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Nano-Phytoremediation approach to remediate contaminated soil

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ABSTRACT

Rapid industrial development, current farming practices, and other harmful human activities enhance the amount of poisonous heavy metals in the atmosphere, which exerts a poisonous effect on all forms of living beings and changes their properties. The non-biodegradable metals accumulate in soil /environment and thus contaminate the food chain. Many efforts have been made to increase the efficiency of phytoremediation technology such as the inclusion of chelating agents, the application of rhizobacteria, genetic engineering, etc. In this context, the integration of nanotechnology with phytoremediation has introduced new dimensions for renovating the remediation methods. Thus the combination of phytoremediation approaches and nanotechnology may increase the adsorption/absorption and deterioration of pollutants. The nanoparticles tend to absorb a large variety of pollutants and also catalyze reactions by reducing the energy required to break them down, owing to their unique surface properties. As a result, this Nano-phytoremediation process reduces the accumulation/deposition of pollutants into soil/ environment. The spread of pollutants may also reduce by this approach. Thus, the present investigation reports on the future trends to remediate the contaminated site by nano-phyto approach.

Keywords-Bioremediation, Nanomaterials, Nanoparticles, Phytoremediation, Environment, Pollution

INTRODUCTION

Anthropogenic activities like the combustion of fossil fuel, phosphate fertilizers, agrochemicals, mining, industrial effluents, etc. are adding harmful pollutants and toxic metals and excess nutrients to the soil/environment [1]. Various engineering-based methods such as soil excavation, soil washing air burning, or pump and treat systems are already being used to remediate contaminated soils. However, non-biological techniques are not fully accepted as they destroy the biotic components of soil and the environment. Nowadays phytoremediation is an emerging technology used to remediate the contaminated environment [2 & 3]. The term "phytoremediation" is a combination of the Greek "phyto" (meaning plant) and Latin "remedium" (meaning to correct or remove evil). Green plants have a great ability to pick up pollutants and carry out their functions in various ways. A phytoremediation is a group of technologies that uses the plant to reduce, remove, degrade or immobilize environmental contaminants, primarily those of anthropogenic origin, to restore the site to a condition usable for private or public application.[4]. Certain plants (hyper-accumulator) have endogenous, genetic, biochemical and physiological inherent qualities to fight against soil, water, and air pollution [5],[6]. Hyper-accumulator plants' root systems have the capability to accumulate, translocate, and store the contaminants in the plant body.

Recent advances in nanotechnology have impacted industries including manufacturing, biomedical applications, electronics/telecommunications, agriculture, and renewable energy, among others [7]. Nanoparticles (NPs) are broadly defined as particles having at least one dimension between 1 and 100 nm in diameter [8]. Nanoparticles have unique properties and novel features. They have been widely used in many aspects of daily life and energy production, including in catalysts, semiconductors, cosmetics, drug carriers, and environmental energy [9]. The biosynthesis of nanoparticles using microorganisms has emerged as a rapidly developing research area in green nanotechnology across the globe, with various biological entities being employed in the synthesis of nanoparticles constantly forming an impute alternative for conventional chemical and physical methods. The advancements in nanotechnology open a window globally to remediate the contaminated soil/land effectively [10, 11]. It has been claimed that nanotechnology has great potential as an environmentally cleaner technology, including by alleviation of the toxicities of various metals/metalloids [12]. Besides, nanotechnology has been recognized as a potential method for the remediation of pollutants in a variety of environmental matrices, including soils/land. In this context, soil/land remediation is one of the main domains where nanotechnological approaches have been widely used. By the use of nanoparticles, the hyperaccumulator plants (Marigold, Tagetes, Cardemine, Pteris, etc.) and indigenous soil microbes could increase the biodegradation process, thereby increasing the potential extent of phytoremediation. Such an approach could be called Nano-phytoremediation and Microbial-mediated Nano-Bioremediation. Due to the small size of nano-particles (1-100 nm), the combination of nanoparticles and phytoremediation approaches results in a lot of benefits. Nanomaterials possess significant surface areas, a high number of active surface sites, and high adsorption capacities, which make them a promising solution for the remediation of contaminated soils. Nanomaterials can function in the phytoremediation system by directly removing pollutants, promoting plant growth, and increasing pollutant phytoavailability. Phytoextraction is the most effective and recognized phytoremediation strategy for remediating contaminated soil. Nanoscale zero-valent iron is the most studied nanomaterial for facilitating phytoremediation due to its successful engineering applications in treating contaminated soil and groundwater. Fullerene nanoparticles can increase the phytoavailability of pollutants [13].

Nanoparticles-

Nanotechnology is characterized by the application of very small particles (<100 nm), called nanoparticles (NPs) or ultrafine particles. The size of Nanoparticles (nano-scale particles = NSPs) is ranged between 1 and 100 nm which can drastically modify their Physico-chemical properties compared with the bulk material. Nanoparticles can be made from a variety of bulk materials and they can act depending on the chemical composition, size, or shape of the particles. They are more reactive and more mobile in nature.

