydrophilic on template removal because of their high surface silanol density, leading to low adsorption for hydrophobic pollutants. | [157] |
| Photocatalysis | Economic constraints for the high level of mineralization. Postreaction products of photocatalysis could still remain toxic. Photo corrosion is a typical drawback, postseparation inorganic catalysts. Semiconductor photocatalysts are unstable under light irradiation. | [158, 159] |
| Electro kinetics | There might be ionic motion, crystallization of metal salts, and dehydration which prevented removal of inorganic pollutants. | [160] |
| Electrochemical advanced oxidation processes | High cost, high energy consumption for complete mineralization of pollutant. | [161] |
| Advanced oxidation process | Considerably affected by pollutant nature, type, and concentration of oxidants and catalyst, reactor configuration. Release toxic and less biodegradable by-products in extreme cases. | [162, 163] |
| Electrocoagulation | Myriad of designs for reactor formation. | [164] |
| Ozonation | Difficult mineralization of pollutants due to the presence of hydroxyl ion scavengers. | [165] |
| Classical Fenton process | Unsafe storage, transportation, and handling of hydrogen peroxide for large treatments. | [166] |

11.0. Conclusion and future perspectives

The contemporary era's fast pollution discharge into the environment poses a serious threat to the ecosystem and to human health. One of the most advantageous strategies for cleaning up HM-contaminated soil is phytoremediation, which also offers several benefits. Despite this, its broad usage isn't possible because to the lengthy cleaning procedure, unpredictable weather, phytotoxic effects brought on by too many toxins (HMs), and sluggish repair times. Because many standard strategies are inefficient in eliminating various contaminants, alternative ways are needed to eliminate pollutants as much as feasible. In recent years, it has been clear that using NPs in phytoremediation can significantly increase its effectiveness. This review's main goal is to give a general overview of how nanoparticles are used to address possible problems, such as the remediation of heavy metal-contaminated soil. Large, polluted areas might potentially be cleaned up using nano remediation, which would shorten cleanup times, do away with the need to remove toxins, and bring contamination concentrations down to nearly zero. The effectiveness of the method in real-world settings is crucial to the multidisciplinary effort that is required. One of the key difficulties in doing this research is the collaboration between biology and the science of

materials. The remediation potential of nanoparticles can also be improved by modifying their size and shape.

Future studies are required to address the issues related to the use of biologically derived nanoparticles in heavy metal remediation. These studies should focus on their toxicity to plants and animals, their regeneration, regulation, and degradation, as well as combined methods for utilising their potentials for phytoremediation, synergistic and antagonistic interactions between microorganisms and bionanomaterials, and their stability in the bioremediation of heavy metal.

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