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IMPORTANCE & APPLICATIONS OF NANOTECHNOLOGY

Nanophytoremediation: An Overview of Novel and Sustainable Biological Advancement

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Abstract

Increased threat of metals simultaneous to the biota well-being and the environs is continually causing a major apprehension worldwide. The phytoremediation technique is highly advantageous involving the natural processes of plants viz., translocation, evapotranspiration, bioaccumulation thus degrading contaminants slowly. In particular, nanophytoremediation is a rapid green alternative as it reduces the ancillary impacts of the environment such as green gas emissions, waste generation, and natural resource consumption to the present scenario as there is a great potential of nanoparticles from plants which can be synthesized. Nanophytoremediation is a current methodology for remediation of pollutants, contaminants by using synthesised nanoparticles from plants. In this, the use of different strategies enhances the selective uptake capabilities of plants. The metal elements in excess are affecting the physiological processes in plants; thus, it is necessary to apply nanophytoremediation technology through transgenic plants. In this review paper, we focussed on plant species, which can be used as metal tolerant, hyperaccumulators. Due to the insurmountable pressure of a sustainable cleaner environment, bioremediation can be concurrent with nanoparticles for efficient and effective sustainable measures.

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Introduction

Plants are autotrophic in nature, thus are self-sufficient in the utilization of sunshine and CO₂ as energy and carbon sources. The vegetation mostly depends on its roots for water, nutrients, and minerals from groundwater and soil. The maintenance of the greener environment is mostly integrated with plants. Further, the sustainability of these plants depends on the environment, which is contaminated mostly from anthropogenic activities and pollution. In contrast, plants also absorb diverse compounds that are toxic in nature thus can be considered as an efficient detoxification mechanism for the removal of contaminants. Thus, from this viewpoint, plants are employed effectively in the treatment of contaminants viz., organic contaminants, polyaromatic hydrocarbons, which are potentially viable in contaminant detoxification. Previously the traditional remediation of metal-contaminated soil includes on-site management and subsequent disposal of wastes to another landfill site. However, this makes the site hazardous with additional risks of migration of contamination. There are various clean-up techniques for soils that can be categorised as physical, chemical, and biological. There are reports of the chemical and physical processes which have limitations viz., great price, labour-intensive, variations in properties of soil and disturbance of the native soil microflora whereas chemical techniques increase secondary pollution problems with large volumetric sludge which increases cost. The biological remediation processes consist of bioventing, bioleaching, bioremediation, bioreactors, bioaugmentation, biostimulation, and land forming. In this context, the phytoremediation technology has been in existence in par with other remediation technologies as a novel natural ecological, biological remediation processes.

Phytoremediation created from Greek prefix “*phyto*” means plant and Latin suffix “*remedium*” means remedy or restore. Phytoremediation is a versatile technology to treat polluted soils, pollutants, deposits, and groundwater, in a profitable as well as environmental welcoming the usage of plants [1] thus can be referred to as natural green biotechnology Figure 1 denotes the different phytoremediation technologies. Phytoremediation technology is suitable against several types of contaminants [2] in the atmosphere in a variety of media, as mentioned in Table 1.

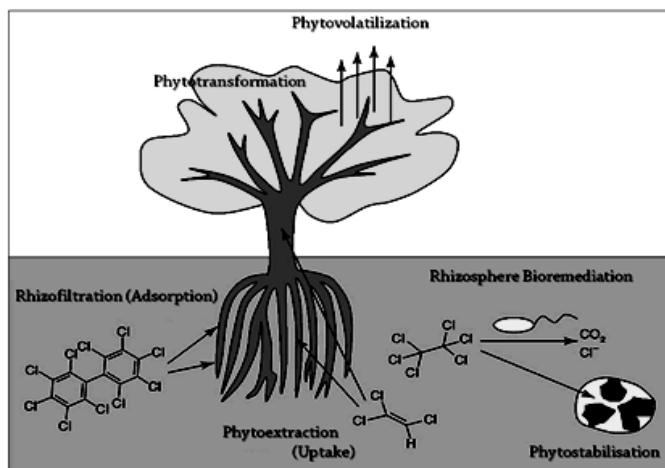


Figure 1: Illustration of physiological processes occurring in plants during phytoremediation.

Table 1: Technologies related to Phytoremediation.

Treatment	Mechanism	Medium
Phytodegradation	Degradation of plant uptake organics.	Surface and groundwater
Rhizofiltration	Roots can uptake metals.	Surface waters and water pumped through troughs
Bioremediation supported by plants	Enhanced microbial degradation in the rhizosphere.	Soils and groundwaters within the rhizosphere
Phytoextraction	Metal uptake and presence of metal concentration directly via plant tissue with the subsequent exclusion of plants for biomass degradation.	Soils
Phytostabilization	Root exudes which causes metal precipitation thus decrease the bioavailability.	Soils, groundwaters and tailings in a mine
Phytovolatilization	Evapo transpires Se, Hg and volatile organics.	Soils and groundwaters
Phytomining	Inorganic substance extraction from mine ore.	Soil
Removal of organics	Volatile organics are left out through the plant.	Air
Rhizosecretion	Molecular farming methodology, which secretes natural products and recombinant proteins from roots.	Soil
Vegetative caps	Rainwater is evapotranspiration, preventing contaminant leaching from a waste disposal site.	Soil

Phytoremediation technique has its limitations,

- a) Slow remediation time
- b) Plant waste after phytoremediation

It is seen previously plants [3] tend to produce nanoparticles under appropriate conditions, as mentioned in Table 2. The deployment of contained contaminants remains equally *in-situ*

and *ex-situ*. One of the newer techniques of *in-situ* remediation, nanotechnology has been in focus with the usage of nanomaterials in various laboratory investigations and field applications, mostly in North America and Europe. But in India nanophytoremediation is not practised. Although nanophytoremediation can be an economically viable process, proper utilization can be ecologically useful.

Table 2: Numerous nanoparticles synthesized from the plants.

Nanoparticles	Plant
Silicon-Germanium (Si-Ge) nanoparticles	Freshwater diatom <i>Stauroneis</i> sp.
Au and Ag nanoparticles	<i>Pelargonium graveolens</i> , <i>Hibiscus rosasinensis</i> , <i>Citrus sinensis</i> , <i>Diopyros kaki</i> (Persimmon), <i>Emblica officinalis</i> , <i>Phyllanthium</i> , Mushroom extract, <i>Coriandrum sativum</i> .
Ag nanoparticles	<i>Elletaria cardamom</i> , <i>Parthenium hysterophorus</i> , <i>Euphorbia huta</i> , <i>Ocimum</i> sp., <i>Nerium indicum</i> , <i>Brassica juncea</i> , <i>Azadirachta indica</i> , <i>Pongamia pinnata</i> , <i>Clerodendrum inerme</i> , <i>Opuntia ficus indica</i> , <i>Gliricidia sepium</i> , <i>Desmodium triflorum</i> , <i>Carica papaya</i> , <i>Coriandrum sativum</i> , <i>Pdargoneum graveolens</i> , <i>Avicennia mania</i> , <i>Aloe vera</i> extract, <i>Capsicum annum</i> , <i>Rhizophora mucronata</i> , <i>Cerriopstagal</i> , <i>Rumexhymeno sepalus</i> , <i>Pterocarpus santalinus</i> , <i>Sonchus asper</i> .
Au nanoparticles	<i>Terminalia catappa</i> , Banana peel, <i>Mucuna pruriens</i> , <i>Medicago sativa</i> , <i>Allium sepa</i> L., <i>Camellia sinensis</i> L., <i>Chenopodium album</i> L., <i>Justicia gendarussa</i> L. <i>Macrotyloma uniflorum</i> (Lam) Verde, <i>Azadirachta indica</i> A. Juss, <i>Magnolia kobus</i> and <i>Dyopiros kaki</i> , <i>Cinnamomum zeylanicum</i> , <i>Menthapiperita</i> L., <i>Mirabilis jalapa</i> L., <i>Syzygium romaticum</i> , <i>Terminalia catappa</i> L., <i>Amaranthus spinosus</i> .
Ag, Ni, Co, Zn and Cu nanoparticles	<i>Brassica juncea</i> , <i>Medicago sativa</i> and <i>Helianthus annuus</i> .
Platinum nanoparticles	<i>Diospyros kaki</i> , <i>Ocimum sanctum</i> L.,
Palladium nanoparticles	<i>Cinnamomum zeylanicum</i> Blume, <i>Cinnamomum camphora</i> L., <i>Gardeniaja sminoides</i> , Ellis. Soybean (<i>Glycine Max</i>) L.,
Lead nanoparticles	<i>Vitus vinifera</i> L., <i>Jatropha curcas</i> L.
Indium oxide nanoparticles	<i>Aloe vera</i> (<i>Aloe barbadensis</i> Miller),
Gold/Silver bimetallic nanoparticles	<i>Azardicta indica</i> (Neem)

Several studies report the usage of nanoparticles to have an affirmative effect on plants. Mixed TiO₂ (nano) and SiO₂ (nano) were presented into soybean (*Glycine max*) increasing activity of nitrate reductases which sped the plant propagation by increasing the water absorption and fertilizer utilization. Similarly, it was found by studies that Carbon Dots (CDs) promotes growth in mung bean at 0-1.0 mg/mL concentration. This result supports that nanoderivatives like carbon dots can absorb and utilize nutrients that induce a physiological response. Although there studies on nanoparticles that can cause toxicity, it has not been yet elucidated for most nanoparticles. It is vividly important to study nanoparticles and their effect on plant growth mechanisms to prevent the ecological risk of nanoparticles and to promote sustainable development of nanotechnology shortly, particularly in the Indian context. Thus the different integrated approaches to producing nanoparticles and apply nanoderivatives eliminating the metal impurities from soil and water, thus a flawless, in-depth study of nanoparticles are required, which can be applied. Nanophytoremediation study is based as an alternative remediation advanced technology in addition to the phytoremediation, the current scenario of reducing the contaminants more safely.

Publications

Publications wise not many were found in the literature databases; for example, probing sciencedirect database, it has found none on nanophytoremediation. Since the year 1995 to date, 2018, the number of publications found to be 764. Of which highest published were found to be research articles (567) followed by review articles (78), short communications (34), and rest others.

Among journals trends, the highest number was found to be in Journal: Chemosphere (99) followed by Ecotoxicology and Environmental Safety (61), Ecological Engineering (52), the lowest number published was in Journal of Biotechnology (18) over the years 1995-2018. Publication trends for phytoremediation, as observed from the ScienceDirect Database year-wise publications, a) category wise and b) journal wise were shown in Figure 2. Nanophytotechnological remediation was published in the *J. of Environ. Protec.* (JEP) (2016, <http://dx.doi.org/10.4236/jep.2016.75066>).

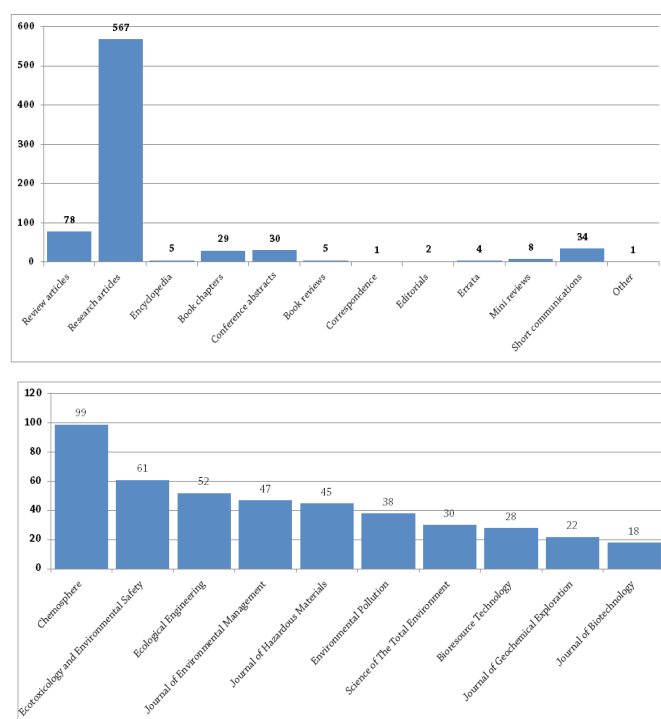


Figure 2: Publication trends for phytoremediation as per the ScienceDirect database - year-wise publications, a) Category wise and b) Journal wise.

Phytoremediation classification

Phytoremediation technologies are classified in general into a

- Phytoextraction**-Metal concentration reduction in the soil through plants that can accumulate metals in the shoots.
- Phytostabilization**-Immobilise the utilization of soil metals via adsorption onto roots; rhizosphere precipitation.
- Phytostimulation**-The process where root releases certain compounds enhancing the microbial activity in the rhizosphere of the plant. It is a type of rhizosphere phytoremediation which is used as an inexpensive approach to remove soil organic pollutants.

- d. Phytovolatilization**-A technique, where the soil contaminants are cleaned up by plants and discharge them as atmospheric volatiles through transpiration.
- e. Phytotransformation/Phytodegradation**-Breaking down of organic contaminants seized through plants via
- i. *Plant metabolic processes; or*
 - ii. *The outcome of metabolites, such as enzymes, produced by the plant.*
- f. Phytoremediation**-Re-vegetation of the drylands by plants can prevent the spread of pollutants into the environment [14].

An overview of metal contaminants in several phytoremediation processes is provided in Table 3. In the case of contaminated water, the following processes in phytoremediation technologies are utilised as,

a. Rhizofiltration-Roots were used to remove aqueous toxic metals, mainly the heavy metals like lead (Pb) and radioactive elements [5]. The plants are employed as filters in wetlands

or as a hydroponic setup [6]. Wetlands are often widely considered as sinks for pollutants and there are countless instances where the wetlands plants are considered to remove contaminants [7] used which includes metals viz., Se, perchlorate, cyanide, nitrate and phosphate [8].

b. Hydraulic control-It is a process in which bulk amount of water is absorbed by the wildy growing plants preventing the increase of pollutants into the unpolluted surrounding zones [4].

The phytoremediation methods chosen depend upon,

- i. Specifically high growth rates in the polluted sites
- ii. Huge surface area proportionately in contact with the water body
- iii. High translocation potential [9]

These factors say both the Bioconcentration Factor (BCF) and Translocation Potential (TP) are related to plants sensitivity for phytoremediation.

Table 3: Synthesis of iron nanoparticles/derivatives.

Type of nanoparticles	Biochemical Agents	Size / Morphology	Environmental Applications
Stabilized bimetallic Fe/Pd nanoparticles	Starch	14.1 nm distinct, well dispersed	Degradation of chlorinated hydrocarbons in water
Fe ₃ O ₄	Na-Alginate	27.20 nm spherical	Urea Decomposition
Fe ₃ O ₄ - Polymer Composite	Agar (Reducing & Stabilising Agent)	50-200 nm spherical, 24 nm diameter & Hexagonal	Magnetic Storage Media
Nano-Shell (Fe, Cu)	Ascorbic Acid (Antioxidant)	<100 nm Cubic	Functions in catalysis, Biosensors, Energy storage problems, nanodevices.
nZVI	Ascorbic Acid (Vit-C)	20-75 nm, spherical	Cd removal
Superparamagnetic Iron oxide (Coatings & Functionalisation)	Ascorbic acid (Vit-C)	5 nm - 30 nm (Hydrodynamic Size)	Contrast enhancement agent for MRI Applications
Fe ₃ O ₄ (MNPs)	L-Lysine (A. Acid)	17.50 nm & Spherical Crystalline	Biosensors, Drug Delivery
nZVI	L-Lysine (A. Acid) L-Glutamic Acid L-Glutamine L-Arginine and L-Cysteine	-	Low-molecular, biocompatible
FeNPs	Haemoglobin & Myoglobin	2-5 nm aggregates, crystalline	Bioconjugated nanoparticles for biological applications
Fe ₃ O ₄	D-glucose Gluconic Acid	12.5nm roughly spherical, crystalline	Drug delivery, Cell transplantation
Fe ₃ O ₄	Glucose & Glyconic Acid	4-16 nm Crystalline	Removal of waste in the biomedical field
Carbon capsulated Iron NPs	Wood-derived sugar	100-150 nm nanospheres, 10-25 nm diameter of iron-core	Acts as catalysts in the conversion of wood-derived syngas to liquid hydrocarbons
Iron oxide	Tannic acid	<10 nm	Utilization of biomass causes the reduction of metal ions
Fe core-shell structure	Chitosan-Gallic acid	11 nm cubic	Increased thermal stability of drug Gallic Acid, Anticancer activity was higher for HT29 and MCF7 cell - lines

In Brake fern (*Pteris vittata*), the best phytoremediation process is established as it consists of a high root to shoot metal transduction; thus, it is observed that the BCF value is greater than one. Out of the several phytoremediation technologies, phytoextraction is the most effective, which depends upon hyperaccumulation of metals into the whole plants. For phytoextraction, a heavy metal tolerant plant that grows rapidly with high biomass yield per hectare also should possess a prolific

root system. When the cultivation is over by the season's end plants are harvested, dehydrated and the enriched mass with contaminants is dumped or sent into the smelter. To be active phytoextraction, the dehydrated biomass, ash extracted from the above-ground parts of a phytoremediator crop, consists of a greater concentration of the pollutants than the contaminated soil [10]. The biomass rich product exudes as the secondary metabolic waste, which requires further treatment. The phyto-

extraction process can be natural and induced. The energy can be recovered from biomass burn or pyrolysis thus phytoextraction can be used as a cost-effective technology by giving biomass yields. *Salix* and *Populus* species are also used for phytoremediation technology.

Bio elements and their effects on pollution

Pollution is an undesirable change observed, which is deteriorating our raw materials, especially land and water. An overall representation of the contamination process, which can cause microorganisms to pollute soil and surface water, is shown in (Figure 3). At normal concentration, soil comprises bio-elements, particularly metals. These bio elements serve as micro and macronutrients for the soil. They can be classified as light metals (Mg, Al) metalloids (As, Se) and heavy metals viz., Cd, Hg, Pb, Cr, Ag and Sn. Light metals have a greater significance to health and environment [11] whereas substantial metals are the bioelements (At. No., Z >20) with a density >5.0 g/cc and have definite metal properties like conductivity, ductility, ligand specificity, cationic stability, etc. Beneficial heavy metals include elements like Cu, Cr, Zn, Mn, Fe, Co, and Ni, which are essential in smaller amounts in metabolism but may be lethal in higher concentrations. Geogenic, anthropogenic and contamination by heavy metal is shown can cause microorganisms [12] to affect the normal molecular process as shown in (Figure 4). Heavy metals sieve through the soil and are terminated into the soil by geogenic and anthropogenic processes [13].

Geogenic contamination can be exemplified by extensive arsenic contamination, as seen in the groundwaters of the Indian state of West Bengal and Bangladesh [14]. The other contamination source includes anthropogenic activities like generating huge amounts of effluents, which is a constant threat to environmental pollution. Fertilizers incorporate phosphate compounds containing Cd, which are being used in horticulture, agriculture as well as in animal industries as a trace element nutrient. Cd, Hg, and Pb metals attack the activity of the enzyme, which contains the -SH group which initiates chronic diseases. These heavy metals/metalloids and organics form a grave danger to animals (including humans) and plants. Heavy metal pollution on land and water show a severe impact on the ecosystem. In Western Europe, a large mass of approx 14,00,000 sites affected as the reports of [15] out of which 3,00,000 are contaminated, but the projected number in Europe could be greater, as the problem was progressively occurring in the Central and East European countries. In the US, around 600,000 contaminated brownfields with heavy metals requiring reclamation [16]. Land pollution has been a great challenge in the Asian continent as seen in China, where 1/6th of arable land is with heavy metal pollution, and over 45% has been ruined either due to erosion or desertification. This becomes the consequence because of human-dominated ecological problems viz., urban ecology, and agricultural ecology [17]. Thus it is vital to eliminate these pollutants from the contaminated sites in which phytoremediation are one of the processes which include complexation, accumulation, volatilization and degradation of pollutants both of organic and inorganic origin.

Biosynthesis of nanoparticles from plants

Nanoparticles are aggregates between 1-100 nm, this particular size that alters the physicochemical properties equated to other material. A variety of nanoparticles are produced by bacteria, fungi, and plants [18], which have wider applications in several sectors. Plants are more appropriate than bacteria or fungi towards the synthesis of NPs, as less incubation time is required for metal ion reduction. The procedures like Plant Tissue Culture (PTC) and downstream processing techniques make more promising in synthesising metal and oxide NPs at a larger scale. The documentation of hyperaccumulator exclusive genes and their succeeding transfer to the other species of transgenic plants can improve phytoremediation capacity. The plant's remediation volume shall be greatly enhanced by genetic manipulation and other viable plant-based transforming techniques. In plants, it is seen to have an inherent ability to lessen metals through their specific metabolic pathways [19]. Stampoulis et al., 2009 [20] have examined the impact of ZnO, Cu, Si, and Ag NPs on the root elongation, seed germination, and biomass production of *Cucurbita pepo* grown as hydroponics. Accordingly, experimental findings suggested, root length reduced by 77% when seeds exposed Cu nanoparticles and 64 % when exposed to bulk Cu powder when equated to the untreated controls.

Plant biomass was reduced by 75% when exposed to Ag NPs. Shekhawat and Arya, 2009 [21] used *Brassica juncea* seedlings to produce Ag NPs *in vitro*. There are reports from of synthesized gold nanoparticles by *Terminalia catappa* leaf extract in an aqueous medium [22]. Beattie and Haverkamp, 2011 [23] and Masarivoca and Kralova, 2009 [4] examined metal ions Ag⁺ and Au³⁺ to Ag⁰ and Au⁰ NPs in *Brassica juncea* for the reduction sites. Nevertheless, Ag NPs in plants are mostly modelled as Ag not only forms NPs in plants but it also exhibits higher catalytic properties as it consists of high electrochemical reduction po-

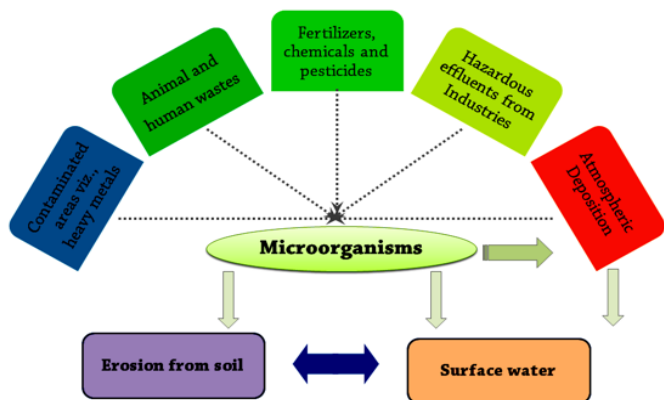


Figure 3: An overall representation of the contamination process - that can cause microorganisms to pollute soil and surface water.

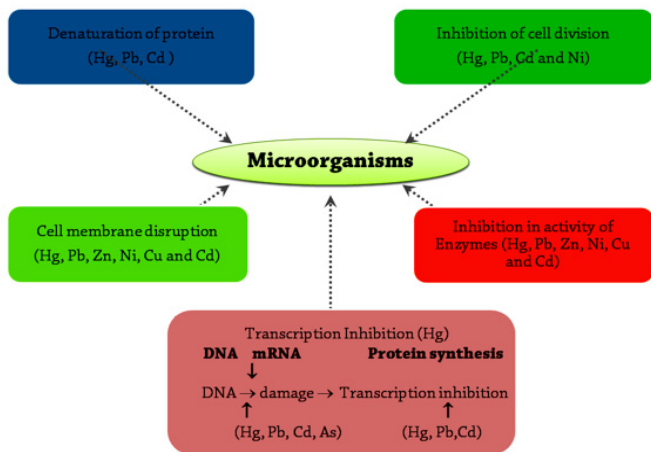


Figure 4: Geogenic, anthropogenic and contamination by heavy metal is shown can cause microorganisms to affect the normal molecular process.

tential and several additional useful properties. Although the research on the production of nanoparticles is in a nascent stage in plants, more qualitative work is required to realise the physiological, biochemical and molecular mechanistic process relative to nanoparticles.

Nano-iron and its derivatives

Reactive Nanoscale Iron Product (RNIP) and Nanoscale Zero-Valent Iron (NZVI) are mostly the elementary forms of iron (nano) technology [24]. Nano zero-valent iron because of its nano-size (1-100nm) enables high-level remedial adaptability. NZVI, a product of nanotechnology is used to treat a range of impurities in perilous wastewater (See Table 3) represents the synthesis of iron nanoparticles [25]. For example, NZVI was tested in the removal of As (III) seen in groundwater. NZVI can be used in Permeable Reactive Barriers (PRBs) form to intercept plumes on the subsurface and remediate them. The sustained zero-valent iron nanoparticle "*ferragels*" swiftly dispersed and immobilize Cr (VI) and Pb (II) from aqueous solutions, reducing the Cr (VI) to Cr (III) and Pb (II) to Pb (0) while oxidizing Fe to goethite (α -FeOOH) [26]. Anionic hydrophilic carbon (Fe/C) and poly (acrylic acid)-supported (Fe/PAA); Fe (0) NPs were further considered as sensitive material for the dehalogenation of chlorinated HCs in soils and groundwaters [27]. Nickel-iron NPs in the ratio 1:3 were employed in the dehalogenation of Trichloroethylene (TCE) [28].

Single-enzymed nanoparticles

Enzymes serve as effective biocatalysts in bioremediation. Nevertheless, less stability as a result of diminutive catalytic lifetimes of enzymes limits their effectiveness being inexpensive due to oxidation. The usage of nanotechnology provides a novel method where the enzymes are stabilized in the form of Single Enzyme Nanoparticles (SEN). Enzymes can be devoted to the magnetic iron NPs increasing stability, longevity and reusability. The enzyme separation from the magnetic iron NPs is usually done by the use of a magnetic field. The two different catabolic enzymes-trypsin and peroxide subjected to unvarying core-shell Magnetic Nanoparticles (MNPs). SEN requires the involvement of modification of enzyme surface, vinyl polymer growth from the enzyme surface. There are immobilized enzymes in biopolymers and carbon nanotubes, which can add as environmental biosensors.

Exopolysaccharides

Exopolysaccharides (EPSs) are polymers of the polysaccharide of high mol. wt., secreted by microorganisms. EPSs are sustainable as it has good adsorption capacity, environmentally friendly. Therefore the usage of EPS for bioremediation in the metallic and dye-based environmental pollution attracted researchers in the past years. Polysaccharides are very rich in-OH groups using them as a stabilizer for the production of metal NPs, an environment friendly alternate for the chemical-reducing method [29].

EPS are used as a reducing agent and stabilizer. They are further used for the synthesis of metal NPs viz., lentinan, carboxymethylated chitosan, glucan, carboxymethyl cellulose, carboxylic curdlan [30]. Apart from exopolysaccharides, the Au and Ag nanoparticles also consist of good dispersible capability and uniformity. EPS produced from *A. fumigatus*, [31] *Lyngbya putealis*, *Lactobacillus plantarum* [32] and *Bacillus firmus* [33] removed heavy metals viz., Cu^{2+} , Pb^{2+} , Cr^{4+} , Cd^{2+} and Zn^{2+} within the

adsorption capability of 50-1120 mg/g. EPS-605 obtained from newly identified *L. Plantarum*-605 was obtained from a Chinese fermented food, Fuyuan pickles. When EPS-605 was self-assembled in H_2O , monodispersed nanoparticles were detected that are useful for bioremediation and record heavy metal and dye adsorption.

Dendrimers

Dendrimers are multivalent, globular, highly branched, monodispersed molecules with synthetic elasticity. Dendrimers have proper architecture and controlled composition, which consists of three components and has an extensive assortment of applications ranging from catalysis, electronics to drug release. With its unique structural characteristics viz., nanoscopic size, spheroidal surface, vast interior with exhilarating properties which consists of low viscosity, extraordinary solubility, and reactivity. Dendrimers first dendrimers were synthesized by Fritz Vogtle in 1978 [34] consists of three constituents – a vital core, internal branch cells or radiated symmetry and terminal branch cell or marginal group. The void spaces in dendrimers interact with nanoparticles which enhances the catalytic activity. The dendrimer nanocomposites were also set for the treatment of water and dye removal from industrial waters to enhance the reactivity by creating more surface area with a reduced amount of toxicity. PAMAM dendrimers using group of hydroxyl-terminated (G4-OH) poly (amidoamine) also acts as templates in the production of Cu NPs formed by coordination of Cu ions with dendrimer interior amines and subsequent reduction forming dendrimer-encapsulated Cu NPs (Cu-DEN).

Cowpea Mosaic Virus (CPMV), a plant virus, is adequate to endorse the templated mineralization of metal and metal oxide. CMV particles used for templated fabrication of metallic NPs by an electron less deposition metallization process. In the virus capsid Pd ions are electrostatically bound to the virus capsid and upon reduction acts as a nucleation site to deposit metal ions from solution. Further, dendrimer-modified and plain Magnetite Nanoparticles (MNPs) have been widely studied in environmental decontamination. Dendrimers can enhance drug targeting efficacy mainly to be used in drug delivery systems [34].

Nanocrystals and carbon nanotubes

Nanomaterial based applications in the field of environment are in multiples, that provide both large and portable scale also cleans up impurities that are present in our environment. Carbon-based nanomaterials viz., nanocrystals and Carbon Nanotubes (CNT) have wider applications as antimicrobial agents, environmental sensors, biosensors, sorbents, depth filters, renewable energy technologies, high flux membranes, and in pollution prevention [35]. CNTs are both Single-Walled (SWCNT) or Multi-Walled (MWCNT), functionalized and hybrids were evaluated for the elimination of Et-C₆H₆ from aqueous solution and remediating pollution to avert diseases from ethylbenzene (Et-C₆H₆) viz., cyclodextrins (CD). Nickel ions from water were remediated using MWCNT based materials [36]. CNT-based polymeric materials incorporating nanomaterials, Calixarenes, and Thiacalixarenes were synthesised to remove both organic (p -NO₂-C₆H₅OH) and inorganic contaminants (Cd^{2+} , Pb^{2+}) from water bodies [37]. CNTs immobilized by calcium alginate (CNTs/CA) materials investigated the Cu removal efficiency (69.9% at pH 2.1) via equilibrium studies [37]. Magnetic-MWCNT nanocomposites reported eradicating cationic dyes in aqueous solutions [38].

Engineered polymeric nanoparticles application in bioremediation for removal of hydrophobic contaminants

Hydrophobic contaminants, say, Polycyclic Aromatic Hydrocarbons (PAHs) are globally persistent in the atmosphere. PAHs are hydrophobic, strongly sorbed to the soil thus sorption limits the bioavailability of these pollutants on the surface. Sequestration in Non-Aqueous Phase Liquids (NAPLs) shrinks the mobility and bioavailability of hydrophobic contaminants [39]. Although surfactant micelles have shown an increased rate of PAHs and hydrocarbon solubilisation in contrast also causes biodegradation.

Synthesis of non-ionic Amphiphilic Polyurethane (APU) NPs from a mixture of Polyethylene Glycol (PEG) Altered Polyurethane Acrylate (PMUA) and polyurethane acrylate precursor chains solubilise PAHs from the contaminated soil. Unlike surfactant micelles, PMUA NPs are cross-linked, so not easily breakable when it comes in contact with soil interacting with liposomes of microorganisms, but have excellent properties to improve desorption and the agility of Phenanthrene (PHEN) in aquifer sand [40].

Polymeric nanoparticles used in soil remediation

Research-based on nanoparticles usage in soils and groundwater remediation processes increased greatly with promising results. Using nanotechnologies polluted soils remediation becoming an emerging area with an enormous impending to advance the performance over traditional remediation technologies in a large way. Effective application for soil contaminants contexts, predominantly, for heavy metals, other inorganic and organic contaminants and emerging contaminants, like pharmaceutical, cosmetic, personal care products etc.

Polynuclear Aromatic Hydrocarbons (PAHs) that absorb intensely to soil are very challenging to eliminate. In such cases, Amphiphilic Polyurethane (APU) nanoparticles are used in soil remediation which is polluted with PAHs. Desired properties of APU particles can be achieved by engineering, experimental results have shown that these designed particles make sure hydrophobic interior regions that confer a high affinity for PHEN and hydrophilic surfaces that encourage soil particle mobility. APU NPs (17-97 nm) are prepared of Polyurethane Acrylate (PA) and ionomer (UAA) or PEG, Modified Urethane Acrylate (PMUA) precursor chains which are emulsified and cross-linked in water. APU particles are stable, independent to their concentration in the aqueous phase, have interiors regions exhibiting hydrophobic property enhances PAH desorption. APU particles contrived to give the anticipated properties. APU particles affinity towards pollutants like, PHEN is precisely managed by varying hydrophobic segment size required for the chain propagation. Mobility of soil APU suspensions is controlled by the charge density or the size of the water-soluble chains [40].

Biogenic uraninite nanoparticles

There is evidence of the widespread prevalence of uranium in India's groundwater. A variety of sources and studies has indicated the link between exposures to uranium in drinking wa-

ters which causes chronic kidney diseases. Although the main source is geogenic but still anthropogenic factors play their part in the decline in groundwater table and nitrate pollution promote uranium mobilisation. The term *Uraninite* defines compositionally complex, nonstoichiometric, cation-substituted forms of UO_2 , which are found in nature. Biogenic uraninite being nanoscale biogeological material is significant due to usage in bioremediation strategies. Uraninite is utmost preferred product in-situ stimulated subsurface uranium U (VI) has its solubilisation much lesser compared to other uranium species.

Uraninite nanoparticles have its properties viz., solubility and dissolution kinetics, which are crucial for microbial bioremediation which mitigates subsurface uranium contamination through uranium reduction. Uraninite exhibits structural chemistry thus derives its properties from its open fluorite structure. Biogenic uraninite forms by reduction of U (VI) to U (IV) considered as the first stage. After the reduction process, the second step formation requires the precipitation of the mineral. In situ U (VI) reduction has been observed and reported at a large number of contaminated U.S. Department of Energy (DoE) nuclear legacy sites has shown potential results. The success in uranium bioremediation should be maintained strictly in anaerobic conditions. The surface chemistry of nanoparticulate uraninite is important for the construction of geochemical models of uranium behaviour which follows the bioremediation. This may be challenging for research in nano-bio geosciences in the future [41].

Soil trace element biomonitoring plants

Soil contamination manifested by trace elements, organic and inorganic compounds is an extensive problem occurring worldwide. Common techniques in soil remediation include waste disposals, incinerations, leaching of soil thermal desorption, and vapour abstraction, but all these types of actions may be responsible for secondary pollution which ultimately affects soil properties. Plants are the major factors to keep our environment clean and green by remediation of soil and water. The soil organic and inorganic contaminants are removed by phytoremediation. Ryegrass, oat plant, tall fescue, sunflower, and green gram grow in diverse contaminated conditions useful for phytoremediation. Certain plants known as hyperaccumulators are good in phytoremediation in particularly towards heavy metal removal. Some hyperaccumulators families represent their metal content [42].

Table 4 defines the hyperaccumulator plants of various families which are used to accumulate specific metals at different concentrations. Phytoextraction seems to be a feasible alternate to the traditionally conventional practice used in the decontamination of soils with heavy metals [43]. In phytoextraction, methodology plants absorb pollutants from soil. Metals that are deposited as ions in the plant's roots, stems, leaves and inflorescences are burnt to recover metals and the subsequent biomass is removed to dispose of safely. The build-up of heavy metals is connected to the total concentration of the metals and suggestively segregated as macro-and micro-nutrients and soil acidity.

Table 4: Hyperaccumulator plants for varied metals.

Metals	Plant species	Accumulated Metal concentration (mg/kg)
Cadmium		
<i>Thlaspi caerulescens</i>	Brassicaceae	2,130
Zinc		
<i>Thlaspi caerulescens</i>	Brassicaceae	43,710
<i>Thlaspi rotundifolium</i>	Brassicaceae	18,500
<i>Dichopetalum gelonioides</i>	Brassicaceae	30,000
Nickel		
<i>Thlaspi Sps.</i>	Brassicaceae	2,000-31,000
<i>Allyssium Sps.</i>	Brassicaceae	1280-29,400
<i>Berkheya codii</i>	Asteraceae	11,600
<i>Pentacalia Sps.</i>	Asteraceae	16,600
<i>Psychotria coronata</i>	Rubiaceae	25,540
Copper		
<i>Ipomoea alpina</i>	Convolvulaceae	12,300
Lead		
<i>Minuartia verna</i>	Caryophyllaceae	20,000
<i>Agrostis tenuis</i>	Poaceae	13,490
<i>Vetiveria zizanioides</i>	Cyperaceae	>1500
Cobalt		
<i>Crotalaria cobalticola</i>	Fabaceae	30,100
<i>Haumaniastrum robertii</i>	Lamiaceae	10,232

Table 5: Synthesis of diverse nanomaterials.

Nanomaterials	The methodology used in the synthesis	Examples
Nanoparticles biosynthesis from metals (NPs)	Photochemical Biochemical Electrochemical Thermochemical	Cu, Au, CoNi, CdTe, CdSe, ZnS, Rh, Pt, Ir, Pd, Co, Ag, Au, Cu, Fe & Ni
Nanomaterials from carbon	Arc-discharge Chemical vapour deposition Laser ablation	Cylindrical nanotubes (SWNT, MWNT) Fullerenes
Nanomaterials from Polymers	Electrochemical Polymerization	Nanowires of PPy, PANI, Poly (3-4 ethylene dioxy thiophane, PAMAM, dendrimers)
Metal oxide Nanoparticles	Hydrothermal Reverse Micelles Solvo-thermal Sol-gel Method Electrochemical deposition	BaCO ₃ , BaSO ₄ , TiO ₂ , ZnO, Fe ₂ O ₃ , Fe ₃ O ₄ , MgO
Bionanomaterials	Biological	Plasmids, nanoparticles from protein viruses

Cystoseira indica (brown algae) after its chemical treatment become greatly effective against chromium. Metal uptake is seen in algae species such as in *Spirulina* used for chemisorptions of metals with few heavy metals like chromium and copper [57]. *Ranunculus peltatus*, *Ranunculus trichophyllus*, *Lemna minor*, *Azolla caroliniana* viz., serve as an arsenic indicator [Favas et al., 2012]. *Ulothrix cylindricum* (green algae) has biosorption capacity of 65.6 mg/g, forming an inexpensive method for biosorption of As(III) [58]. Aquatic macrophytes grow quickly and due to their high biomass production, the greater capacity

Vascular plants

Water pollution is dangerous and one of the ecological risk factors suggests the need to cultivate water plants that absorb trace elements. Usually, there is a quick dilution of the contaminants in water thus investigating the plant tissues provides combined evidence about the quality and components of water and the method of phytoremediation [44]. The various nanomaterials which can be synthesized through several methods have been represented in Table 5. Further, it is observed that species viz., duckweed (*Lemna gibba*), water spinach (*Ipomoea aquatica*) and fern (*Azolla pinnata*) are prominent to phytoremediate metals [45] like boron, chromium, and manganese, respectively [46-48]. Aquatic macrophytes such as water hyacinths are used extensively in phytoremediation of water contaminated with dyes [49]. Hasan et al., 2007 [50] stated the efficacy of water hyacinth in sorption of Zn(II) and Cd(II) from the water. The species from Lemnaceae family, eliminate dyes such as acid blue (azo dye, AB92) transforms to form dissimilar transitional compounds [51]. Aquatic plants viz., *Azolla pinnata* (water-fern) and *Hydrilla verticillata* (water-thyme) used for elimination of fly ash and uranium respectively [52,53]. *Micranthemum umbrosum* observed [54] removal of As and Cd by phytofiltration method. *Oenothera picensis* plant was quite extensively considered towards phytoextraction of copper [55]. Algae such as charaphytes viz., *Chara aculeolata* and *Nitella opaca* were used to remove Pb, Cd, and Zn [56].

in accumulating heavy metals widely used for wastewater treatment compared to soil-grown plants.

A macrophyte grows in or near the water body and is emergent, submerged or floating. Aquatic plants have adjusted to living in aquatic environments (hydrophytes or macrophytes) to differentiate from algae and other microphytes. Water hyacinth (*Eichhornia crassipes*), Sensitive Plant (*Neptunia aquatica*), Lucky 4-Leaf Clover (*Marsilea mutica*) water lettuce (*Pistia stratiotes*), Moneywort (*Bacopa monnieri*), Mosaic Flower (*Ludwigia sedioides*), Water poppy (*Hydrocleys nymphoides*) and

duckweed (*Lemna minor*) are a few of the aquatic macrophytes widely intended for heavy metal phytoremediation [59]. *Pistia stratiotes* have relatively high growth rate thus ideally chosen in phytoremediation study as it is proposed to accumulate As [60]. Water lettuce is observed to be a probable plant for phytoremediation for manganese contaminated waters [59]. In the elimination of Pb, Cd, Cr from the water, *Lemna minor*, a native of Europe, North America, Asia and Africa is naturalised for its advantage to grow in several climatic conditions; also a potential accumulator of Cd to remediate the aquatic environment. *Eichhornia crassipes* was used for the tertiary treatment of wastewater phytoremediation as it has broader leaves and fibrous root system which assists in the absorption of heavy metals [61]. There has been experimentation on water hyacinth (*Eichhornia crassipes*), two algal species (*Chlorodesmis sp.* and *Cladophora sp.*) found in As-contaminated water bodies are used to determine the arsenic tolerance capability. *Cladophora* species are found to be appropriate for co-treatment of sewage and As-contaminated brine in algal ponds. *Typha latifolia* and *Eichhornia crassipes* are freshwater plants used to clean up the effluents that usually contain high concentrations of Co, Cd and As. *Eleocharis acicularis* commonly known as dwarf hair grass and needle spike rush acts as hyperaccumulator as it uptakes several metals Fe, Pb, Mn, Cr and Zn from drainages and mines [62,63]. *Myriophyllum aquaticum* consists of enzymes that play a vital part in the transformation of organic compound contamination and is effective in the phytoremediation of an aquatic environment [9]. *Ludwigia palustris* (marsh seedbox; creeping primrose) and *Mentha aquatica* (water mint) effectively remove Cu, Fe, Hg and Zn. Among the freshwater vascular plants, the most efficacious plants are *E. crassipes* and *L. minor*.

Hyperaccumulator plants for different metals

Bioconcentration factor and factor of translocation are multiplied to get the phytoextraction efficiency. It is observed that accumulated metal concentration in soil modifies its biological properties. Different plant species vary concerning the uptake

of heavy metal. The hyperaccumulation of heavy metals mainly rests on several factors viz., plant species, soil circumstances, (pH, temperature, humidity, soil organic content, cation capacity), types of heavy metals. The uptake of metals is determined by the metal type and metal chemical speciation and habitat characteristics of the plant [64]. Hence, the plant selection became significant for the remediation of the containment location. The accumulation efficacy of heavy metals in any plant species is calculated via a bioconcentration factor [65]. The willow plant consists of the highest biomass thus identified itself as an appropriate plant for soil remediation [66]. In a prior experiment, plant species of Brassicaceae family, such as *Brassica juncea L.*, *Brassica napus L.* and *Brassica rapa L.* can accumulate Zn and Cd moderately. In *Brassica juncea* the nuts showed the bioaccumulation ability towards Cu [67]. *Pistia stratiotes L.* (water lettuce) has the potential to remove Cd from surface water [68]. Canola (*Brassica napus L.*) is very effective for Cu, Cd, Pb and Zn in comparison to *B. juncea L.* (Indian mustard). Application of Ethylene Diamine Tetraacetic Acid (EDTA) increases heavy metal availability thus making the plant uptake showing the prominence of organic chelates in increasing metal solubility/availability, thus applicable to enhancing the efficiency of phytoremediation technique.

Table 6 represents the advantages and limitations of phytoremediation technologies. In Brassicaceae family, plants are used for biofumigation. *Helianthus annuus* (Sunflower) has the capability for soil remediation contaminated by Pb. Soybean plants characteristically synthesise homophytochelatin alternative to phytochelatin when heavy metals are exposed. For the soybean seeds and young seedlings, Cr metal is found to be extremely toxic at higher concentrations [69]. Crops are affected as it is seen that soil contamination by heavy metals causes a considerable loss in seed production of soybean canopies [70]. Agricultural soils accumulate toxic metals in edible portions of crops which grow in contaminated soils that described in crops viz., rice, soybean, maize and vegetables.

Table 6: Advantages and limitations of phytoremediation.

Advantage	Limitation
Phytoextraction	
Plant with high biomass within lesser time should be successful to remove contaminants from soil.	<ol style="list-style-type: none"> Hyperaccumulators exhibit slow growth and less bio-productivity due to shallow root systems. Biomass/ Phytomass must be disposed of cautiously.
Phytostabilization	
Cost-effective and less disruptive which enhances the ecosystem restoration/re-vegetation.	<ol style="list-style-type: none"> The requirement of extensive fertilization/soil modification. Proper maintenance is required to prevent leaching.
Phytovolatilization	
Contaminants/Pollutants are transformed into less toxic forms. e.g volatilization of mercury(Hg) by conversion to the elemental form in transgenic <i>Arabidopsis</i> and yellow poplars which contains bacterial mercuric reductase (<i>merA</i>)	<ol style="list-style-type: none"> Contaminants/ hazardous metabolites might accumulate in vegetation viz., fruits/ lumber. Low levels of metabolites can be found in plant tissues.
Phytofiltration/Rhizofiltration	
<i>In situ</i> (pond floating rafts) or <i>ex-situ</i> (tank system); aquatic. Absorption and adsorption play an important role.	<ol style="list-style-type: none"> Constant pH monitoring of the medium is required for optimizing the uptake of metals. Influent chemical speciation and all the species interactions are to be understood. Intensive maintenance is needed. Large root surface area is usually required.

Effect of metals on the physiological process

Generally, metals play a significant part in the metabolic pathways in plants during the growth and development in appropriate amounts but lethal in excess. Soil gets contaminated due to several activities like mining, disposal of solid wastes, automobile exhausts and engineering activities. Therefore, there is a possibility of augmented uptake of metals by food crops which cause human health risks thus affecting food quality and safety. Metals viz., iron (Fe), molybdenum (Mo), copper (Cu), cobalt (Co), manganese (Mn) and zinc (Zn) are crucial for plant growth, categorized as essential micronutrients. The non-essential metals found as pollutants comprise mercury (Hg), chromium (Cr), selenium (Se), uranium (U), nickel (Ni), cadmium (Cd), arsenic (As), lead (Pb), vanadium (V) and wolfram (W). Prior published reports by [71] provided information on the impact of metal on the seed of crops and medicinal plants regarding biochemical and molecular implications which provides an important role in seed germination. It has been noted that metals applied exogenously in the range, micro to mili molar concentrations could affect seed variability. Seeds from metal tolerant plants and hyperaccumulators possess higher threshold toxicity than the seeds of non-tolerant plants. Nonetheless, data on their effects on *insitu* seed germination is in the nascent stage which is required to be investigated. Cd and Cu inhibit water uptake, obligatory for seed germination. One can overcome seed dormancy with metal treatment although the actual mechanism of action yet to be understood. But the process of deposition and toxicity of metals is unknown in developing seeds, to embryos and cotyledons.

Similarly, few experiments have focussed on the detoxification of metals by Phytochelatins (PC) and Metallothioneins (MT). Similarly, [72] have studied extensively about the chromium toxicity in plants which predominantly hinge on valence states of chromium ions. Cr has toxic effects on plant development which includes modifications in the germination process, development of roots, leaves and stems which ultimately affects entire dry mass production and yield. Chromium too has harmful effects on the plant's physiological processes such as photosynthesis, water channelling and mineral nutrition. Shukla et al., 2003 [73] inspected the effects of cadmium in wheat (*Triticum aestivum* L) plant. Gupta and Gupta, 1998 [74] reported in their publication that nutrient toxicities in crops due to manganese and boron are more compared with other nutrients. The foremost toxicity symptoms in crops include burning, chlorosis and yellowing of leaves. The toxicity of metals is influenced by metal concentration, the composition of minerals, and organics in the soil, pH, redox potential and the existence of other metals in the soil. Metal toxicity is also affected by the association to mineral constituents of the polluted sites. Since, there is a lack of basic understanding of metal behaviour for a precise condition a precise protective method towards metal additions to soils is warranted [75].

Besides, the requirement to know the proper metal toxicity in food products and their nutritional intake in evaluating their risk to human wellbeing is more. However, the problem of metal toxicity persists due to contamination of the environment which worsens intensively due to negative human activities. Hyperaccumulators grows on metalliferous soils, leaves possess toxic metal accumulation compared with other plant species. Studies aimed regarding these hyperaccumulators to understand their physiological role and molecular mechanisms and thus these plants can be used as a tool in removing met-

als from natural metal-rich soils (ores) and contaminated areas. Metal tolerant species *Hordeum vulgare*, *Brassica juncea*, *Triticum aestivum*, *Brassica napus*, *Helianthus annuus* accumulates toxic metals in high concentrations in their shoot system.

Transgenic plants usage in phytoremediation

Transgenic plants with wide geographic distribution and are used owing to their enhanced tolerance and phytoextraction potential. Transgenic plants are fast-growing seem to possess high biomass, much-elongated roots and greener leaves than unmodified plants. Herbivores are repulsive to transgenic plants, thus making it greatly an encouraging candidate in phytoremediation efforts [76].

Transgenic plants when grown in Cu-contaminated soil, leaves contain 2-3 times more Cu compared to other plants [77]. *Arabidopsis thaliana* also possess greater Cu accumulation as reported by overexpression of a pea MTgene [78]. PsMTA from *Pisum sativum*, when overexpressed in *A. thaliana*, accumulated 8 times more Cu in roots [79]. *Nicotiana glauca* (shrub tobacco) has a high tolerance towards Pb and Cd when grown in a metal-contaminated soil, the transgenic plants accumulated higher Pb concentrations in the shoot system (50% more) and the root system (85% more).

An attempt was made towards transferring and expression of genes from bacteria, yeast, animals or other plants and improvised for potentially high yield. One of the encouraging advances in transgenic technology is the use of multiple genes (cytochrome P450s, GSH, GT etc.) for thorough degradation of xenobiotics within the plant system that was involved in metabolism, uptake and transport of specific pollutants in transgenic plants [80-82]. A published review focussed on the development of transgenic plants for remediation of 2,4,6-trinitrotoluene, hexahydro-1,3,5-trinitro-1,3,5-triazine and glycerol trinitrate [81] by introducing and expressing bacterial nitroreductases and cytochrome p450s.

As hyperaccumulators have a high metal tolerant trait, probable detoxification capacity is maximum thus efficiently used in phytoremediation. But there is an alternative to hyperaccumulators due to sluggish growth and condensed biomass production, hence it requires numerous years for sanitization of contaminated sites. Thus, to facilitate faster decontamination the remedial property can be extensively improvised by genetic manipulation, plant tissue culture, imbursement of transgenic approaches viz., genes, traits can be manipulated thus the production of transgenic plants; mainly industrialized for remediating heavy metal contaminated soil sites. Examples include *Nicotiana tabacum* expressing a yeast metallothionein gene for higher cadmium tolerance or *Arabidopsis thaliana* overexpressing a mercuric ion reductase gene for higher mercury tolerance [83]. [84] Stated about arsenic sequestration which happens largely in vacuoles by complexation with glutathione (-GSH) and Phytochelatins (PCs).

