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Review Article

Raw Materials Synthesis from Heavy Metal Industry Effluents with Bioremediation and Phytomining: A Biomimetic Resource Management Approach

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Heavy metal wastewater poses a threat to human life and causes significant environmental problems. Bioremediation provides a sustainable waste management technique that uses organisms to remove heavy metals from contaminated water through a variety of different processes. Biosorption involves the use of biomass, such as plant extracts and microorganisms (bacteria, fungi, algae, yeast), and represents a low-cost and environmentally friendly method of bioremediation and resource management. Biosorption-based biosynthesis is proposed as a means of removing heavy metals from wastewaters and soils as it aids the development of heavy metal nanoparticles that may have an application within the technology industry. Phytomining provides a further green method of managing the metal content of wastewater. These approaches represent a viable means of removing toxic chemicals from the effluent produced during the process of manufacturing, and the bioremediation process, furthermore, has the potential to save metal resources from depletion. Biomimetic resource management comprises bioremediation, biosorption, biosynthesis, phytomining, and further methods that provide innovative ways of interpreting waste and pollutants as raw materials for research and industry, inspired by materials, structures, and processes in living nature.

1. Introduction

Heavy metals are hazardous and dangerous, especially when introduced into the environment via pollution. However, they do have a valuable role to play; for example, heavy metal nanoparticles are used in various nanoscience and nanotechnology applications. Biomimetic resource management refers to a way of dealing with resources that is inspired by living nature regarding materials, structures, and processes. Such an approach offers innovative new ways to deal with heavy metal-loaded waste effluents and provides raw materials for industry. Plants and microorganisms are used to redefine "waste" to "revenue" for new industries [1]. Heavy metal-loaded effluents from industry could be the base material for metallic nanoparticles used in nanoscience and nanotechnology. Plants (such as the sunflower plant) and microorganisms (such as bacteria, fungi, algae, and yeast) can be used to accumulate these heavy metals and to safely remove the pollutants from the water and the soil. The first goal regarding heavy metal effluents should be their prevention. However, in cases where they cannot (yet) be completely prevented, biomimetics can come into the game: we could learn from living nature how to deal with such effluents not by treating them as waste but by treating them as resource (waste-to-wealth concept). Metallic nanoparticles are currently used in important nanotechnology research areas and are also heavily used in applications. They are important (and acceptable) in our current early phases of nanotechnology research and development, where we need to understand the basics. Future resource management might increasingly realize the paramount biomimetic principle of "shape rather than material" to achieve functionalities that are currently fulfilled by unsustainable metal- and plastic-based resources by benign materials that would allow for sustainable engineering. Apart from biomineralized structures and specific biomolecules, where the chemistry (as opposed to the physics) of the metal is necessary for the function (such as in hemoglobin or chlorophyll), living nature rarely uses metals. In most cases, elaborated structures from hierarchically composed metal free materials yield the functionality that we, with our current conventional engineering, mainly achieve with the use of many different materials, including metals.

The main purpose of this paper is to explore the potential of using heavy metals that are extracted from the environment with the help of organisms as a resource for metallic nanoparticles. This has a number of potential benefits. The particles are removed from the environment and research, development, and industry are provided with a novel source of nanoparticles and their constituents. Since some nanoparticles can be derived directly from natural sources, such as plants and microorganisms, they can be accessed at a lower cost and in a more biofriendly manner than those fabricated via conventional production mechanisms. Another advantage of extracting heavy metals from the environment is that the natural nanoparticles accessed via this method exhibit reproducible shapes and sizes, whereas such shape and size uniformity remains a challenge in man-made nanoparticles. A variety of physical and chemical procedures are used for the synthesis of metallic nanoparticles, with "bottom-up" and "top-down" approaches as two broad categories.

This review predominantly concentrates on the management and recovery of heavy metals from industrial wastewater through the application of a biosorption-desorption process. The production of metal nanoparticles from heavy metal industrial effluent is also discussed. A particular focus will be placed on the bioremediation process, since this method holds great promise as a potential technique of biosynthesizing metal nanoparticles from polluted heavy metal industrial effluent. It is envisaged that developments in this area provide a means of removing toxic effluent from wastewater and/or soil and also represent a viable and sustainable technique for obtaining nanoparticles for high technology applications in a manner that is environmentally friendly and cost effective.

2. The Bioremediation Process as an Approach for Designing Materials for Environmental Applications

In order to ensure that industrial practices are sustainable on a long-term basis, it is critical that we develop an awareness of the environment and the ecological effects of manufacturing techniques that produce toxic metals. Contaminated soil in the environment as a result of manufacturing practices is common throughout the world. Numerous countries face issues as a result of contaminated wastewater and have taken action to raise awareness via relevant policies and the development of technologies [2]. However, many of the physiochemical processes that are traditionally employed in the remediation of soils and polluted sites are expensive and do not permanently alleviate hazardous pollution [3]. Bioremediation represents one method of using biological systems, such as microorganisms or microbial-like bacteria, fungi, and other agents, to clean up and degrade organic and inorganic pollutants [4]. Bioremediation is a general concept that encompasses all the processes and actions required to biotransform an environment in which contaminants exist back into its original pristine condition. Various factors are involved in the bioremediation process and this process uses various agents, such as bacteria, yeast, fungi, algae, and higher plants, as major tools to treat oil spills and remove heavy metals from the environment [5]. A number of sophisticated technologies for the remediation of polluted sites are currently in use.

2.1. The Bioremediation Process: Current Situation. Effluents produced by the metal industry are often found as contaminants in water sources, rivers, seas, and soils. Fu and Wang [6] published a review on the use of bioremediation to remove heavy metal ions from wastewaters; remediation technologies used to treat heavy metal contaminated groundwater were summarized by Hashim et al. [7]. Heavy metals are defined as metals that have an atomic weight between 63.5 and 200.6 and a specific gravity greater than 5 [7]. They include Zinc, Copper, Nickel, Mercury, Cadmium, Lead, Chromium Arsenic, Silver, Platinum, and Gold [6]. Some heavy metals are toxic and poisonous, especially to humans, while noble metals are very valuable and can be used in high-tech nanotechnology applications or in the production of high-value goods.

The management of toxic heavy metals that are introduced into the environment via industrial wastewater is very important, as toxic wastewaters pose serious threats to the environment and to human health [8]. The technologies that are currently used in the commercial remediation of heavy metal effluent rely on immobilizing the heavy metal by leachability [9]. Those techniques include chemical fixation, chemical alteration/complexation, stabilisation, capping, soil washing, and ferric iron remediation stabilisation. Additional methods that are currently being used to remediate heavy metal contamination are chemical precipitation, ion exchange, adsorption, membrane filtration, electrochemical treatment technologies, floatation, coagulation, and flocculation [6]. Each method has its own advantages and limitations. The chemical precipitation, ion exchange, and membrane filtration methods are widely used for wastewater remediation with high efficiency. In the chemical precipitation method, the heavy metal ion is altered by changing it from a soluble to an insoluble substance so that it can later be removed via a process of flocculation and sedimentation. Through a combination of chemical precipitation and nanofiltration methods, it is possible to recover heavy metal ions for reuse.

The main limitations of these methods are that they are costly, involve complex processes, and are environmentally unfriendly. For example, the ion exchange method is expensive and the chemical handling process it employs could cause secondary pollution. Even though the use of natural resin, zeolites, is low-cost and environmentally friendly and offers the same performance as synthetic resin, its availability is limited and, at present, its use is limited to the experimental laboratory only.

The adsorption process has long been recognized as a low-cost alternative to the removal of contaminants from wastewater. This flexible, low-cost method works even in wastewater that contains a low concentration of metal effluents. However, the efficiency of this method varies according to the type of adsorbents, since certain sorbents have high selectivity towards heavy metals.

In commercial adsorption-based remediation processes, commercial activated Carbon (AC) is widely used as a high efficiency absorbent [6]. However, the price of AC is increasing. Furthermore, when used as absorbents, Carbon nanotubes, for example, pose a risk to humans when they are discharged into the water. To avoid various limitations, especially the risk to humans, there is a need to identify a means of improving this method so that it is more environmentally friendly and of zero risk to life forms. Furthermore, as a result of the rapid growth of industrialization, which has increased the volume of heavy metal pollution, there is a need to identify a low-cost method of removing contaminants from wastewater. Biology-based remediation processes are attractive because they have lower operation costs than physicochemical processes [10]. Thus, the use of biological materials for absorption holds great promise as they are highly cost effective and environmentally benign. As such, a large amount of research has been conducted into the use of biological materials for the absorption of heavy metals in wastewater with much of this research placing a particular emphasis on the types of biosorbents that are available.

Biosorbents from living cells, dead cells, or biomass are the key components in biosorption technology and, for the last 20 years, various researchers have focused on these materials [10]. As reported by Atkinson et al. [10], the earliest investigation into microbial biomass as a biosorbent was performed in the 1980s, potentially earlier. Current studies on bacterial biosorbents for the bioremediation of heavy metals were reviewed by Dhankhar and Guriyan [11] and Vijayaraghavan and Yun [12]. Studies on marine algae as biosorbents were comprehensively reviewed by He and Chen [13]. Bankar et al. [14] and Viraraghavan and Srinivasan [15], respectively, discussed recent reviews on yeasts and fungal-based biosorption. Studies on biomass from agricultural waste and byproducts for the removal of heavy metals have become a new interest in recent years [16–18].

2.1.1. Removing Heavy Metals. Heavy metals are present in soil, aqueous solution, or streams as the result of a variety of human waste activities, which include intensive agriculture, sludge dumping, metal-rich mine tailings, metal smelting, electroplating, energy conversion, and fuel production [19]. All heavy metals have a toxic effect if they are found in high concentrations in soil and therefore need to be removed or transformed. Microorganisms can be used as cation sorbents for the removal of heavy metal cations from industrial wastewater or for the recovery of metals from their solutions [20]. Dave and Chopda [21] described how a surface modification strategy could enhance the stability and efficiency of iron oxide nanomaterials in the removal of heavy metals for remediation in water. Metal oxide nanoparticles as antimicrobial additives have been the subject of extensive research [22]. Ahluwalia and Goyal [23] described the removal of heavy metals such as Lead, Zinc, Cadmium, Chromium, Copper, and Nickel from wastewater through the use of microbial and plant-derived biomass of *Aspergillus niger, Penicilium chrysogenum, Rhizophus nigricans, Ascophyllum nodosum, Sargassum natans, Chrorella fusca, Oscillatoria anguistissima, Basillus firmus*, and *Streptomyces* sp. The ability of algae to remove heavy metals from aqueous solution has been recognized for some decades. Li and coworkers [24] carried out an experiment using the yeasts *Zygosaccharomyces rouxii* and *Saccharomyces cerevisiae* in Cadmium removal in a complex food environment. Their results indicated that *Z. rouxii* had a powerful Cadmium removal ability at low Cadmium concentrations, which mainly depended on the intracellular Cadmium bioaccumulation. The percentage of intracellular Cadmium bioaccumulation of both *Z. rouxii* and *S. cerevisiae* decreased as the initial biomass and Cadmium concentrations increased. The metal content of algae can be used to predict the level of metal pollution in a water body [25]. The high accumulation capacity can even be used for the enrichment or recycling of valuable metals. Their relative comparison is generally made using an accumulation factor (AF). The metal accumulation factor (AF) is defined as the ratio of metal concentration in plant cells (μg/g) and the metal concentration in water (μg/mL) and it is also known as bioconcentration ratio, concentration ratio, or enrichment ratio. Toxic metals can be transferred to their surroundings or to the wider environment through numerous ways including industrial production processes, incineration emissions, and waste disposal. The majority of deposition of metals in the environment is within soil or sediment. Microorganisms can detoxify metals by valence transformation, extracellular chemical precipitation, or volatilization, through which they enzymatically reduce some metals through metabolic processes [26] (Table 1). New technologies to improve the remediation process are continually being developed and adopted and a system known as “pump-and-treat” has been established; however, this is time consuming and inefficient [27].

2.1.2. Phytoremediation. Phytoremediation technology can be applied as a solution to the major environmental and human hazards caused by contaminated soils and waters [31]. