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 synthesized 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.

Keywords: Nanoparticles; Phytoremediation technologies; Hyperaccumulators; Bioelements; Contaminants; Transgenic plants.

**Introduction**

Plants are autotrophic in nature, thus are self-sufficient in the utilization of sunshine and CO$_2$ 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.

**Table 1: Technologies related to Phytoremediation.**

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

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.

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon-Germanium (Si-Ge) nanoparticles</td>
<td>Freshwater diatom Stauroneis sp.</td>
</tr>
<tr>
<td>Au and Ag nanoparticles</td>
<td>Pelargonium graveolens, Hibiscus rosasinensis, Citrus sinensis, Diopyros kaki (Persimmon), Emblica officinalis, Phyllanthium, Mushroom extract, Coriandrum sativum.</td>
</tr>
<tr>
<td>Ag nanoparticles</td>
<td>Elletaria cardamom, Parthenium hysterophorus, Euphorbia huta, Ocimum sp., Nerium indicum, Brassica juncea, Azadirachta indica, Pongamia pinnata, Clidemia inermis, Opuntia ficus indica, Gliotyledon sepium, Desmodium triflorum, Carica papaya, Coriandrum sativum, Pdargoneum graveolens, Avericennia mania, Aloe vera extract, Capsicum annum, Rhizophora mucronata, Ceriopstagia, Rumex hlymeno sepalus, Pterocarpus santalinus, Sonchus asper.</td>
</tr>
<tr>
<td>Ag, Ni, Co, Zn and Cu nanoparticles</td>
<td>Brassica juncea, Medicago sativa and Helianthus annuus.</td>
</tr>
<tr>
<td>Platinum nanoparticles</td>
<td>Diospyros kaki, Ocimum sanctum L.,</td>
</tr>
<tr>
<td>Palladium nanoparticles</td>
<td>Cinnamomum zeylanicum Blume, Cinnamomum camphora L., Gardenia aminoides, Ellis. Soybean (Glycine Max) L.,</td>
</tr>
<tr>
<td>Lead nanoparticles</td>
<td>Vitus vinifera L., Jatropha curcas L.</td>
</tr>
<tr>
<td>Indium oxide nanoparticles</td>
<td>Aloe vera (Aloe barbadensis Miller),</td>
</tr>
<tr>
<td>Gold/Silver bimetallic nanoparticles</td>
<td>Azadiricta indica (Neem)</td>
</tr>
</tbody>
</table>

Several studies report the usage of nanoparticles to have an affirmative effect on plants. Mixed TiO$_2$ (nano) and SiO$_2$ (nano) were presented into soybean (Glycine max) increasing activity of nitrate reductases which speed 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 sciedirect 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).

Phytoremediation classification

Phytoremediation technologies are classified in general into a

a. Phytoextraction-Metal concentration reduction in the soil through plants that can accumulate metals in the shoots.

b. Phytostabilization-Immobilise the utilization of soil metals via adsorption onto roots; rhizosphere precipitation.

c. 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

- **Plant metabolic processes; or**
- **The outcome of metabolites, such as enzymes, produced by the plant.**

f. **Phytoretransaturation** - 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 wildly 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.

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### Table 3: Synthesis of iron nanoparticles/derivatives.

<table>
<thead>
<tr>
<th>Type of nanoparticles</th>
<th>Biochemical Agents</th>
<th>Size / Morphology</th>
<th>Environmental Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stabilized bimetallic Fe/Pd nanoparticles</td>
<td>Starch</td>
<td>14.1 nm distinct, well dispersed</td>
<td>Degradation of chlorinated hydrocarbons in water</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Na-Alginate</td>
<td>27.20 nm spherical</td>
<td>Urea Decomposition</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ - Polymer Composite</td>
<td>Agar (Reducing &amp; Stabilising Agent)</td>
<td>50-200 nm spherical, 24 nm diameter &amp; Hexagonal</td>
<td>Magnetic Storage Media</td>
</tr>
<tr>
<td>Nano-Shell (Fe, Cu)</td>
<td>Ascorbic Acid (Antioxidant)</td>
<td>&lt;100 nm Cubic</td>
<td>Functions in catalysis, Biosensors, Energy storage problems, nanodevices.</td>
</tr>
<tr>
<td>nZVI</td>
<td>Ascorbic Acid (Vit-C)</td>
<td>20-75 nm, spherical</td>
<td>Cd removal</td>
</tr>
<tr>
<td>Superparamagnetic Iron oxide (Coatings &amp; Functionalisation)</td>
<td>Ascorbic acid (Vit-C)</td>
<td>5 nm - 30 nm (Hydrodynamic Size)</td>
<td>Contrast enhancement agent for MRI Applications</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ (MNP)s</td>
<td>L-Lysine (A. Acid)</td>
<td>17.50 nm &amp; Spherical Crystalline</td>
<td>Biosensors, Drug Delivery</td>
</tr>
<tr>
<td>nZVI</td>
<td>L-Lysine (A. Acid)</td>
<td>-</td>
<td>Low-molecular, biocompatible</td>
</tr>
<tr>
<td></td>
<td>L-Glutamic Acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>L-Glutamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>L-Arginine and L-Cysteine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeNPs</td>
<td>Haemoglobin &amp; Myoglobin</td>
<td>2-5 nm aggregates, crystalline</td>
<td>Bioconjugated nanoparticles for biological applications</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>D-glucose Gluconic Acid</td>
<td>12.5nm roughly spherical, crystalline</td>
<td>Drug delivery, Cell transplantation</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Glucose &amp; Glyconic Acid</td>
<td>4-16 nm Crystalline</td>
<td>Removal of waste in the biomedical field</td>
</tr>
<tr>
<td>Carbon capsulated Iron NPs</td>
<td>Wood-derived sugar</td>
<td>100-150 nm nanospheres, 10-25 nm diameter of iron-core</td>
<td>Acts as catalysts in the conversion of wood-derived syngas to liquid hydrocarbons</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>Tannic acid</td>
<td>&lt;10 nm</td>
<td>Utilization of biomass causes the reduction of metal ions</td>
</tr>
<tr>
<td>Fe core-shell structure</td>
<td>Chitosan-Gallic acid</td>
<td>11 nm cubic</td>
<td>Increased thermal stability of drug Gallic Acid, Anticancer activity was higher for HT29 and MCF7 cell - lines</td>
</tr>
</tbody>
</table>

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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-
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Geogenic and anthropogenic processes [13]. Metals sieve through the soil and are terminated into the soil by affecting the normal molecular process as shown in (Figure 4). Heavy metal is shown to cause microorganisms [12] to affect the normal molecular process. Heavy metals 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].

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].

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 invitro. 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 Au0 to Ag+ 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.
Importance & Applications of Nanotechnology

Nanotechnology, with its ability to manipulate matter at the nanoscale, has the potential to solve some of the world's biggest challenges. By understanding and applying the principles of nanotechnology, we can address issues ranging from environmental remediation to the development of new medical treatments. In this section, we will explore the importance and applications of nanotechnology, focusing on its potential to impact various fields.

**Nanomaterials in Environmental Remediation**

Nanomaterials such as nanoscale iron products (NSIPs) and nanoscale zero-valent iron (NZVI) are being extensively studied for their potential to remediate contaminated sites. NZVI is a type of nanomaterial that is capable of reducing contaminants such as heavy metals and organic pollutants. This is achieved through several mechanisms, including reduction, precipitation, and adsorption.

For example, NZVI has been used in the remediation of groundwater contaminated with heavy metals. NZVI can effectively reduce metals such as lead, cadmium, and chromium to their elemental forms, making them less toxic and easier to remove from water. This is particularly important in areas where water contamination is a significant issue, as it allows for the recovery of water resources without the need for immediate disposal or replacement.

**Dendrimers**

Dendrimers are another class of nanomaterials that have significant potential in environmental remediation. These highly branched, spherical macromolecules can be used to encapsulate and deliver a variety of substances, including enzymes and therapeutic agents. This makes them ideal for the removal of pollutants from water and soil.

One example of their use is in the remediation of water bodies contaminated with ethylbenzene. Dendrimers can be functionalized with specific groups that interact with the contaminant, allowing for selective adsorption and removal. This approach not only enhances the remediation process but also ensures minimal disturbance to the environment.

**Nanocarbons and Carbon Nanotubes**

Carbon nanotubes (CNTs) and graphitic phases such as carbon nanofibers (CNFs) and carbon nanodots (CNDs) have shown great potential in environmental remediation. These materials can be used for the remediation and stabilization of heavy metals, organic pollutants, and even act as filters for groundwater.

For instance, CNTs can be used to adsorb heavy metals from water, demonstrating high adsorption capacity and selectivity. This is achieved through the strong van der Waals forces between the CNTs and the metal ions, allowing for efficient removal and subsequent concentration in a solid form.

**Conclusion**

Nanotechnology offers a promising avenue for environmental remediation, providing solutions to longstanding problems such as heavy metal contamination and organic pollutants. As research and development continue, we can expect to see more targeted and effective applications of nanomaterials in the field of environmental science.
Importance & Applications of Nanotechnology

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 Polyethene 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].

Polymorphic 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-
Table 4: Hyperaccumulator plants for varied metals.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Plant species</th>
<th>Accumulated Metal concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>Thlaspi caerulescens</td>
<td>Brassicaceae</td>
</tr>
<tr>
<td>Zinc</td>
<td>Thlaspi caerulescens</td>
<td>Brassicaceae</td>
</tr>
<tr>
<td></td>
<td>Thlaspi rotundifolium</td>
<td>Brassicaceae</td>
</tr>
<tr>
<td></td>
<td>Dichopteris gelonioides</td>
<td>Caryophyllaceae</td>
</tr>
<tr>
<td>Nickel</td>
<td>Thlaspi Sps.</td>
<td>Brassicaceae</td>
</tr>
<tr>
<td></td>
<td>Allopyrum spp.</td>
<td>Brassicaceae</td>
</tr>
<tr>
<td></td>
<td>Berkhedia codii</td>
<td>Asteraceae</td>
</tr>
<tr>
<td></td>
<td>Pentacalia Sps.</td>
<td>Asteraceae</td>
</tr>
<tr>
<td></td>
<td>Psychotria coronata</td>
<td>Rubiaceae</td>
</tr>
<tr>
<td>Copper</td>
<td>Ipomoea alpina</td>
<td>Convolvulaceae</td>
</tr>
<tr>
<td>Lead</td>
<td>Minuartia verna</td>
<td>Caryophyllaceae</td>
</tr>
<tr>
<td></td>
<td>Agrostis tenuis</td>
<td>Poaceae</td>
</tr>
<tr>
<td></td>
<td>Vetiveria zizaniodes</td>
<td>Cyperaceae</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Crotalaria cobaltica</td>
<td>Fabaceae</td>
</tr>
<tr>
<td></td>
<td>Haumaniastrum robertii</td>
<td>Lamiaceae</td>
</tr>
</tbody>
</table>

Table 5: Synthesis of diverse nanomaterials.

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>The methodology used in the synthesis</th>
<th>Examples</th>
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</thead>
<tbody>
<tr>
<td>Nanoparticles biosynthesis from metals [NPs]</td>
<td>Photochemical</td>
<td>Cu, Au, CoNi, CdTe, CdSe, ZnS, Rh, Pt, Ir, Pd, Co, Ag, Au, Cu, Fe &amp; Ni</td>
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<tr>
<td></td>
<td>Biochemical</td>
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<td></td>
<td>Electrochemical</td>
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<td>Nanomaterials from carbon</td>
<td>Arc-discharge</td>
<td>Cylindrical nanotubes (SWNT, MWNT) Fullerenes</td>
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<td></td>
<td>Chemical vapour deposition</td>
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<td>Laser ablation</td>
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<tr>
<td>Nanomaterials from Polymers</td>
<td>Electrochemical Polymerization</td>
<td>Nanowires of PPy, PANi, Poly [3-4 ethylene dioxy thiophane, PAMAM, dendrimers</td>
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<td>Metal oxide Nanoparticles</td>
<td>Hydrothermal</td>
<td>BaCO₃, BaSO₄, TiO₂</td>
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<td></td>
<td>Reverse Micelles</td>
<td>ZnO, Fe₂O₃, Fe₃O₄, MgO</td>
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<td>Sol-gel Method</td>
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<td>Electrochemical deposition</td>
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<td>Bionanomaterials</td>
<td>Biological</td>
<td>Plasmids, nanoparticles from protein viruses</td>
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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 (Lemma gibba), water spinach (Ipomoea aquatica) and fern (Azolla pinnata) are prominent to phytoremedicate 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]. Microcystis umbraculum observed [54] removal of As and Cd by phytofiltration method. Oenothera piscensis plant was quite extensively considered towards phytoextraction of copper [55]. Algae such as charophytes viz., Chara aculeolata and Niellia opaca were used to remove Pb, Cd, and Zn [56].

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]. Ullothrix 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 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). 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 (Lemma 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, Lemma 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 homophytochelatins alternative to phytochelatins 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>
<thead>
<tr>
<th><strong>Table 6</strong>: Advantages and limitations of phytoremediation.</th>
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<td><strong>Phytoextraction</strong></td>
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<td>Plant with high biomass within lesser time should be successful to remove contaminants from soil.</td>
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<tr>
<td><strong>Phytostabilization</strong></td>
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<tr>
<td>Cost-effective and less disruptive which enhances the ecosystem restoration/re-vegetation.</td>
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<tr>
<td><strong>Phytovolatilization</strong></td>
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<tr>
<td>Contaminants/Pollutants are transformed into less toxic forms. e.g volatilization of mercury(Hg) by conversion to the elemental form in transgenic Arabidopsis and yellow poplars which contains bacterial mercuric reductase (merA)</td>
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<tr>
<td><strong>Phytodestruction/Rhizofiltration</strong></td>
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<td>In situ (pond floating rafts) or ex-situ (tank system); aquatic. Absorption and adsorption play an important role.</td>
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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 molar concentrations could affect seed viability. 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) 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 organisms 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 extensively 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 metals 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 nitro-reductases 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, imburement 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 tabaccum expressing a yeast metallothioinein gene for higher cadmium tolerance or Arabidopsis thaliana over-expressing 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 (atZ) 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 metal stress [90]. The SH-peptide GSH (γ-Glu-Cys-Gly) and its variation homoglutathione (h-GSH, γ-Glu-Cys-δ-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. ~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 [Rauer, 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. Nano-phytoremediation 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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