Nanoparticles may be of two types-organic and inorganic nanoparticles. The organic nanoparticles include carbon nanoparticles (fullerenes) whereas the inorganic nanoparticles include magnetic nanoparticles, noble metal nanoparticles (e.g. gold and silver), and semiconductor nanoparticles (e.g. Titanium dioxide and Zinc oxide). According to Ruffinironment-Castiglione and Cremonini [14] nanoparticles may be of three types: natural, incidental, and engineering. The natural nanoparticles include volcanic or lunar dust, and mineral composites, incidental includes such NPs which result from anthropogenic activity, e.g. diesel exhaust, coal combustion, welding fumes, and engineered NPs are artificially synthesized. Smaller particle size enables the development of smaller sensors, which can be deployed more easily in remote locations. Recently, nanomaterials (NMs) have been suggested as efficient, cost-effective, and environmentally-friendly alternatives to existing treatment materials, in both resource conservation and environmental remediation [15].

Biosynthesis of Nanoparticles-

Nanoparticles are synthesized by a variety of organisms like plants, bacteria, fungi, etc.

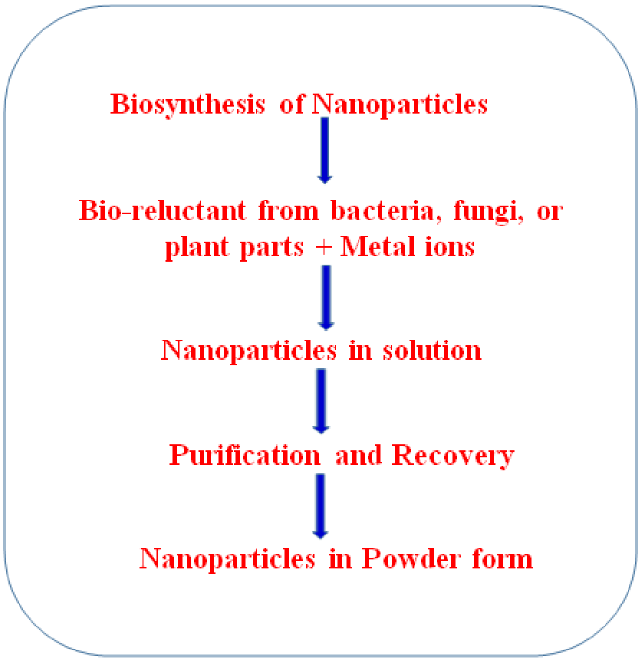

Figure 1: Flowchart outlining the biosynthesis of nanoparticles.

A number of plants are currently being used to synthesize the nanoparticles. While fungi and bacteria require a comparatively much more incubation time for the reduction of metal ions. Water soluble chemicals produced by plants do this in a much lesser time. Thus, plants are a better option to synthesize nanoparticles than bacteria and fungi. Taking the use of plant tissue culture techniques and downstream processing procedures, it is possible to synthesize metallic as well as oxide nanoparticles on an industrial scale once issues such as the metabolic status of the plant are properly addressed. It is proved from compiled information that the impact of nanoparticles varies from plant to plant and depends on their mode of application, size, and concentration.

Synthesis of Nanoparticles by Plants-

The biosynthesis of nanoparticles by plants is a widely accepted technology for the rapid production of nanoparticles. Plants are considered chemical factories of nanoparticles [16]. Plants have various cellular structures and metabolic processes to combat the toxicity of metals and maintain homeostasis. It is a dynamic solution to detoxify metals and hence scientists have now turned it into phytoremediation [17].

Plants have the ability to tolerate the inimical concentrations of heavy metals and accumulate high concentrations of heavy metals in them. In plants or plant-derived materials, a wide range of metabolites with redox potential is determined, which are playing a principal role as a reducing agent in the biogenic synthesis of nanoparticles. In comparison to the microbial synthesis of nanoparticles, highly stable nanoparticles are synthesized by plant or plant extract with a higher rate of production. Consequently, the advantages of the plant-mediated preparation of metal nanoparticles lead researchers to in search of further exploration of the bio-reduction mechanism of metal ions by plants and possible mechanism of formation of metal nanoparticles in and by the plants [18].

Generally, the bio-reduction mechanism of the metal nanoparticles in plants and plant extracts includes three main phases [19] (i) The activation phase in which the reduction of metal ions and nucleation of the reduced metal atoms occur., (ii) the growth phase, referring to the spontaneous coalescence of the small adjacent nanoparticles into particles of a larger size, accompanied by an increase in the thermodynamic stability of nano-particles, or a process referred to as Ostwald ripening and (iii), the termination phase in which the final shape of the nanoparticles formed.

