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Nanotechnology for the bioremediation of heavy metals and metalloids

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ABSTRACT

Contamination of soil and water by heavy metals and metalloids is one of the major issues that are being raised and addressed globally as it has adverse effects on the environment as well as on human health. Since each technique has its own pros and cons, integration of a few methods helps in getting effective and efficient results. Application of nanotechnology has led to the overcoming of various drawbacks of conventional methods of remediation. Nano-bioremediation is an extended branch of nanotechnology that deals with the removal of pollutants from the site of contamination by utilizing biogenic nanoparticles or materials synthesized from biological sources that are of nano size. This technique has an edge over other methods because of size of the material; smaller the size, higher would be the surface area to volume ratio and higher the ratio, more surface would be available for the reaction to occur. In recent years, the green synthesis of nanoparticles has gained enormous attention because of the economic and ecological aspects. This review highlights the implications and health risks of heavy metals and metalloids along with the application of nanotechnology in the bioremediation of these contaminants.

1. INTRODUCTION

With the increase in urbanization and industrialization, the content of heavy metals and metalloids has also risen, leading to immense damage to the whole ecosystem. According to Global Agenda 2015, rising pollution in the developing countries has become the sixth most important global trend and according to the World Economic Forum, it is the third most significant issue in Asia [1]. With each passing year, the fuel and power industries tend to generate around 2.4 million tonnes of heavy metal waste while 2 million tonnes of the waste is produced by the agricultural industries [2].

Elements that are metallic in nature and occur naturally with density 5 times greater than that of water and have relatively high atomic weight can be defined as heavy metals while metalloids are the ones possessing properties of both metals and non-metals and typically fall under the category of heavy metals [3]. The density of these metals is greater than 4 g/cm^3 and, thus, is known as "heavy metals and metalloids." Out of various heavy metals and metalloids, contamination of arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), mercury (Hg), and nickel (Ni) has gained the maximum attention because of their existence in values greater than the critical values determined by agencies like ATSDR [4]. Comparative to others, mercury, cadmium, and lead are the most toxic ones and are recognized as the "big three" due to their intense impact on the environment [5].

According to a study conducted by Bhardwaj *et al*., the Delhi (India) stretch of river Yamuna was found to be critically polluted with heavy metals such as iron, lead, chromium, cadmium, nickel, zinc, and copper [6]. Data from the study conducted by Kumar *et al*. indicated cadmium and arsenic to be the major contaminants of different soils of India [7]. According to Agency for Toxic Substances and Disease Registry's (ATSDR) Priority List of Hazardous Substances (ATSDR), As ranks No. 1 while Pb, Hg, and Cd rank No. 2, No. 3, and No. 7, respectively [8]. Since heavy metals pose detrimental risk to environment, their standard limits should be kept into consideration for economic sustainability and viability. List of acceptable limits of heavy metals and metalloids in drinking water is mentioned in Table 1.

The remediation process of the toxic heavy metals is generally done through four different ways, namely, *in situ* containment, *ex situ* containment, *in situ* treatment, and *ex situ* treatment but the inefficient results and drawbacks of conventional and bioremediation methods led to the application of nanotechnology in this area [9]. The branch of nanotechnology has received great attention lately because of the ability to synthesize a material possessing desired characteristics that are different from the bulk material. Application of nanotechnology improves the existing processes and materials by simply scaling down to a nano level where the unique quantum and surface phenomena can be exploited [10]. Nanoparticles are known to possess properties such as uniform shape and high surface area to volume ratio that greatly influence the ability of the nanomaterial to penetrate the cell

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Table 1: Acceptable limits of heavy metals and metalloids in drinking water.

Heavy metal/ metalloid	Atomic weight (u)	Who limits (mg/L)[(a)]	US-EPA limits (mg/L)[(b)]	BIS limits (mg/L)[(c)]
Arsenic (As)	74.92	0.01	0.010	0.01
Lead (Pb)	207.2	0.01	0.015	0.01
Cadmium (Cd)	112.41	0.003	0.005	0.003
Mercury (Hg)	200.59	0.006	0.002	0.001
Chromium (Cr)	51.99	0.05	0.1	0.05
Nickel (Ni)	58.69	0.07	0.1	0.02

[(a)]Guidelines for drinking water quality: Fourth edition, incorporating the first Addendum. ISBN 978-92-4-154995-0. World Health Organization, 2017. [(b)]2018 Edition of the Drinking Water Standards and Health Advisories Tables, Office of Water, U.S. Environmental Protection Agency. [(c)]Bureau of Indian Standards (BIS) (Source: Indian Standard [IS 10])

membranes and further help in biochemical activities [11]. The eco-friendly nature of organisms that eventually reduces the use of toxic chemicals has become the major reason for the extensive application of biogenic nanoparticles in heavy metal and metalloid removal.

Institutions such as European Observatory for Nanomaterial (EON), USEPA, the OECD Working Party on Manufactured Nanomaterials (WPMN), and ISO Technical Committee TC 229 "Nanotechnologies" have made an effort to establish cooperation at an international level to increase the existing regulations on the use of nanomaterials [12]. In 2015, the Strategic Approach to International Chemicals Management (SAICM) under United Nations Environment Program (UNEP) gave recommendations on the exchange of information, technical and regulatory guidance, and the proper management of nanomaterials. To raise awareness about nano-safety issues and their implications across borders, wide range of activities has been established by the United Nations International Training and Research (UNITAR) [13]. The Indian government in October 2001 came up with an initiative that is addressed as the Nano Science and Technology Initiative (NSTI), and in 2007, another program called nano mission was launched. Under these programs, series of research work has been conducted but the country lacks a robust regulatory framework and does not have any legislation that addresses nanoparticle as hazardous [14]. The present review highlights the impact of heavy metals and metalloids on the environment and human health as well as discusses its remediation through the integration of nanotechnology with bioremediation methods.

2. IMPACT OF HEAVY METALS AND METALLOIDS ON ENVIRONMENT AND HUMAN HEALTH

2.1. Impact on Soil

The release of heavy metals sourced from industrial activities, fertilizers, sewage sludge, animal manure, waste water irrigation, coal combustion, petrochemical spillage, and disposal of high metal waste causes the contamination of soil. Since these are non-biodegradable in nature, they last for longer periods of time in the environment. It is believed that the presence of the heavy metals and metalloids affects the biodegradation rates of organic pollutants and they pose severe impact on the whole ecosystem because of their residence in the food chain [15]. The adverse effects of heavy metal contamination are not only limited to plant yields and quality but are also responsible for affecting the size, composition, as well as the activity of the microbial population. The enzymatic activity of the microbial community is also affected by the heavy metal contamination. Interference with the microbial processes and the reduction in the number as well as the activity of soil microbes exhibit toxic effects on the soil biota. Contrary to that, long-term exposure to heavy metals may lead to enhanced tolerance level of the bacterial community that could help in the restoration of the contaminated ecosystem.

2.2. Impact on Water

Heavy metals and metalloids end up accumulated in water bodies and soil by the runoff from the municipalities, industries, as well as the urban areas. The presence of heavy metals and metalloids in sewage water leads to their accumulation in the irrigation systems. The presence of these contaminants in water affects all organisms even in trace amounts and imposes serious problems to humans and other ecosystems [16]. The pollution causes a decrease in the dissolved oxygen concentration and with the decrease in dissolved oxygen concentration, the aquatic life is negatively impacted [5]. As soon as heavy metals and metalloids enter the river, they get diluted at a fast pace and are transported over hundreds of kilometers. Then, they get accumulated in the aquatic organisms and are deposited in the sediments. Due to the variations in the pH values and hydrological and external redox conditions, the heavy metals in the sediments get released into the overlying water and cause toxicity to organisms [17]. Biomagnification and bioenrichment effects may allow heavy metals to exist in the food chain because of their toxicity, easy enrichment, and refractory degradation. This may lead to adverse effects on the ecosystem as well as jeopardize the safety of water supply to humans [18].

2.3. Impact on Human Health

The biological activities of native proteins get affected by the interference of heavy metals and metalloids through various modes of interaction; the metals may interact and bind with the free thiols or other functional groups in proteins or in case of metalloproteins, they may displace the essential metal ions or get involved in catalyzing oxidation of amino acid side chains. Studies have shown that heavy metals and metalloids are also responsible for inhibiting the process of refolding of denatured proteins (*in vitro*), interfering with the protein folding (*in vivo*), and causing nascent protein aggregates in the living cells. Any sort of interference with the protein folding affects the cell viability and protein homeostasis [19]. The presence of lead even in amounts as low as 5 ug/l can cause development problems such as behavioral disorders, impaired cognitive function, impaired hearing and stunted growth as well as inhibits porphobilinogen synthase that is majorly involved in the heme biosynthesis. It also hinders Vitamin D metabolism and gets accumulated in the bones and interferes with maturation of erythroid elements in the bone marrow. Similarly, nickel toxicity can lead to allergic contact dermatitis, bronchitis, emphysema, and impaired pulmonary function [20]. Arsenic is responsible for issues related to skin damage, circulatory system, and cancer while chromium causes denaturation and mutation of proteins and nucleic acids. Thus, the presence of heavy metals and metalloids above the permissible limit has adverse effects on the human as well as animal health [21].

2.4. Impact on Microorganisms

Interaction between the microorganisms and heavy metals leads to altered enzymatic expression that is indicative of the jeopardizing effects of heavy metals on the ecosystem [22]. Different microorganisms show different types of tolerance response; the hyphal extension rate and spore germination get affected in case of fungi due to their interaction with heavy metal contamination, the cell density and species richness are affected in protozoans [23], inhibition of photosynthesis, and reduction in chlorophyll content is observed in case of algae [24], and in lichens, similar to algae, the photosynthesis is inhibited [25].

2.5. Impact on Air

With the increase in the global population, industrialization and urbanization have become leading cause for the presence of particulate matters in the air. Natural processes such as volcanic eruptions, storms, soil erosion, and weathering of rocks are also the sources of air pollution along with anthropogenic activities. Heavy metals such as lead, cadmium, and zinc are emitted from the traffic as well as from various industries. These heavy metals impact the health of the living organisms as well as cause infrastructure deterioration, formation of acid rain, and eutrophication [15,26].

3. BIOREMEDIATION

Bioremediation is a technique that is used for the removal and conversion of contaminants such as heavy metals and metalloids, hydrocarbons, oil, dye, and pesticides into a less toxic and less harmful form by the aid of biological agents. This process involves the degradation and mineralization of organic substances into nitrogen, water, carbon dioxide, etc., by utilizing biomass [27]. Bioremediation triangle has three main components, namely, microorganisms, food, and nutrients. The presence of contaminant in soil or water serves the purpose of providing a carbon source for the microbial growth as well as the microbes obtain energy as a result of carrying out the redox reaction that leads to electron transfer. Desired efficiency of bioremediation can be only achieved when microorganisms are capable of enzymatically attacking the contaminants and further convert them into non-toxic products. For this to happen, optimum levels of essential nutrients and chemicals are needed to be supplied for microorganisms to detoxify the pollutants. The reason for microorganisms to be suited for this process is that they possess enzymes that are able to utilize contaminants as food. The manipulation of environmental parameters is necessary to allow the microbial growth as well as activity to occur at a faster rate [28]. Principally, the process of bioremediation is based on biodegradation which involves complete removal and degradation of contaminants into harmless forms that are safe for the ecosystem.

Irrespective of various advantages of bioremediation such as high specificity and selectivity, economic feasibility, and environment friendly nature, these processes have several drawbacks as well. Ample of time is needed for the degradation of toxic compound to be carried out and the use of bioremediation at extremely contaminated sites becomes restricted. The *in situ* bioremediation poses problems such as seasonal difference in microbial activity, problems with the use of additives for the purpose of treatment, and sometimes, the process get out of control and becomes difficult to manage. Furthermore, *the ex situ* method is inefficient for the remediation of heavy metals and chlorinated hydrocarbons. This necessitates the need for applying nanotechnology to bioremediation in order to remediate contaminated sites [29,30]. By integrating nanotechnology with bioremediation, excellent and extraordinary adsorption capacities can be achieved due to the surface effect, small size effect, quantum effect, as well as macroquantum surface effect.

4. NANOBIOREMEDIATION

Nanotechnology is a branch capable of improving the activity and effectiveness of conventional remediation and bioremediation methods by accelerating the contaminant transformation rate because of the smaller sizes of the nanoparticles [31]. Integration of nanotechnology and bioremediation technique is a feasible method that helps in nurturing the environment through the removal of contaminants as well as accelerates the rate of advancement [32,33]. In simple words, the process of removal of contaminants such as heavy metals, metalloids, organic, and inorganic pollutants from the site of contamination using nano-sized particles or materials synthesized by plant, fungi, or bacteria by the aid of nanotechnology is known as nanobioremediation. Three major attributes important for the applicability of nano-bioremediation are, (1) use of green and clean nanomaterials, (2) solution for the removal of contaminants, and (3) to be used as sensors for environmental agents [34]. Nanotechnology for the purpose of remediation has become popular because of small size (<100 nm), larger surface area, and attractive chemical characteristics [35]. Principle of this technique is the degradation of waste utilizing nano-catalyst that allows deep penetration within the contaminant and further treating it safely without harming the surrounding environment by the aid of few microorganisms. Microorganisms are capable of converting heavy metals and metalloids into non-toxic forms by mineralization of organic contaminants to products such as carbon dioxide and water. The nano size of the nanoparticles allows their penetration into the contaminated site and this provides better results compared to bioremediation methods.

4.1. Properties of Nanoparticles

Nanoparticles can be defined as aggregates (atomic or molecular) that have a dimension between 1 and 100 nm possessing ability to modify their physiochemical properties comparative to bulk materials. Their classification depends on the number of dimensions in which electrons can be confined, such as 0-dimensional (0D) and 1-dimensional (1D). Thin films (2D), wires and rods (1D), and spheres (0D) are a few geometries in which the nanoparticles can exist [36]. They possess unique properties that do not exist in their bulk counterparts and, therefore, have wider range of applications. The uniqueness lies in the large surface area to volume ratio because of the smaller size and this imparts physical and chemical properties that are different from the bulk counterparts. Nanoparticles can be categorized into organic (micelles, fullerenes, and dendrimers) and inorganic (ceramic, steel, and metal oxide nanoparticles) nanoparticles. Single crystalline nanoparticles are termed as nanocrystals and other than that the nanoparticles can either be polycrystalline or amorphous with various morphologies such as platelets, spheres, and cubes [37].

For the synthesis of nanoparticles, both chemical and biological methods have been adapted. Due to the eco-friendly nature, low cost, rapid synthesis, control over size characteristics, and toxicity, the biological synthesis method is preferable [38]. Biological systems have an ability to self-organize and to synthesize molecules possessing highly selective properties. Various parameters on which the physical properties of nanoparticles depend include size, shape, state of size distribution, surface area, solubility, and the structure. Increased surface area to volume ratio of nanoparticles helps in making the surface more available for reaction as the number of molecules at the surface increases exponentially. Furthermore, with the variation in size and shape of the nanoparticle, the optical properties also vary [39]. The chemical properties of nanoparticles are defined by the zeta potential, surface chemistry, photocatalytic properties, and the chemical composition [40]. Nanoparticles that are synthesized using a green nanotechnology approach make use of living organisms, microbes, and plants. Microbes have gained attention for the production of nanoparticle because of their high tolerance, rapid decontamination, and reproduction power. Biologically generated nanoparticles have been reported to show high catalytic reactivity and high specific surface area [41]. The presence of capping agent secreted by microorganisms helps in avoiding aggregation of nanoparticles. Extracellular biosynthesis of nanoparticles requires no downstream processing as well as is not expensive [42].

4.2. Synthesis of Nanoparticles

Top-down (physical) and bottom-up approaches (chemical and biological) are the two main approaches through which the nanoparticles can be synthesized, as depicted in Figure 1. In the top-down approach, without any atomic level control, the larger particles are broken systematically into smaller particles and as a result of which nanoparticles are produced [43,44]. The bottom-up approach involves the self-assembly of smaller particles to form nanoparticles. Various techniques for the synthesis of nanoparticles in case of bottom-up approach are laser pyrolysis, sol-gel, aerosol-based procedure, plasma spraying process, and green synthesis [45]. Since the physical and the chemical methods are expensive, form toxic by-products, and require the addition of toxic chemicals, the biological method for the synthesis of nanoparticles has gained a lot attention [46]. Nanoparticle synthesis using non-biogenic methods requires an additional step of functionalization wherein polymers and surfactants are used for surface coating [47]. The formation of capping occurs simultaneously with nanoparticle formation during biogenic methods of nanoparticle synthesis, and therefore, no additional step is required, as depicted in Figure 2. Excellent adsorption, catalytic activity, and environment-friendly nature of biogenic nanoparticles have made them the best candidates for the clean-up of the environment [48]. To list a few, good polydispersity, dimension, stability, and low cost, removal of processing conditions and synthesis at physiological pH, temperature, and pressure are the advantages of biogenic synthesis over other conventional methods [49]. Proteins that are secreted by the biomolecules cause the reduction of metal ions and further lead to the synthesis of nanoparticles. These biogenic nanoparticles can be applied in various fields such as medical, food industry, chemical, electrochemical, environmental remediation, and biotechnology [50]. The ability of microorganisms to grow and survive in high concentration of toxic metals is due to their chemical detoxification and energy-based efflux from the cell by membrane proteins that generally function as either chemo-osmotic or protein anti-transporters or ATPase. Microbes are capable of synthesizing nanoparticles either using intracellular or using extracellular processes. The positively charged metal ion diffuses into the cell wall (negatively charged) by the aid of electrostatic interactions in case of the intracellular process. Endocytosis, carrier channels, and ion channels are responsible for the cytoplasmic influx of the heavy metals and metalloids, and further, the enzymatic machinery converts toxic forms into the non-toxic nanoparticles. The extracellular process is marked by the enzymatic secretion, bioreduction, and particle capping [51]. The basic mechanism for the extracellular synthesis of nanoparticles is the metal ion aggregation on cell surface and involvement of reducing ions through enzymes [36]. Microbial nanoparticles are highly affected by parameters such as temperature, pH, pressure, time, and particle size [52]. The temperature requirement is different for all the synthesis methods, namely, physical (>350°C), chemical (<350°C), and biological (<100°C) [53]. pH of medium affects the size and texture of biogenic nanoparticles. Ambient pressure is ideal as rate of reduction of metal ions is maximum at ambient conditions. The incubation time of the reaction medium affects the quality and type of nanoparticle. For instance, long time of storage can lead to aggregation or shrinkage of the nanoparticles, can become uniform or it can react with the environment. Other factors like composition of metabolites vary from plant to plant and thus affect the nanoparticles synthesis as these act as reducing agents and stabilizing agents. The source of bioactive compounds is one of the limiting factors to standardize green synthesis of metal nanoparticles [54]. Varying type and quality of enzymes secreted intracellularly and extracellularly by microbes may affect nanoparticle synthesis. The quantity and quality can be influenced by the type of purification method chosen [55,56].

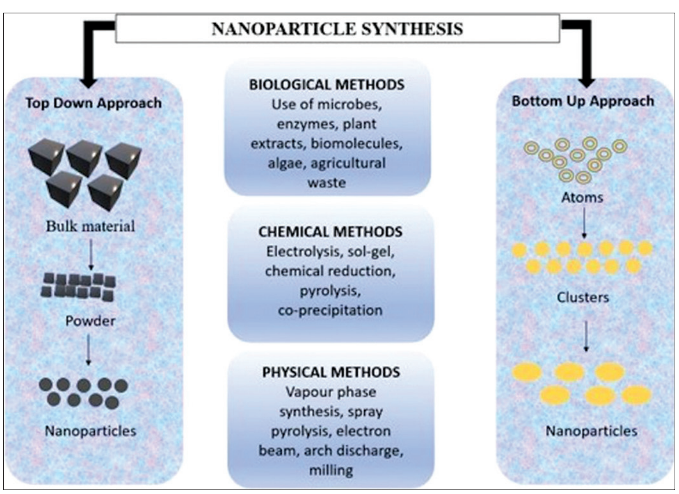

Figure 1: Approaches for nanoparticle synthesis.

4.3. Characterization Techniques

Clarity regarding the surface area, shape, chemical composition, size, and dispersity can be achieved by the characterization of the biogenic nanoparticles. Characterization of nanomaterials is crucial as their application is highly dependent on the size and shape. Various techniques that are used for serving the purpose of characterization include scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier-transform infrared (FTIR) spectrum analysis, X-ray diffraction (XRD), UV–Visible spectrum analysis, energy-dispersive X-ray spectroscopy (EDX), and Brunauer-Emmett-Teller (BET) [37]. One of the most commonly used characterization tools is SEM that helps in achieving a high enlargement of 3D images for morphological and topographical analysis of the surface of the material at a micrometer and sub-micrometric scale. The UV–Vis spectroscopy quantifies the light that is absorbed and scattered by the sample and, thus, characterizes the optical properties of the sample. For the chemical or the elemental analysis, energy-dispersive X-ray spectroscopy is used that depends on the interaction of source of X-ray excitation and the sample. XRD technique is an important tool for the topographic analysis of the sample. The XRD spectra are a result of the measurement of the angles at which an X-ray beam is diffracted by crystalline phases of the sample. To characterize the chemical properties of the specimen, FTIR is used, wherein, light rays between the wavelengths of near infrared and far infrared are absorbed by the specimen's molecules to determine the type of bonds that are present within the molecules. The physical surface assimilation of gas molecules present on a solid surface is clarified by the BET theory and it is very crucial for the measurement of material's particular expanse [57,58].

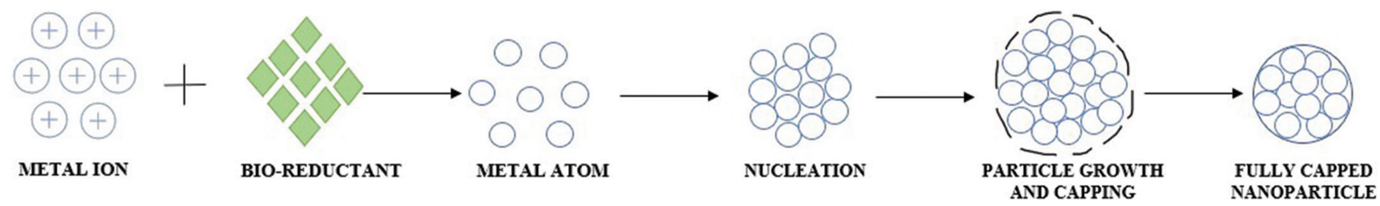

Figure 2: Microbial synthesis of nanoparticle.

4.4. Nanoparticle Synthesis by Biological Sources

4.4.1. Synthesis of nanoparticles by bacteria

Bacteria have an ability to bind and concentrate dissolved metal and metalloid ions. They are capable of converting toxic metal ions into non-toxic nanoparticles. Bacterial mobilization, immobilization, and metal precipitation allow the facilitation of nanoparticle synthesis. Diversity and high adaptability to extreme conditions of nanoparticles synthesized by bacteria make it a promising approach [51]. The immediate cell environment is detoxified by bacteria through reducing the toxic metal species into metal nanoparticles. The bacterial biomolecules are used as stabilizing as well as capping agents during nanoparticle synthesis. The extracellular synthesis of biogenic nanoparticles is comparatively more efficient and easier to extract nanoparticles. Huge quantities of nanoparticles can be synthesized extracellularly in a pure form. Bacteria have been exploited for the synthesis of nanoparticles such as palladium, titanium, magnetite, gold, silver, and so on. Bacteria have a potential to be used as a biocatalyst for the synthesis of inorganic material; can also act as bio-scaffold for the mineralization purpose; and take active part in the synthesis of nanoparticles. The biosynthesis by the aid of bacteria is a flexible, reasonable, and suitable large-scale production technique [59,60]. Few examples of nanoparticles synthesized by bacteria for the remediation of environmental contaminants are biogenic manganese oxide nanoparticles by *Pseudomonas putida* [61], silver nanoparticles by *Bacillus cereus* [62], gold nanoparticles by *Rhodopseudomonas capsulata* [63], biogenic selenium nanoparticles by *Citrobacter freundii Y9* [64], etc.