In another example, the arsenic fall was seen in the transgenic plant developed by using bacterial genes ArsC from *E. coli* with co-expression of γ -glutamylcysteine synthetase to provide sufficient -GSH for subsequent conjugation [85]. By the expression of bacterial genes merA gene encoding organo-mercurial lyase, transgenic plants show better resistance against the toxic effects of mercury [86]. When merB was expressed in endoplasmic reticulum resistance was further improved. Therefore findings on chloroplast are the primary target for mercury poi-

soning is leading the ongoing research in chloroplast genome engineering. Further, the expression of bacterial genes atrazine chlorohydrolase (*atzZ*) and 1-aminocyclopropane-1-carboxylate deaminase has shown a promising result in the remediation of atrazine and alachlor [87]. Transgenic plants expressing these genes show significantly increased tolerance, uptake and detoxification of targeted explosives. Expression of cytochrome p450 as in CYP2E1 in tobacco and poplar plants have not only increased TCE metabolism but also is metabolizing vinyl chloride, benzene, toluene and chloroform [82]. Also, trace element detoxification systems have been implemented at the molecular level in yeast and bacteria. A vivid study and approaches by manipulation of molecular genetic techniques to regulate the discharge of metals as contaminants can be controlled through the use of the transgenic plant.

Metal homeostasis in plants

Metal homeostasis is defined as the metal uptake, trafficking, efflux, and sensing pathways, which allowing organisms to maintain a narrow intracellular concentration range of essential transition metals. The molecular and genetic basis for these mechanisms will be vital in the development of plants that can be agents for phytoremediation of contaminated sites. One among the recurrent general mechanism requires metal homeostasis, chelation of the metal by a ligand and subsequent compartmentalization of ligand-metal complex. Plants evolved a variety of mechanisms managing heavy metal stress which include the synthesis of the Sulphur rich metal chelators, Glutathione (GSH), Phytochelatins (PCs) and Metallothioneins (MTs) [88,89]. Organic acids like citrate, maleate which chelate extracellularly have significant tolerance to aluminium. Peptide ligands comprise Metallothioneins (MTs), small gene-encoded, Cys-rich polypeptides. GSH, abundantly the low-weight molecular SH-compound in plants is synthesized through ATP-dependent enzymatic pathway. GSH protects plants from environmental and oxidative stresses, xenobiotics and heavy metals. Glutathione acts as a precursor of Phytochelatins (PCs) during excessive mental stress [90]. The SH-peptide GSH (ζ -Glu-Cys-Gly) and its variation homoglutathione (h-GSH, ζ -Glu-Cys- $\hat{\alpha}$ -Ala) has a stimulus in the form and toxicity to heavy metals such as Cu, Cd, As, Hg and Zn in different ways. Inventive measures of remediation technologies are of paramount importance thus plants can be an introduced as supplementary alternative renewable source thus used insitu remediations.

Metallothioneins

Metallothioneins (MT) are cytoplasmic proteins [91], a family of small, vastly conserved, cysteine-rich metal-binding proteins (M.W. \sim 7000), that are rich in sulfhydryl groups (thiols, make them bind to several trace metals) that are significant small proteins that bind towards Zn and Cu homeostasis, small amounts of Fe, Hg and perhaps other heavy metals [92], safeguard against oxidative stress, and buffering against toxic heavy metals. MTs were recognized firstly as Cd-binding proteins in mammalian tissues. Comparably proteins are recognized in large numbers of animal species [93]. Cysteine-rich proteins known for their high affinity towards cations Cd, Cu, Zn etc.; also known to deliberate heavy-metal tolerance and accumulation in yeast and plants.

To mention,

- a. Enhanced Cd tolerance is a result of overexpression of MT genes in tobacco and oilseeds.

- b. A 16-fold greater Cd tolerance was observed by MT yeast gene (CUP 1) overexpression in cauliflower.
- c. The yeast metallothionein (CUP1) encourages Cu uptake in tobacco - 7 times more in older leaves than fresh leaves, during Cu stress.
- d. Likewise, high accumulation of Cu was found in *Arabidopsis thaliana* by overexpression of a pea MT gene.

Phytochelatins

Phytochelatins (PC) are oligomers of glutathione [94], produced by the enzyme phytochelatin synthase from GSH, seen in plants, fungi, nematodes and all the algal groups including cyanobacteria. Phytochelatins are central for heavy metal detoxification and act as chelators [95], Cysteine-rich metal-chelating (post-translationally synthesized) peptides which suggestively show heavy-metal tolerance in plants and fungi by chelation and thus decrease their unrestricted availability. It is projected that PCs are the functionally alike MTs [96].

PCs aren't reported in animal species, which supports that MTs performs normal functions well in animals, as a contribution by PCs in plants. Heavy metal toxicity in plants is seen in diverse ways; these include chelation, exclusion, compartmentalization of the metal ions, immobilization, and the expression of more stress response mechanisms in general such as ethylene, other stress proteins etc [11].

To mention,

- a. In the *Agrobacterium*-mediated transformation, the induction and overexpression of phytochelatin synthase (PCS1) in *Nicotiana glauca* bring about high concentrations of Pb and Cd.
- b. Accumulation of high Pb concentrations in aerial parts and roots were also observed in transgenic plants.
- c. Longer roots, greener higher leaves than unmodified plants were seen in transgenic seedlings.
- d. Overexpression of an Arabidopsis PC synthase (AtPCS1) in transgenic which increases PC synthesis thus accumulating and tolerating metals.

As PCs are found in tissues of the plants and cell cultures upon open to trace levels of crucial metals and the level of PCs were seen in cell cultures is correlated with the medium by reduction of metal ions. These remarks are inferred to designate the role of PCs in the crucial metal ion metabolism homeostasis [Rausser, 1995; 97].

Conclusion

Amongst several regions of the world, cultivation of plants is significant in the maintenance of the ecosystem. Environmental contamination occurs due to geogenic and anthropogenic activities as discussed in the review paper. Although a few metals are true bio elements at normal concentration they can cause a potentially hazardous impact on excessive usage causing environmental contamination. There are a variety of measured steps taken through the different aspects of phytoremediation to curb the menace of contaminants and pollution but there is always a step of further progress which can be implemented in this scenario.

Plants are naturally found to synthesize nanoparticles. Nanophytoremediation is an innovative and encouraging technology

which has gathered a wider reception due to its current area of research in plants. As in the review paper, there are several plant families which act in the biosynthesis of nanoparticles. It is significant to study on metal nanoparticles formation, types of nano-particles, derivatives of these nanoparticles, and their action on the physiological process will further eliminate the bioaccumulation of toxic nanoparticles in the plants. Numerous countries globally use plants as a primary source of energy for food; fodder thus toxicity, contamination of metals in crops, medical plants may have a huge impact. In our review paper, we have made a significant effort to understand the phytoremediation processes in general, the nanoparticles occurrence, the need to biomonitor the trace elements in the environment, the physiological effects of the bioelements, transgenic plants which can be used effectively in nanophytoremediation. Thus, in conclusion, nanophytoremediation can be a complementary biological clean up technique thus maintaining the sustainability of the environment.

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