Synthesis of Nanoparticles by Fungi

Fungi are an excellent source of different extracellular enzymes which influences nanoparticle synthesis. The Fungi have been widely used for the biosynthesis of nanoparticles. In addition to monodispersity, nanoparticles with well-defined dimensions can be obtained using fungi. In comparison to bacteria, fungi could be used as a source for the production of larger amounts of nanoparticles. This is because, the fungi secrete a greater volume of proteins which directly translates to higher productivity of nanoparticle formation. Instead of fungi culture, isolated proteins have also been used successfully in nanoparticle production. The use of specific enzymes secreted by fungi in the synthesis of nanoparticles is promising. Understanding the nature of the biogenic nanoparticle is equally important. Microbiological methods generate nanoparticles at a much slower rate than that observed when plant extracts are used. In the biosynthesis of metal nanoparticles by a fungus, enzymes are produced which reduce a salt to its metallic solid nanoparticles through the catalytic effect. This is one of themajor drawbacks of biological synthesis of nanoparticles using microorganisms and must be corrected if it is to compete with other methods. For industrial applications, fungi should have certain properties which include high production of specific enzymes or metabolite, high growth rate, easy handling in large-scale production and low- cost requirement for production procedures which provides advantages over other fungus methods. Fungi have an edge over other biological systems due to wide diversity, easy culture methods, reducing time and increasing cost-effectiveness. This, in turn provides an eco-friendly approach for nanoparticle synthesis. Genetic engineering techniques can be employed to improve the particle properties in near future. In synthesis of numerous enzymes and rapid growth with the use of simple nutrients, yeast strains possess certain benefits over bacteria and the synthesis of metallic nanoparticles employing the yeast is being considered [20].

Synthesis of Nanoparticles by Bacteria

Microbes (Bacteria) have a remarkable efficiency to produce reduced metal ions under stress conditions. Therefore, supernatants of some bacteria such as Pseudomonas and Arthrobacter act as microbial cell factories synthesizing silver nanoparticles [21]. The ZnO nanoparticles are synthesized by Lactobacillus plantarum bacteria [22]. The gram-negative bacterial strain Aeromonas hydrophila has been explored for the biosynthesis of ZnO nanoparticles with further antimicrobial applications [23]. Triangular CuO nanoparticles have been developed using Halomonas elongate which displayed antimicrobial activity against E. coli and S. aureus [24]. In another experiment, super paramagnetic iron oxide nanoparticles of about 29.3 nm dimensions were produced using Bacillus cereus strain. As an application, their anti-cancer effects were reported against the MCF-7 (breast cancer) and 3T3 (mouse fibroblast) cell lines in a dose-dependent manner [25]. A rapid, method for the synthesis of manganese and zinc nanoparticles by reducing manganese sulfate and zinc sulfate using Streptomyces sps. has been reported. The scale of NPs for manganese and zinc was between 10 and 20 nm [2 6] . Escherichia coli E-30 and Klebsiella pneumoniae K-6 have been reported to synthesize cadmium sulfide nanoparticles with average size ranging from 3.2 to 44.9 nm and showed highest antimicrobial activity on A. fumigatus, B. subtilis, S. aureus, and E. coli strains [27].

Cyanobacteria (Blue- green algae) are a phylum of photosynthetic bacteria widely used for their capacity to synthesize nanoparticles due to the presence of bioactive components, which help in stabilizing and functionalizing the nanoparticles, resulting in fewer steps insynthesis. Their high-growth rate also facilitates higher biomass production to aid in nanoparticle synthesis. Aqueous extracts of the cyanobacterium Oscillatoria limnetica has been useful in synthesizing Ag nanoparticles by reduction and further stabilizing them. The size of the nanoparticles was 3.30–17.97 nm and they showed anti-cancer and anti-microbialactivity [28].

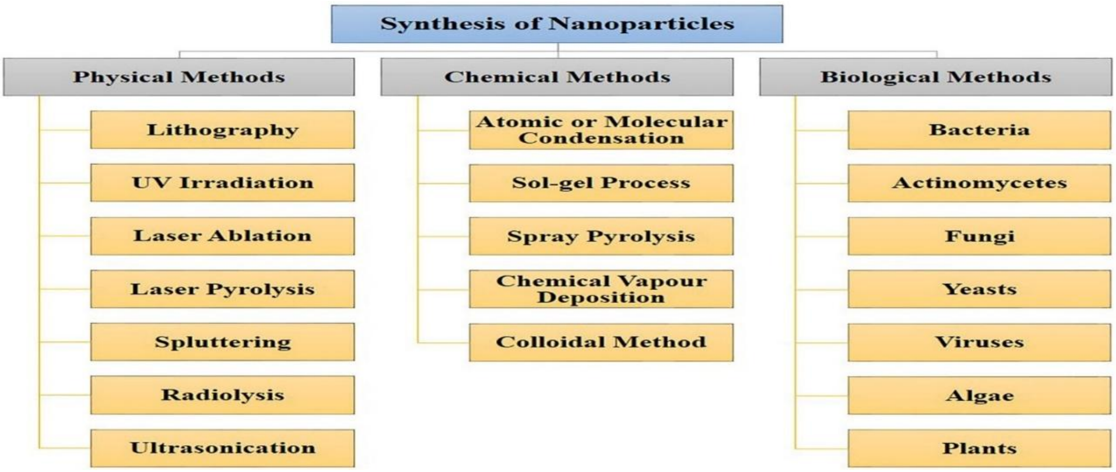

Figure 2- Different approaches for nanoparticles synthesis. Nanoparticles can be synthesized through physical, chemical, and biological routes.

Phytoremediation

Presently phytoremediation is an emerging promising approach to remediate polluted environments. This technology is an alternative or complementary one that could be applied along with or instead of mechanical congenital cleaning methodologies which mostly require high capital input, labor, and, intensive energy. Certain plants have endogenous, genetic, biochemical, and, physiological qualities to combat soil, water, and air, pollution. Phytoremediation takes advantage of the uptake capabilities of plant root systems, together with the translocation, bioaccumulation, and pollutant storage/degradation abilities of the entire plant body [29].

Phytoremediation exploits plants' innate biological mechanisms for human benefit. Seven subsets of this technology as applicable to toxic metal remediation from soil and water are: Phytoextraction, Phytofilteration, Phytostabilization, Phytovolatilization Phytodegradation Rhizodegradation, and Phytodesalination.

Phytoextraction

It is the best approach to remove the contaminant especially heavy metals, from soil or water by plant roots and their translocations in above-ground parts [29, 30]. In metal-polluted soil hyperaccumulating plants seeded/transplanted are cultivated under established agriculture methodologies. When maximum plant growth and metal accumulation are achieved, plants from above-ground levels are harvested which results in the permanent removal of metals from the site [31]. The efficiency of phytoextraction depends on many factors like soil properties, speciation of heavy metals, bioavailability, heavy metals, and plant species concerned. The plants which have to be used in phytoextraction should possess the following characteristics.

I. Easy cultivation and harvest.
II. Enhanced growth rate.
III. Profusely branched root and shoot system.
IV. Widely distributed.
V. Hyperaccumulating nature.
VI. Translocation of accumulated heavy metals from roots to shoots.
VII. Tolerant to heavy metals.
VIII. Production of high biomass.
IX. Resistance to pathogens & pests.

Phytofilteration:

In Phytofiltration plant roots (rhizofiltration) or seedlings (blasto filtration) are grown in aerated water from where they participate and concentrate toxic metals from contaminated effluents [32]. In other words, phytofiltration is the removal of pollutants from contaminated surface waters of or waste water by plants [33]. The techniques involve growing plants hydroponically and transplanting them into metal-polluted water from where plants absorb and concentrate the metal in their roots & shoots [34]. The plants which have to be utilized in rhizofiltration must possess-fast growing roots with the capability for removing toxic metals from solution over an extended period of time. After saturation with metal contamination which forms precipitation over the root surface, whole plants or roots are harvested for disposal. This precipitation is caused by root exudates and changes in rhizospheres [34]. The mechanisms of phytofiltration are not necessarily similar for different metals. Precipitation and exchangeable sorption are involved in the case of Pb . The advantages of rhizofiltration include it ability tube used as in-situ or ex-situ applications and species other than hyperaccumulators can also be used [35].

Phytostabilization:

It is also termed phyto-restoration or phyto-immobilization. It is a technique used for the stabilization of contaminants in a contaminated environment [36]. In this remedial technique, the plant stabilizes wastes and prevents exposure pathways through wind & water erosion, enables hydraulic control that restricts the vertical migration of pollutants into groundwater, and immobilizes the pollutants physically and chemically by root sorption and chemical fixation with different soil amendments. Metals of different valances vary in toxicity. By excreting special redox enzymes, plants skillfully convert hazardous metals to a relatively less toxic state and decrease possible metal stress and damage [30]. The reduction of Cr (VI) to Cr (III) is widely studied, the latter being both less mobile and less toxic [37]. The research of Smith and Bradshaw [38] led to the development of two cultivars of *Agrosists tenuis,* Sibth, and one of *Festuca rubra* L. which are now commercially available for the phytostabilization of Pb, Zn, & Cu contaminated soil. The combination of tree and grasses work best for phytostabilization. Fast transpiring trees such as *Poplar* maintain an upward flow to prevent downward leaching, while grasses prevent wind erosion and lateral runoff with the dense root systems. Further, grasses do not accumulate as many metals in their shoots as dicot species, minimizing exposure of wildlife to toxic elements [39]. However, phytostabilization is a temporary solution to the problem but not permanent because heavy metals remain in the soil. Only their environment is limited. Actually, it is a management strategy for stabilizing potentially toxic contaminants [40].

Phytovolatilization:

Phytovolatilization is the uptake of pollutants from the soil by plants, their conversion to volatile form, and subsequent release into the atmosphere. It works well for organic pollutants but can be used for a few inorganics that can exist in volatile form i.e. Se, Hg, and As. The mentioned process is controversial of all techniques due to its dubious nature that whether the release of these volatilized elements in the atmosphere is safe. The disadvantage is the volatilized element could be recycled by precipitation and then deposit back into the ecosystem [41]. It is fact that it does not remove the pollutant completely, only transfer from one segment (Soil) to another (atmosphere) [42]. Members of the Brassica genus and some microorganisms are particularly good volatilizers of Se [43]. Amongs the aquatic species, rice, rabbit foot grass, Azolla, and pickleweed are the best Se volatilizers [44]. Volatilization of Se involves the assimilation of inorganic Se into the organic selenoaminoacids selenocysteine (SeCys) and selenomethionine (SeMet). The latter can be methylated to form dimethyl selenide (DMSe), which is volatile [43]. In Hg, contaminated soil and sediments, microbial activity converts the highly toxic Hg (II) into organo-mercurials and, under optimum conditions, elemental Hg (which is far less toxic) enters the biogeochemical cycle upon volatilization [45]. After genetic modification of Arabidopsis thaliana L. and Nicotiana tobaccum L. with bacterial organomercurial lyase (Mer B) and mercuric reductase (Mer A) genes [46], plants have developed abilities to absorb elemental Hg (II) and methyl mercury (Mer Hg) to the atmosphere. Although it is a passive process, it may be maximized by using plant species with high transpiration rate, by overexpression of enzymes such as Cystathionine _V_ synthases that mediates S/Se volatilization [47], and by the transferring gene for Se volatilization from hyperaccumulator to nonaccumulators [48].

Phytodegradation

Phytodegradation is the breakdown of organics, taken up by the plant to simpler molecules that are incorporated into plant tissues. Phytodegradation is not dependent on rhizospheric microorganisms [49] Plants contain enzymes that can break down and convert ammunition wastes, chlorinated solvents such as trichloroethylene, and other herbicides. The enzymes are usually dehalogenases, oxygenases, and reductases [50]. According to Zazouli [51], many organic hazardous pollutants such as bisphenol A (BPA) which are toxic and not easily biodegradable can concerns for environmental pollution words wide. They studied whether *Azolla filiculoides* is able to remove BPA from an aqueous solution. They noticed that *Azolla filiculoides* have 60-90% BPA removal efficiency. The removal efficiency was more than 90% when the BPA concentration was 5 ppm and the amount of biomass was 0.9 gm. They concluded that *Azolla* has a good ability to remove the organic compound from aqueous solution and removal efficiently depended on the reaction time, initial BPA concentration, fern water weight pH, and temperature. The conventional methods such as AOP (Advance oxidation process) adsorption etc. or high cost and consume high energy and because all countries are faced with energy shortage problems today; thus natural systems, for instance, the use of *Azolla* can be a good alternative to the conventional system to remove of this compounds from waste-water. Recently, scientists have shown their interest in studying the phytodegradation of various organic pollutants including synthetic herbicides & insecticides [30].

Rhizodegradation

Rhizodegradaion is the breakdown of organic pollutants in the soil through soil microorganisms of the rhizosphere

[52]. The rhizosphere extends about 1mm around the root and is under the influence of the plant [39]. The main reason for the increased degradation of pollutants in the rhizosphere is likely the increase in the number and metabolic activities of the microbes. Plants can stimulate microbial activity about 10-100 times higher in the rhizosphere by the secretion of root exudates containing amino acids, carbohydrates, flavonoids, and amino acids. According to Spaczynski [53], soil microorganisms living in the rhizosphere play an invaluable role in the degradation of harmful organic compounds; they are often much more involved in the mineralization of xenobiotics than plants.

Through rhizodegradation many toxic compounds such as pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons petroleum compounds, etc can easily be removed from the microorganisms to secrete organic substrates for facilitating the growth and activities of rhizosphere microorganisms, plants also provide certain enzymes capable of degradation organic contaminants in soil [54].

Phytodesalination

It is a recently reported and emerging technique to reclaim salt-affected soil [55]. Phytodesalination refers to the use of halophytic plants for the removal of salts from salt-affected soils in order to enable them for supporting normal plant growth [56 & 57]. It was postulated that salt affected the soil cover of about 6% (more than 800 million ha) of the world's lands, which is mainly due to natural causes Salt accumulation over a long period of time in arid and semi-arid regions) or to human-induced causes that affected in 2008 about 2% (32 million ha) of the dry land formed areas and 20% (45 million ha) of the irrigated lands in the world [55]. To overcome this problem, several authors [58 &59] have been encouraging this biological approach proving the efficiency of Na^+ -hyperaccumulating plants to desalinize the soil on which they are cultivated, especially in arid and semiarid regions, where low precipitations expectations and inappropriate irrigation system are unable to leach salts from the rhizosphere. Soil phytodesalition is based on the capacity of some halophytes to accumulate enormous sodium quantities in their shoots. Halophytic plants have been suggested to be naturally better adapted to cope with heavy metals compared to glycophytic plants [56]. According to an estimation two halophytes, *Suaeda maritima* and *Sesuvium portulacastrum* could remove 504 and 474 kg of sodium chloride (Nacl) respectively from 1 hectare of saline soil in a period of 4 months. Therefore, *S. maritima* and *S. portulacastrum* could be successfully used to accumulate NaCl from highly saline soils and enable them for crop production after a few repeated cultivation and harvest [58].

Nano-phytoremediation

Nano-phytoremediation is a cost-effective technique of utilizing plants and microbes to break down pollutant compounds, ultimately improving soil quality and reducing pollution. Nano-phytoremediation involves both nanotechnology and phytoremediation together to clean up the contaminated environment. Nanotechnology increases the phytoremediation, efficiency, and nanoparticles, can also be used for remediation of soil and water contaminated with heavy metals, organic, and inorganic pollutants. Nanoparticles used in enzyme-based bioremediation, can also be used in combination with phytoremediation [60 & 61]. Nanomaterials can function in phytoremediation systems, by directly removing pollutants, promoting plant growth, and increasing pollutant's phytoavailability. Among various phytoremediation techniques, phytoextraction, is the most effective technique, to remediate soil contaminated with heavy metals [62]. The zero-valent iron is the most effective nanomaterial, facilitating phytoremediation due to its successful engineering applications in treating contaminated soil and groundwater. Crons et.al, [63] Investigated that nanomaterials decontaminated organic pollutants like PCB (Polychlorinated Binyl), PAHS (Poly Acromated Hydrocarbons), and organic solvents, etc. present in the soil. Contaminants, ranging from heavy metal to volatile organic compounds, can easily be treated by this technology with high efficiency of its uptake by the plant. Nano-phytoremediation is particularly effective for organic pollutants and more efficient removal of site contaminants. The recent studies has been reported that the application of nanoparticles can also improve the stress tolerance of plants in ex-situ and in-situ conditions, thereby, promoting phytoremediation potential [64].

Selection of Nano-particles used for Phytoremediation

The nanoparticles should have following characteristics to be used for phytoremediation (i) the nanoparticle should be non-toxic for plant

(ii) Seed germination, seedling growth, root-shoot elongation, plant height, and biomass of the plant should be increased by application of Nanoparticles.

(iii) By, use of nanoparticles, the phyto-enzyme production should be increased.

(iv) Abilities to enhance the plant growth hormones.

(v) Should have the capability to binds with contaminants and increase the bioavailability for plant.

(vi) Enhance the phytoremediation process.

The application of selected nanoparticles results in enhanced plant growth and nano augmentation increased phytoremediation potential which can significantly remove the contaminants from the soil environment. Many nanoparticles have been proved to be a plant growth promoters due to their ability to enhance the plant growth promoter hormones and better uptake of minerals by the plant species. Various plant species were also found to increase growth from the nano-treatment procedures. Several studies also indicate the positive effects of metal and metal oxide nanoparticles on the growth of higher plants [65].

Interaction in between Nanoparticles and Plants

The application of Nanomaterials is site specific and their efficiency is influenced by pollutant types, concentration, size, charge/ ion-charge material and organic content and also by other physical and chemical Properties of soil such as soil aggregates texture etc. along with plants causing many physiological and morphological changes, and the plant responses will be strongly depending on the nanoparticle types, dose and speciation as well as, on the plant species involved [66].The effectiveness of nanoparticles also depends on their physical and chemical composition,size, shape, surface covering, reaction and most importantly the concentration on which they are effective which varies from plant to plant.[67 and 68]. In many studies, increasing, evidence suggests that various nanoparticles increase plant development and growth. According to Khan and Bano[69],silver nanoparticles significantly increased the ABA (Abscisic Acid) and GA (Gibberellic Acid) production by greater than 90%, which helps plants to tolerate stress conditions as well as increase the uptake of nutrients and water for improved growth. The uptake of nitrogen, its assimilation, and plant metabolism increased with the application of Mn nanoparticles. The positive effects of Mn nanoparticles were also noticed by Pradhan et.al [70] on root and shoot elongation. Nanoparticles in the form of nano fertilizers also help to regulate nutrients release in soil system, catalyze soil fertility, and promote enzymatic activities in plants. Increasing chlorophyll content and seed germination [71,72 & 73].

Nanobioremediation

Nanobioremediation implies both nanotechnology and bioremediation where the process is executed at the molecular level. It is a technique that helps in transforming harmful pollutants into safer molecules using various microorganisms in combination with nanoparticles that range in size less than 10 nm. Several nanoparticles like Zn, Ag, Au, Cu, etc. synthesized with numerous microorganisms in literature help in degrading harmful pollutants. Recently several researchers have used Iron and Zinc nanoparticles in cleaning-up environments. Iron nanoparticle technologies are currently used in cleaning up the ground waters & contaminated soil, by the process of absorptive/immobilization techniques and are even used as reductive technologies whereas, Zinc nanoparticles used as a semiconductor photocatalyst having the capacity to degrade the organic dye. These nanoparticles are found efficient in degrading the wide variety of compounds, dyes, organic acids, etc. which are left in sewage systems [74].

Principle of Nanobioremediation

The basic principle of nanobioremediation is referred to as the degradation of organic waste using nanocatalysts as a medium which allows them to penetrate deep inside the pollutants/ contaminants and treat them safely without affecting the surroundings with the help of several microorganisms (75). These microorganisms are present everywhere in the environment and compete with the population of the world. However, microorganisms have been found to have various advantages like converting heavy metals into non-toxic forms with the help of mineralization of organic contaminants to end product like CO_2 H2O or can lead to various metabolic intermediates which can be used to meet abnormalities for the growth of these microorganisms and moreover the utilization of these toxic compound lead to difference of their cell wall by the production of degradative enzymes which make them resistant to various heavy metal which they consume [76].

Metabolic Pathways involved in degradations of Contaminants

According to Das and Chandran [77] the contaminants are degraded under aerobic conditions. When the organic pollutants come in contact with the microorganisms, intracellular attacks take place by the microorganisms on pollutants. In this process, the oxygen molecules are incorporated by the activation of several enzyme groups known as oxygenase and peroxidase (Fig. 3). The degradation of the organic compounds is carried out in a step-by-step process, where several intermediates are formed through intermediated control metabolism. During the degradation process, various enzymes like cytochrome P_{450} play an important role. This enzyme is involved in the degradation of several oils and hydrocarbon. Several other enzymes like alkane hydroxylases, dioxygenases eukaryotic cytochrome P_{450}, bacteria cytochrome P_{450}, soluble methane monooxygenases etc. also involved in the degradation of fatty acids, alkyl benzene, cycloalkanes alkenes etc.

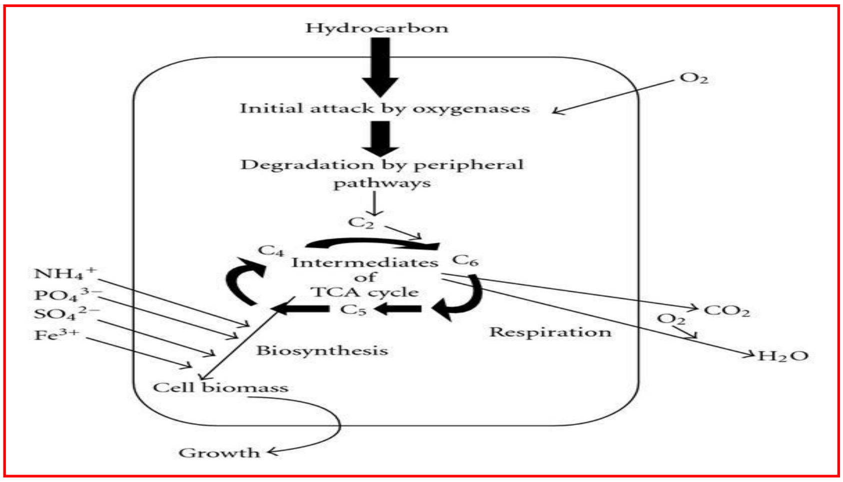

Figure 3: The metabolic pathway for degradation of hydrocarbons.

Application of Nanophyto and Nanobioremediation-

Plant species to be used in the nano-phytoremediation techniques for decontaminating, the contaminated soil is based on the application of nanoparticles and phytoremediation methods by using pl;ants.This technique exhibited a great potential to the environmental remediation and decontamination of organic pollutants in sediments. The various plant species and varieties of nanoparticles, are used in nano-phytoremediation experiments of contaminants, and their removal efficiencies are listed in table. Heavy metal pollution in soil is a very serious problem worldwide and poses a significant threat to food safety and human health. It has been finally reported that phytoremediation of soils contaminated with heavy metals by hyperaccumulator plants is enhanced by applying nano-materials (78 & 79).

Lead is a very common industrial metal pollutant that is widely used in storage batteries, gasoline additives, ammunition, etc., exerts great health effects. Nanomaterials enhance the phytoextraction efficiency of ryegrass (Lolium perennae) to Pb. Liang et.al [78] studied the effects of nano-hydroxyapatite on the lead phytoextraction by ryegrass and noticed that phytoextraction efficiency increased 31.76% in 1.5 months. Cadmium is a toxic metal commonly released into the soil from various industrial processes and products such as mining, smelting, electroplating, storage batteries, color pigments and phosphate fertilizers [80 &81].

Using hyperaccumulators to extract Cd from contaminated soils is the principal phytoremediation strategy, but available Cd hyperaccumulator species are in limited amount and capacity [82]. Some nano-materials have been noticed to increase the phytoextraction of cadmium in soil. Singh and Lee[83] noticed the positive effects of TiO2 nanoparticles on Cd accumulation in soybean plants.

Arsenic is also a very toxic and carcinogenic heavy metal. Arsenic contamination has been increased due to its enhanced uses in pesticides, herbicides, phosphate fertilizers, wood preservatives etc. [84]. Phytoextraction and phytostabilization, are two main phytoremediation strategies used to abate soil arsenic contamination. Souri [85] also reported the increased phytoextraction of arsenic by Isatis cappadocia.

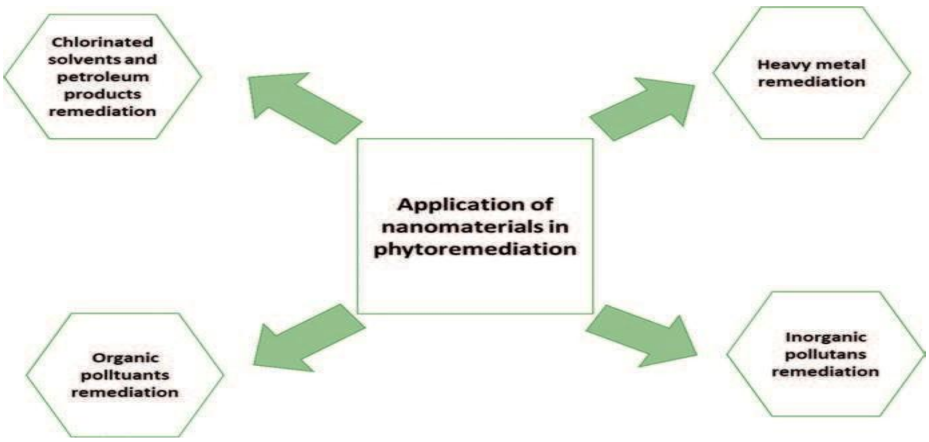

Figure 4: Application of nanomaterials in phytoremediation.

Nanobioremediation is a technique in which microbes convert harmful pollutants into safer molecules by using nanoparticles that range in size less than 100 nm. Many nanoparticles like zinc, silver, gold, copper, etc. are synthesized by microbes and plants, useful in degrading harmful pollutants. Nanobioremediation has the potential to reduce the overall cost in cleaning up large- scale pollutants with reduced cleaning-up. The basic principle of biodegradation is that the nanocatalyst produced by microorganisms penetrates deep inside the contaminants and treat them safely without affecting the surroundings[86].The microorganisms like bacteria, fungi etc. are mostly used to break down the organic pollutants. Life is dependent on the overall quality of the environment. Thus, to preserve and sustain the environment, it is important to use the nanobioremediation technique which is possible through the application of biotechnology. Environmental biotechnology employs the application of genetic engineering, or recombinant DNA technology, which improves the efficiency of microorganisms to reduce the environmental burden of toxic substances. Many of the microbes found in a variety of habitats/ environmental niches like the Dead Sea, the Himalayas, the Yellowstone National Park etc. play an essential role in recycling the gases present in the environment. Microbes are also responsible for developing the liable pools of N, H, & S etc. There are various microorganisms have even developed their cell wall structures to protect themselves through various damages caused by pollutants,by releasing wastes into the freshwater lakes etc. by various mechanisms like oxidation,reduction and absorption.When these microorganisms used with various Nanomaterials/ nanoparticles, are very much helpful integrating the environmental pollutants at a faster rate then bioremediation. When the process of Nanobioremediation start, the microorganism which are present at the contaminated site releases the extracellular enzyme help in the degradation of organic contaminants [87]. Recently, Nanobioremediation is also used in hydrocarbons, groundwater, wastewater, uranium, heavy metals, and solid waste remediation.

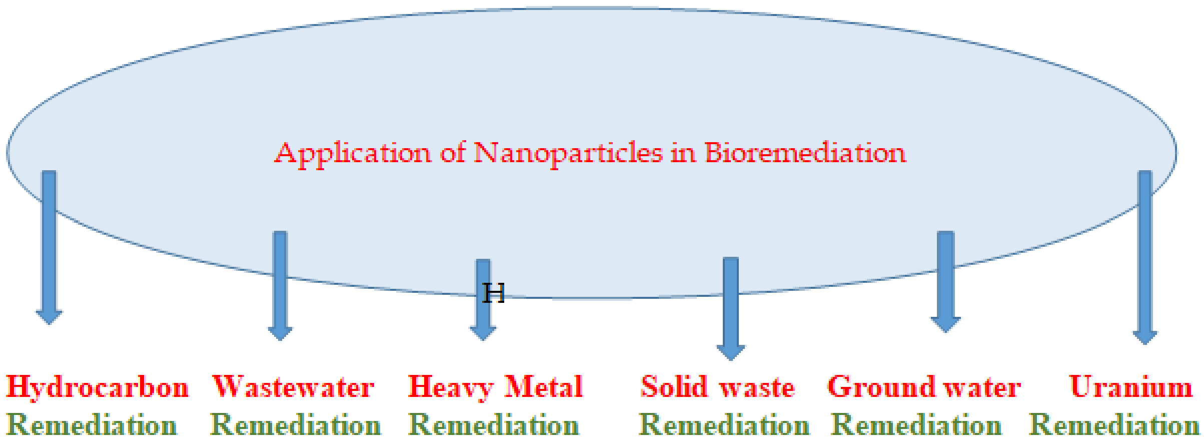

Figure 5: Application of Nanoparticles in Bioremediaton (Nanobioremediation)

CONCLUSION AND FUTURE PERSPECTIVES

Nanotechnology has made our life simpler and easier. Nanomaterials/ nanoparticles are being used in various fields of application like in building materials, in the treatment of environmental pollutants, providing food for microorganisms etc. The biosynthesis of these nanoparticles helps in minimizing the use of harmful chemicals and solvents. The nano-phyto and nano-bioremediation technologies can provid a green and eco-friendly alternative for the removal of environmental contaminants without harming nature. In nature several plants, bacteria and fungi are found, which have the ability to accumulate a large amount of material in their body. Such organisms are called as hyperaccumulators. Such plants and microbes can be used to remediate the soil and water contaminated with heavy metal. Their hyperaccumulation efficiency can be improved much more times by the application of nanoparticles/ nanomaterials. These nanomaterials/ nanoparticles have unique physical and chemical properties and hence, they have received much more attention from scientists and researchers in different areas of environmental sciences. With the use of genetic engineering, nanotechnology, and phytoremediation, environmental clean-up may be more effective and cost-effective. Furthermore, the specific control and design of nanoparticles at the molecular level will increase the capacity, affinity, and selectivity of contaminants. This may cause the reduced release of hazardous substances into air water and soil.

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