4.4.2. Synthesis of nanoparticles by algae

Algae are hyper-accumulators that are photoautotrophic, oxygenic, and eukaryotic in nature known for accumulation of heavy metal ions and later, remodel them into malleable forms [65]. Various advantages of algae for nanoparticle synthesis are ability of bioaccumulation of metals, economic viability, ease of handling, and high tolerance. The cell walls of brown algae are known to be rich in mucilaginous polysaccharides and carbonyl groups that play an important role in the metal uptake [47]. Algal extracts are rich in pigments such as chlorophyll, phycobilins and carotenoids, carbohydrates, minerals, proteins, and antioxidants that help in the reducing the metal ions as well as help in stabilization by capping. The inorganic nanoparticle synthesis involves first, the mixing of extract with water or some organic solvent, and boiling it for certain time and then, after the preparation of metal ion solution, mixing of the algal extract with metal ion solution with stirring. Nucleation is marked by the change in color, and thus, thermodynamically stable nanoparticles with variable shapes and sizes are formed [66]. One such example demonstrating the color change is the synthesis of silver nanoparticles by Fatima *et al.* using red algae *Portieria hornemannii* where the color change was observed from pink to dark brown [67]. The intracellular synthesis of nanoparticles completely relies on pathways such as photosynthesis, respiration, and nitrogen fixation while the extracellular synthesis requires pre-treatment such as washing and blending and is supported by metabolites, ions, enzymes, pigments, DNA, RNA, lipids, hormones, and antioxidants [65]. Iron nanoparticles by *Chlorococcum* sp. MM11 [68], gold nanoparticles by *Euglena gracilis* [69], silver nanoparticles by *Caulerpa racemosa* [70], etc., are a few examples of nanoparticles synthesized by algae for the remediation of environmental contaminants.

4.4.3. Synthesis of nanoparticles by plants

Synthesis of nanoparticles by plants is a single-step procedure with the presence of natural capping agents and absence of toxicants. The major advantage of plant-based biosynthesis is the easy availability, safe handling, as well as availability of various metabolites capable of aiding the reaction. Comparative to bacteria and fungi, the incubation time for metal reduction is much less with phytochemicals, and therefore, plants are considered to be better option for the nanoparticle's biosynthesis [71]. Phytochemicals that are the plant-derived chemicals act as eco-friendly reducing agents for metal ions. Plant-based nanoparticles are not only eco-friendly but are also stable and the presence of proteins, polyphenols, and carbohydrates aid the synthesis of these nanoparticles [72]. Either the powder form or extract of plant biomass can be used and be mixed with a solution of the metal salt. The synthesis of nanoparticles by plants gets completed within a short time span [73]. Biomolecules such as amino acids, terpenoids, flavones, proteins, ketones, tannins, alkaloids, saponins, phenolics, and polysaccharides are the major compounds responsible for the reduction of metals [74]. Extracts such as eugenol (natural reducing agent) and carbazoles were found to be responsible for nanoparticle synthesis from *Syzygium aromaticum* bud extract and *Murraya koenigii* leaf extract [75,76]. Copper oxide nanoparticles by *Psidium guajava* [77], zero valent iron nanoparticles by *Rosa damascene, Thymus vulgaris,* and *Urtica dioica* [78] are a few examples of plant-based nanoparticles.

4.4.4. Synthesis of nanoparticles by fungi and yeast

Fungal cells can be used for biosynthesis of nanoparticles by following two mechanisms – intracellular or extracellular synthesis routes. The nanoparticles are produced and localized in the cytoplasm, cell membrane, or cell wall, in case of intracellular route. Metal ions interact with the cell surface moieties that are oppositely charged where they get reduced simultaneously and they may diffuse to cell membrane or cytoplasm or remain bound to cell surface [79]. Fungi-based synthesis of nanoparticles produces excellently defined dimensions of nanoparticles along with monodispersity. Proteins and reducing agents that are secreted by fungi helps in stabilizing nanoparticles synthesized extracellularly [80]. Properties that fungi must possess for its industrial applications include high enzymatic and metabolite production, easy handling in large scale, good growth rate, and low cost [81]. The fungal mycelium exposed to metal ion prompts the production of enzymes and metabolites for the survival and during this process, metal ions get reduced to non-toxic forms of solid nanoparticles through catalytic effect. Fungi are considered a better source for nanoparticle synthesis than other biological systems because of advantages such as easy culture methods, diversity, cost effective, and take lesser time. Genetic engineering techniques can also be applied to get desired/improved particle properties. A few examples include synthesis of silver nanoparticles by *Cylindrocladium floridanum* [82] and *Penicillium citrinum* [83] and gold nanoparticles by *Penicillium aurantiogriseum, Penicillium citrinum,* and *Penicillium waksmanii* [84].

Synthesis of nanoparticles through yeast is known to be a cellular detoxification method wherein the presence of metal ions causes stress that leads to a series of chemical reactions. These reactions are induced to synthesize stress eliminating compounds such as glutathione and phytochelatin synthase that have nucleophilic and redox properties. The stress eliminating compounds bind to metal ions and reduce to lower valances and form nanoparticles. Quinones and oxidoreductases are involved in other mechanism for synthesis of nanoparticles by yeast. With the absorption of metal ions, the pH is increased and with the increase in pH, pH sensitive oxidoreductase gets activated and reduces the metal ions as well as provides stability by capping [85]. Only a few species of yeast have been exploited and reported as being capable of synthesizing nanoparticles. Silver-tolerant strain MKY3 has been able to successfully synthesize silver nanoparticles [49]. Furthermore, two strains of *Saccharomyces cerevisiae* have been used for gold nanoparticle synthesis [86]. A marine yeast, *Rhodosporidium diobovatum,* was used for intracellularly synthesizing lead sulfide nanoparticles [87]. Synthesis of selenium nanoparticles and titanium oxide nanoparticles by *Saccharomyces cerevisiae* [88,89] and gold nanoparticles by *Yarrowia lipolytica* NCIM 3589 [90] has also been successfully done.

4.5. Application of Nanotechnology in the Bioremediation of Heavy Metals and Metalloids

Due to the fact that nanotechnology enhances the process of bioremediation to a great extent, its application in the bioremediation of heavy metals has widely been exploited. Various approaches that are applied for the purpose of monitoring and treating the contaminants include control of the pollutants, sensing, and remediation of the pollutants by nanoparticles. For the purpose of remediation of heavy metals from wastewater, myco-synthesized iron oxide nanoparticles were formulated by Chatterjee *et al*. *Aspergillus niger* BSC-1, a mangrove fungus, was used for the extracellular synthesis of nanoparticles that led to successful synthesis of biogenic (fungus) nanoparticles in the form of nanoflakes (20–40 nm) that could remove chromium through adsorption with excellent efficiency at specific pH and temperature [91]. Keskin *et al*. formulated efficient *Lysinibacillus* sp. encapsulated nanofibers using cyclodextrin for the remediation of hexavalent chromium, nickel, and dye. These nanofibers had a dual role of: (i) carrier matrix and (ii) feeding source for the encapsulated bacterium [92]. Magnetic iron nanoparticles were synthesized in presence of a reducing biomolecule in a living *D. radiodurans* R1 strain and it showed exceptional arsenic removal capacity [93]. Subramaniyam *et al*. successfully synthesized iron nanoparticles from *Chlorococcum* sp. MM11 with a capacity to remediate and reduce 92% of hexavalent chromium to trivalent chromium [68]. Plant-based biogenic nanoparticles were formulated using *Aloe vera* leaves by Mukherjee *et al*. This eco-friendly method was proved to be highly efficient for the adsorption as well as the remediation of arsenic from contaminated water [94]. Another study conducted by Al-Qahtani who showed the effective removal of cadmium (Cd^{2+}) by the zero valent silver nanoparticles synthesized by *Ficus benjamina* leaf extract. Synthesis of silver nanoparticles was marked by the change of color to brown and it was observed that the initial metal ion concentration had an influence on the contaminant removal [95]. Biogenic iron oxide ferromagnetic nanoparticles functionalized using 3-mercaptopropionic acid were synthesized and further used as adsorbent for the removal of nickel from aqueous solution [96]. Another study conducted by Wang *et al.* resulted in successful synthesis of selenium nanoparticles using bacterium *Citrobacter freundii* Y9 and led to effective mercury removal from the groundwater as a result of reaction between selenium (Se) and mercury (Hg), leading to the formation of Hg-Se [97]. A very effective material for heavy metal remediation was designed by Choudhury *et al*. In this study, for the preparation of nanocomposite, *Saccharomyces cerevisiae* was immobilized on Titania nanopowder. This formulation was found to be exceptionally effective in Cr(VI) removal (99.92%) from contaminated water [98]. Various other examples of biogenic nanoparticles utilized in the remediation of heavy metals and metalloids are mentioned in Table 2.

4.6. Methodologies of Nanobioremediation

Adsorption and reduction are the two major mechanisms through which the biogenic nanoparticles interact with and remediate the heavy metals and metalloids. The mechanism of adsorption can be categorized into physical and chemical adsorption wherein the former completely relies on the presence of permeable structure while the latter requires the presence of functional groups on the surface of the adsorbent for the purpose of remediating heavy metals through electrostatic attraction or chemical binding forces. Comparatively, the chemical method of adsorption is considered to be a better method for the purpose of remediation [110]. In simple words, the reduction of heavy metals is done through two mechanisms: (1) Direct reduction of heavy metals by the nanoparticles or (2) first, adsorption of heavy metals onto the nanoparticle surface occurs, and then, they are further reduced to lower valances. On reduction to low toxic levels, these nanoparticles can easily be biodegraded with the increase in the rate of biodegradation [111].

5. FUTURE PERSPECTIVE AND CHALLENGES

A greener approach toward the removal of heavy metals has been established due the integration of biological systems and nanotechnology. Nanobioremediation offers sustainability because of the environmental advantages as well as has a huge contribution in providing possibilities to face environmental challenges. Nanoparticle technology is not only limited to heavy metal remediation but it also has a huge potential in the removal of microplastics as they are highly toxic to flora and fauna in the marine ecosystem [112,113]. The global nanotechnology market is expected to reach US$125 billion and beyond by 2024. Incorporation of nanotechnologies along with biological methods for the treatment of various ecosystems can provide new opportunities and can strengthen world trade [12]. However, the major issue lies within the commercialization of these aspects and as a matter of fact, as low as 1% of these nanotechnological aspects have been commercialized. Continuous support from the researchers and funding from the government for cost effective and sustainable production is a necessity for nanobioremediation to become a game changer at a commercial level [114]. Another significant issue is with the long-term effects of biogenic nanoparticles on animals and human beings and their accumulation in the environment. Nevertheless, it cannot be

Table 2: Examples of nano-bioremediation of heavy metals and metalloids.

Nanoparticle	Biological agent	Class of bioagent	Contaminant	References
Iron	*Chlorococcum sp.* MM11	Algae	Hexavalent chromium	[68]
Nano zero valent iron-immobilized calcium alginate beads	*Bacillus subtilis, E. coli,* and *Acinetobacter junii*	Bacteria	Hexavalent chromium	[99]
Zinc oxide	*E. coli*	Bacteria	Lead and cadmium	[100]
Titanium oxide	*Syzygium cumini*	Plant	Lead	[101]
Iron oxide	*Fusarium oxysporum*	Fungus	Arsenic	[102]
Mercury-selenium	*Shewanella putrefaciens* 200	Fungus	Mercury	[103]
Nanoscale zero valent iron	*Azadirachta indica and Mentha longifolia*	Plant	Nickel and lead	[104]
Iron	*Deinococcus radiodurans* R1	Bacteria	Arsenic	[93]
Copper oxide	Extracts of mint leaves (*Mentha*) and orange peels	Plant	Lead, nickel, and cadmium	[105]
Iron oxide	*Enterococcus faecalis*	Bacteria	Hexavalent chromium	[106]
Silver	*Catharanthus roseus*	Plant	Chromium and cadmium	[107]
Filtrate-chitosan	*Fusarium solani* YMM20	Fungus	Nickel, cadmium, iron, and lead	[108]
Palladium	*Shewanella loihica* PV-4 and *Enterococcus faecalis*	Bacteria	Hexavalent chromium	[109]

denied that the toxic effects of chemically synthesized nanoparticles are far more extreme as compared to the biogenic ones [115,116].

6. CONCLUSION

Over the years, several remediation strategies have been developed to deal with the heavy metal contamination that source from anthropogenic as well as industrial activities. Nanobioremediation has proven itself to be a game changer as the remediation efficiency is high and the synthesized material is non-toxic in nature. Switching to a greener approach has led to commendable reduction in heavy metal contamination as well as in the toxic effects along with the reduction in overall cost and remediation time. Irrespective of the fact that the mechanism behind microbial synthesis of nanoparticles is still unclear, stable nanoparticles with excellent properties are developed by the aid of microorganisms and plants. Use of biomolecules as reducing agents saves the cost of expensive chemical reductants that are used in physiochemical methods. Biogenic nanoparticles have greater surface area that affects the adsorption capacity positively. Some biogenic nanoparticles have lipid bilayer that gives stability and better physiological solubility. Size and shape can also be manipulated by varying pH, substrate availability, and contact time of reaction. Use of biological approach for nanoparticle synthesis helps in providing an easier approach, ease in multiplication, size uniformity, as well as easy increase in biomass. Thus, the integration of nanotechnology with bioremediation has not only proven to be a successful method in terms of efficiency but is also a safer alternative to the conventional techniques.

7. AUTHORS' CONTRIBUTIONS

All authors made substantial contributions to conception and design, acquisition of data, or analysis and interpretation of data; took part in drafting the article or revising it critically for important intellectual content; agreed to submit to the current journal; gave final approval of the version to be published; and agreed to be accountable for all aspects of the work. All the authors are eligible to be an author as per the International Committee of Medical Journal Editors (ICMJE) requirements/guidelines.

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The authors report no financial or any other conflicts of interest in this work.

10. ETHICAL APPROVALS

This study does not involve experiments on animals or human subjects.

11. DATA AVAILABILITY

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

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REFERENCES

1. Rising Pollution in the Developing World. Outlook on the Global Agenda 2015; 2021. Available from: http://www.wef.ch/1yt62cz

[Last accessed on 2021 Dec 18].
2. Dhillon GS, Kaur S, Verma M, Brar SK. Biopolymer-based nanomaterials: Potential applications in bioremediation of contaminated wastewaters and soils. In: Farré M, Barceló D, editors. Comprehensive Analytical Chemistry. Ch. 3. Amsterdam, Netherlands: Elsevier; 2012. p. 91-129.
3. Bánfalvi G. Heavy metals, trace elements and their cellular effects. In: Banfalvi G, editor. Cellular Effects of Heavy Metals. Dordrecht: Springer Netherlands; 2011. p. 3-28.
4. Substance Priority List Resource Page. ATSDR. Available from: https://www.atsdr.cdc.gov/spl/resources/index.html [Last accessed on 2021 Dec 19].
5. Kahlon SK, Sharma G, Julka JM, Kumar A, Sharma S, Stadler FJ. Impact of heavy metals and nanoparticles on aquatic biota. Environ Chem Lett 2018;16:919-946.
6. Bhardwaj R, Gupta A, Garg JK. Evaluation of heavy metal contamination using environmetrics and indexing approach for River Yamuna, Delhi stretch, India. Water Sci 2017;31:52-66.
7. Kumar V, Sharma A, Kaur P, Singh Sidhu GP, Bali AS, Bhardwaj R, *et al.* Pollution assessment of heavy metals in soils of India and ecological risk assessment: A state-of-the-art. Chemosphere 2019;216:449-62.
8. Substance Priority List. ATSDR. Available from: https://www.atsdr.cdc.gov/spl/index.html#2019spl [Last accessed on 2021 Dec 19].
9. Rahman Z, Singh VP. Bioremediation of toxic heavy metals (THMs) contaminated sites: Concepts, applications and challenges. Environ Sci Pollut Res Int 2020;27:27563-81.
10. Nasrollahzadeh M, Sajadi SM, Sajjadi M, Issaabadi Z. An introduction to nanotechnology. In: Interface Science and Technology. Amsterdam, Netherlands: Elsevier; 2019. p. 1-27.
11. Singh J, Vishwakarma K, Ramawat N, Rai P, Singh VK, Mishra RK, *et al.* Nanomaterials and microbes' interactions: A contemporary overview. 3 Biotech 2019;9:68.
12. Vázquez-Núñez E, Molina-Guerrero CE, Peña-Castro JM, Fernández-Luqueño F, de la Rosa-Álvarez MG. Use of nanotechnology for the bioremediation of contaminants: A review. Processes 2020;8:826.
13. Soltani A, Pouypouy H. Standardization and regulations of nanotechnology and recent government policies across the world on Nanomaterials. In: Advances in Phytonanotechnology from Synthesis to Application. United States: Academic Press; 2019. p. 420-46.
14. Amenta V, Aschberger K, Arena M, Bouwmeester H, Botelho Moniz F, Brandhoff P, *et al.* Regulatory aspects of nanotechnology in the agri/feed/food sector in EU and non-EU countries. Regul Toxicol Pharmacol 2015;73:463-76.
15. Masindi V, Muedi KL. Environmental contamination by heavy metals. In: Heavy Metals. India: IntechOpen; 2018.
16. Musilova J, Arvay J, Vollmannova A, Toth T, Tomas J. Environmental contamination by heavy metals in region with previous mining activity. Bull Environ Contam Toxicol 2016;97:569-75.
17. Wang S, Xing D, Jia Y, Li B, Wang K. The distribution of total mercury and methyl mercury in a shallow hypereutrophic lake (Lake Taihu) in two seasons. Appl Geochem 2012;27:343-51.
18. Yuan Z, Li Q, Ma X, Han M. Assessment of heavy metals contamination and water quality characterization in the Nanming River, Guizhou Province. Environ Geochem Health 2021;43:1273-86.
19. Tamás MJ, Sharma SK, Ibstedt S, Jacobson T, Christen P. Heavy metals and metalloids as a cause for protein misfolding and aggregation. Biomolecules 2014;4:252-67.
20. Nkwunonwo UC, Odika PO, Onyia NI. A review of the health implications of heavy metals in food chain in Nigeria. ScientificWorldJournal 2020;2020:6594109.
21. Ali MM, Hossain D, Al-Imran, Khan MS, Begum M, Osman MH. Environmental pollution with heavy metals: A public health concern. In: Heavy Metals-their Environmental Impacts and Mitigation. India: IntechOpen; 2021.
22. De Souza MJ, Nair S, Loka Bharathi PA, Chandramohan D. Metal and antibiotic-resistance in psychrotrophic bacteria from Antarctic Marine waters. Ecotoxicology 2006;15:379-84.
23. Rahman Z, Singh VP. The relative impact of toxic heavy metals (THMs) (arsenic (As), cadmium (Cd), chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: An overview. Environ Monit Assess 2019;191:419.
24. Kumar KS, Dahms HU, Lee JS, Kim HC, Lee WC, Shin KH. Algal photosynthetic responses to toxic metals and herbicides assessed by chlorophyll a fluorescence. Ecotoxicol Environ Saf 2014;104:51-71.
25. Bajpai R, Upreti DK. Accumulation and toxic effect of arsenic and other heavy metals in a contaminated area of West Bengal, India, in the lichen *Pyxine cocoes* (Sw.) Nyl. Ecotoxicol Environ Saf 2012;83:63-70.
26. Aksu A. Sources of metal pollution in the urban atmosphere (A case study: Tuzla, Istabul). J Environ Health Sci Eng 2015;13:79.
27. Kapahi M, Sachdeva S. Bioremediation options for heavy metal pollution. J Health Pollut 2019;9:191203.
28. Abatenh E, Gizaw B, Tsegaye Z, Wassie M. The role of microorganisms in bioremediation-a review. Open J Environ Biol 2017;1:38-46.
29. Koul B, Taak P. *Ex situ* soil remediation strategies. In: Koul B, Taak P, editors. Biotechnological Strategies for Effective Remediation of Polluted Soils. Singapore: Springer; 2018. p. 39-57.
30. Singh R, Behera M, Kumar S. Nano-bioremediation: An innovative remediation technology for treatment and management of contaminated sites. In: Bharagava RN, Saxena G, editors. Bioremediation of Industrial Waste for Environmental Safety, Biological Agents and Methods for Industrial Waste Management. Vol. 2. Singapore: Springer; 2020. p. 165-82.
31. Phenrat T, Skácelová P, Petala E, Velosa A, Filip J. Nanoscale zero-valent iron particles for water treatment: From basic principles to field-scale applications. In: Filip J, Cajthaml T, Najmanová P, Černík M, Zbořil R, editors. Advanced Nano-Bio Technologies for Water and Soil Treatment. Cham: Springer International Publishing; 2020. p. 19-52.
32. Ashok KR. Biostimulation Remediation Technologies for Groundwater Contaminants. United States: IGI Global; 2018. p. 381.
33. Pete A, Bharti B, Benton M. Nano-enhanced bioremediation for oil spills: A review. ACS EST Eng 2021;1:928-46.
34. Tratnyek P, Johnson R. Nanotechnologies for environmental cleanup. Nano Today 2006;1:44-8.
35. Tosco T, Papini M, Viggi CC, Sethi R. Nanoscale zerovalent iron particles for groundwater remediation: A review. J Clean Prod 2014;77:10-21.
36. Mughal B, Zaidi SZ, Zhang X, Hassan SU. Biogenic nanoparticles: Synthesis, characterisation and applications. Appl Sci 2021;11:2598.
37. Goutam SP, Saxena G. Biogenic nanoparticles for removal of heavy metals and organic pollutants from water and wastewater: Advances, challenges, and future prospects. In: Bioremediation for Environmental Sustainability. Amsterdam, Netherlands: Elsevier; 2021. p. 623-36.
38. Mishra A, Kumari M, Pandey S, Chaudhry V, Gupta KC, Nautiyal CS. Biocatalytic and antimicrobial activities of gold nanoparticles synthesized by *Trichoderma* sp. Bioresour Technol 2014;166:235-42.
39. Koul DB, Taak P. Biotechnological Strategies for Effective Remediation of Polluted Soils. Singapore: Springer; 2018.
40. Rao CN, Biswas K. Characterization of nanomaterials by physical methods. Annu Rev Anal Chem (Palo Alto Calif) 2009;2:435-62.
41. Riddin T, Gericke M, Whiteley CG. Biological synthesis of platinum nanoparticles: Effect of initial metal concentration. Enzyme Microb Technol 2010;46:501-5.
42. Sudhakar MS, Aggarwal A, Sah MK. Engineering biomaterials for the bioremediation: Advances in nanotechnological approaches for heavy metals removal from natural resources. In: Shah MP, Rodriguez-Couto S, Şengör SS, editors. Emerging Technologies in

Environmental Bioremediation. Ch. 14. Amsterdam, Netherlands: Elsevier; 2020. p. 323-39.
43. Jeevanandam J, Barhoum A, Chan YS, Dufresne A, Danquah MK. Review on nanoparticles and nanostructured materials: History, sources, toxicity and regulations. Beilstein J Nanotechnol 2018;9:1050-74.
44. Tripathi S, Sanjeevi R, Anuradha J, Chauhan DS, Rathoure AK. Nano-bioremediation: Nanotechnology and bioremediation. In: Biostimulation Remediation Technologies for Groundwater Contaminants. United States: IGI Global; 2018. p. 202-19.
45. Shah M, Fawcett D, Sharma S, Tripathy SK, Poinern GE. Green synthesis of metallic nanoparticles via biological entities. Materials (Basel) 2015;8:7278-308.
46. Sherry Davis A, Prakash P, Thamaraiselvi K. Nanobioremediation technologies for sustainable environment. In: Prashanthi M, Sundaram R, Jeyaseelan A, Kaliannan T, editors. Bioremediation and Sustainable Technologies for Cleaner Environment. Cham: Springer International Publishing; 2017. p. 13-33.
47. Mout R, Moyano DF, Rana S, Rotello VM. Surface functionalization of nanoparticles for nanomedicine. Chem Soc Rev 2012;41:2539-44.
48. Kumari S, Tyagi M, Jagadevan S. Mechanistic removal of environmental contaminants using biogenic nano-materials. Int J Environ Sci Technol 2019;16:7591-606.
49. Ingale A, Chaudhari A. Biogenic synthesis of nanoparticles and potential applications: An eco-friendly approach. J Nanomed Nanotechnol 2013;4:165.
50. Sharma D, Kanchi S, Bisetty K. Biogenic synthesis of nanoparticles: A review. Arab J Chem 2019;12:3576-600.
51. Tsekhmistrenko SI, Bityutskyy VS, Tsekhmistrenko OS, Horalskyi LP, Tymoshok NO, Spivak MY. Bacterial synthesis of nanoparticles: A green approach. Biosyst Divers 2020;28:9-17.
52. Baker S, Harini BP, Rakshith D, Satish S. Marine microbes: Invisible nanofactories. J Pharm Res 2013;6:383-8.
53. Ghosh S, Ahmad R, Banerjee K, AlAjmi MF, Rahman S. Mechanistic aspects of microbe-mediated nanoparticle synthesis. Front Microbiol 2021;12:638068.
54. Peralta-Videa JR, Huang Y, Parsons JG, Zhao L, Lopez-Moreno L, Hernandez-Viezcas JA, et al. Plant-based green synthesis of metallic nanoparticles: Scientific curiosity or a realistic alternative to chemical synthesis? Nanotechnol Environ Eng 2016;1:4.
55. Baker S, Rakshith D, Kumar DK, Santosh P, Kavitha H, Yashavantha Rao HC, et al. Plants: Emerging as nanofactories towards facile route in synthesis of nanoparticles. Bioimpacts 2013;3:111-7.
56. Park Y, Hong YN, Weyers A, Kim YS, Linhardt RJ. Polysaccharides and phytochemicals: A natural reservoir for the green synthesis of gold and silver nanoparticles. IET Nanobiotechnol 2011;5:69-78.
57. Goutam SP, Saxena G, Singh V, Yadav AK, Bharagava RN, Thapa KB. Green synthesis of TiO2 nanoparticles using leaf extract of *Jatropha curcas* L. for photocatalytic degradation of tannery wastewater. Chem Eng J 2018;336:386-96.
58. Kumar A, Dixit CK. Methods for characterization of nanoparticles. In: Nimesh S, Chandra R, Gupta N, editors. Advances in Nanomedicine for the Delivery of Therapeutic Nucleic Acids. United Kingdom: Woodhead Publishing; 2017. p. 43-58.
59. Iravani S. Bacteria in nanoparticle synthesis: Current status and future prospects. Int Sch Res Notices 2014;2014:359316.
60. Salem SS, Fouda A. Green synthesis of metallic nanoparticles and their prospective biotechnological applications: An overview. Biol Trace Elem Res 2021;199:344-70.
61. Furgal KM, Meyer RL, Bester K. Removing selected steroid hormones, biocides and pharmaceuticals from water by means of biogenic manganese oxide nanoparticles *in situ* at ppb levels. Chemosphere 2015;136:321-6.
62. Sunkar S, Nachiyar CV. Biogenesis of antibacterial silver nanoparticles using the endophytic bacterium Bacillus cereus isolated from *Garcinia xanthochymus*. Asian Pac J Trop Biomed 2012;2:953-9.
63. He S, Guo Z, Zhang Y, Zhang S, Wang J, Gu N. Biosynthesis of gold nanoparticles using the bacteria *Rhodopseudomonas capsulata*. Mater Lett 2007;61:3984-7.
64. Wang X, Zhang D, Pan X, Lee DJ, Al-Misned FA, Mortuza MG, *et al.* Aerobic and anaerobic biosynthesis of nano-selenium for remediation of mercury contaminated soil. Chemosphere 2017;170:266-73.
65. Khanna P, Kaur A, Goyal D. Algae-based metallic nanoparticles: Synthesis, characterization and applications. J Microbiol Methods 2019;163:105656.
66. Uzair B, Liaqat A, Iqbal H, Menaa B, Razzaq A, Thiripuranathar G, *et al.* Green and cost-effective synthesis of metallic nanoparticles by algae: Safe methods for translational medicine. Bioengineering (Basel) 2020;7:E129.
67. Fatima R, Priya M, Indurthi L, Radhakrishnan V, Sudhakaran R. Biosynthesis of silver nanoparticles using red algae *Portieria hornemannii* and its antibacterial activity against fish pathogens. Microb Pathog 2020;138:103780.
68. Subramaniyam V, Subashchandrabose SR, Thavamani P, Megharaj M, Chen Z, Naidu R. *Chlorococcum* sp. MM11-a novel phyco-nanofactory for the synthesis of iron nanoparticles. J Appl Phycol 2014;27:2.
69. Dahoumane SA, Yéprémian C, Djédiat C, Couté A, Fiévet F, Coradin T, et al. Improvement of kinetics, yield, and colloidal stability of biogenic gold nanoparticles using living cells of *Euglena gracilis* microalga. J Nanoparticle Res 2016;18:79.
70. Sundaramanickam A, Kathiraven T, Shanmugam N, Thangavel B. Green synthesis of silver nanoparticles using marine algae *Caulerpa racemosa* and their antibacterial activity against some human pathogens. Appl Nanosci 2014;5:499-504.
71. Kumar V, Shanmugam R. Plant-based synthesis of nanoparticles and their impact. In: Nanomaterials in Plants, Algae, and Microorganisms. Amsterdam, Netherlands: Elsevier; 2018. p. 33-57.
72. Adil SF, Assal ME, Khan M, Al-Warthan A, Siddiqui MR, Liz-Marzán LM. Biogenic synthesis of metallic nanoparticles and prospects toward green chemistry. Dalton Trans 2015;44:9709-17.
73. Vijayaraghavan K, Ashokkumar T. Plant-mediated biosynthesis of metallic nanoparticles: A review of literature, factors affecting synthesis, characterization techniques and applications. J Environ Chem Eng 2017;5:4866-83.
74. Nath D, Banerjee P. Green nanotechnology-a new hope for medical biology. Environ Toxicol Pharmacol 2013;36:997-1014.
75. Christensen L, Vivekanandhan S, Misra M, Mohanty A. Biosynthesis of silver nanoparticles using *Murraya koenigii* (curry leaf): An investigation on the effect of broth concentration in reduction mechanism and particle size. Adv Mat Lett 2011;2:429-34.
76. Singh A, Talat M, Singh D, Srivastava ON. Biosynthesis of gold and silver nanoparticles by natural precursor clove and their functionalization with amine group. J Nanoparticle Res 2010;12:1667-75.
77. Singh J, Kumar V, Kim KH, Rawat M. Biogenic synthesis of copper oxide nanoparticles using plant extract and its prodigious potential for photocatalytic degradation of dyes. Environ Res 2019;177:108569.
78. Fazlzadeh M, Rahmani K, Zarei A, Abdoallahzadeh H, Nasiri F, Khosravi R. A novel green synthesis of zero valent iron nanoparticles (NZVI) using three plant extracts and their efficient application for removal of Cr(VI) from aqueous solutions. Adv Powder Technol 2017;28:122-30.
79. Priyadarshini E, Priyadarshini SS, Cousins BG, Pradhan N. Metal-Fungus interaction: Review on cellular processes underlying heavy metal detoxification and synthesis of metal nanoparticles. Chemosphere 2021;274:129976.
80. Mohanpuria P, Rana NK, Yadav SK. Biosynthesis of nanoparticles: Technological concepts and future applications. J Nanoparticle Res

2008;10:507-17.

81. Vahabi K, Mansoori GA, Karimi S. Biosynthesis of silver nanoparticles by fungus *Trichoderma reesei* (A route for large-scale production of AgNPs). Insciences J 2011;1:65-79.
82. Narayanan KB, Park HH, Sakthivel N. Extracellular synthesis of mycogenic silver nanoparticles by *Cylindrocladium floridanum* and its homogeneous catalytic degradation of 4-nitrophenol. Spectrochim Acta A Mol Biomol Spectrosc 2013;116:485-90.
83. Honary S, Barabadi H, Gharaei-Fathabad E, Naghibi F. Green synthesis of silver nanoparticles induced by the fungus *Penicillium citrinum*. Trop J Pharm Res 2013;12:7-11.
84. Honary S, Gharaei-Fathabad E, Barabadi H, Naghibi F. Fungus-mediated synthesis of gold nanoparticles: A novel biological approach to nanoparticle synthesis. J Nanosci Nanotechnol 2013;13:1427-30.
85. Rana A, Yadav K, Jagadevan S. A comprehensive review on green synthesis of nature-inspired metal nanoparticles: Mechanism, application and toxicity. J Clean Prod 2020;272:122880.
86. Sen K, Sinha P, Lahiri S. Time dependent formation of gold nanoparticles in yeast cells: A comparative study. Biochem Eng J 2011;1:1-6.
87. Seshadri S, Saranya K, Kowshik M. Green synthesis of lead sulfide nanoparticles by the lead resistant marine yeast, *Rhodosporidium diobovatum*. Biotechnol Prog 2011;27:1464-9.
88. Faramarzi S, Anzabi Y, Jafarizadeh-Malmiri H. Nanobiotechnology approach in intracellular selenium nanoparticle synthesis using *Saccharomyces cerevisiae*-fabrication and characterization. Arch Microbiol 2020;202:1203-9.
89. Peiris M, Gunasekara T, Jayaweera PM, Fernando S. TiO_2 nanoparticles from baker's yeast: A potent antimicrobial. J Microbiol Biotechnol 2018;28:1664-70.
90. Agnihotri M, Joshi S, Kumar AR, Zinjarde S, Kulkarni S. Biosynthesis of gold nanoparticles by the tropical marine yeast *Yarrowia lipolytica* NCIM 3589. Mater Lett 2009;15:1231-4.
91. Chatterjee S, Mahanty S, Das P, Chaudhuri P, Das S. Biofabrication of iron oxide nanoparticles using manglicolous fungus *Aspergillus niger* BSC-1 and removal of Cr(VI) from aqueous solution. Chem Eng J 2019;2019:123790.
92. San Keskin NO, Celebioglu A, Sarioglu OF, Uyar T, Tekinay T. Encapsulation of living bacteria in electrospun cyclodextrin ultrathin fibers for bioremediation of heavy metals and reactive dye from wastewater. Colloids Surf B Biointerfaces 2018;161:169-76.
93. Kim HK, Jeong SW, Yang JE, Choi YJ. Highly efficient and stable removal of arsenic by live cell fabricated magnetic nanoparticles. Int J Mol Sci 2019;20:E3566.
94. Mukherjee D, Ghosh S, Majumdar S, Annapurna K. Green synthesis of α-Fe2O3 nanoparticles for arsenic(V) remediation with a novel aspect for sludge management. J Environ Chem Eng 2016;4:639-50.
95. Al-Qahtani KM. Cadmium removal from aqueous solution by green synthesis zero valent silver nanoparticles with *Benjamina* leaves extract. Egypt J Aquat Res 2017;43:269-74.
96. Venkateswarlu S, Kumar SH, Jyothi NV. Rapid removal of Ni(II) from aqueous solution using 3-mercaptopropionic acid functionalized bio magnetite nanoparticles. Water Resour Ind 2015;12:1-7.
97. Wang X, Zhang D, Qian H, Liang Y, Pan X, Gadd GM. Interactions between biogenic selenium nanoparticles and goethite colloids and consequence for remediation of elemental mercury contaminated groundwater. Sci Total Environ 2018;613-614:672-8.
98. Choudhury PR, Bhattacharya P, Ghosh S, Majumdar S, Saha S, Sahoo GC. Removal of Cr (VI) by synthesized Titania embedded dead yeast nanocomposite: Optimization and modeling by response surface methodology. J Environ Chem Eng 2017;5:214-21.
99. Ravikumar KV, Kumar D, Kumar G, Mrudula P, Natarajan C, Mukherjee A. Enhanced Cr(VI) removal by nanozerovalent iron-immobilized alginate beads in the presence of a biofilm in a continuous-flow reactor. Ind Eng Chem Res 2016;55:5973-82.
100. Somu P, Paul S. Casein based biogenic-synthesized zinc oxide nanoparticles simultaneously decontaminate heavy metals, dyes, and pathogenic microbes: A rational strategy for wastewater treatment. J Chem Technol Biotechnol 2018;93:2962-76.
101. Sethy NK, Arif Z, Mishra P, Kumar P. Green synthesis of TiO2 nanoparticles from *Syzygium cumini* extract for photo-catalytic removal of lead (Pb) in explosive industrial wastewater. Green Proc Synthe 2020;9:18.
102. Balakrishnan GS, Rajendran K, Kalirajan J. Microbial synthesis of magnetite nanoparticles for arsenic removal. J Appl Biol Biotechnol 2020;8:7-5.
103. Jiang S, Ho CT, Lee JH, Duong HV, Han S, Hur HG. Mercury capture into biogenic amorphous selenium nanospheres produced by mercury resistant *Shewanella putrefaciens* 200. Chemosphere 2012;87:621-4.
104. Francy N, Shanthakumar S, Chiampo F, Sekhar YR. Remediation of lead and nickel contaminated soil using nanoscale zero-valent iron (nZVI) particles synthesized using green leaves: First results. Processes 2020;8:1453.
105. Mahmoud AE, Al-Qahtani KM, Alflaij SO, Al-Qahtani SF, Alsamhan FA. Green copper oxide nanoparticles for lead, nickel, and cadmium removal from contaminated water. Sci Rep 2021;11:12547.
106. Samuel MS, Datta S, Chandrasekar N, Balaji R, Selvarajan E, Vuppala S. Biogenic synthesis of iron oxide nanoparticles using *Enterococcus faecalis*: Adsorption of hexavalent chromium from aqueous solution and *in vitro* cytotoxicity analysis. Nanomaterials (Basel) 2021;11:3290.
107. Verma A, Bharadvaja N. Plant-mediated synthesis and characterization of silver and copper oxide nanoparticles: Antibacterial and heavy metal removal activity. J Clust Sci 2021:1-16. Doi: 10.1007/s10876-021-02091-8
108. Mohammed YM, Khedr YI. Applications of *Fusarium solani* YMM20 in bioremediation of heavy metals via enhancing extracellular green synthesis of nanoparticles. Water Environ Res 2021;93:1600-7.
109. Misra M, Chattopadhyay S, Sachan A, Sachan SG. Microbially synthesized nanoparticles and their applications in environmental clean-up. Environ Technol Rev 2022;11:18-32.
110. Latif A, Sheng D, Sun K, Si Y, Azeem M, Abbas A, *et al.* Remediation of heavy metals polluted environment using Fe-based nanoparticles: Mechanisms, influencing factors, and environmental implications. Environ Pollut 2020;264:114728.
111. Wu Y, Pang H, Liu Y, Wang X, Yu S, Fu D, *et al.* Environmental remediation of heavy metal ions by novel-nanomaterials: A review. Environ Pollut 2019;246:608-20.
112. Tiwari N, Santhiya D, Sharma JG. Microbial remediation of micro-nano plastics: Current knowledge and future trends. Environ Pollut 2020;265:115044.
113. Bansal M, Santhiya D, Sharma JG. Behavioural mechanisms of microplastic pollutants in marine ecosystem: Challenges and remediation measurements. Water Air Soil Pollut 2021;232:372.
114. Mandeep, Shukla P. Microbial nanotechnology for bioremediation of industrial wastewater. Front Microbiol 2020;11:590631.
115. Jadoun S, Arif R, Jangid NK, Meena RK. Green synthesis of nanoparticles using plant extracts: A review. Environ Chem Lett 2021;19:355-74.
116. Banu AN, Kudesia N, Raut AM, Pakrudheen I, Wahengbam J. Toxicity, bioaccumulation, and transformation of silver nanoparticles in aqua biota: A review. Environ Chem Lett 2021;19:4275-96.

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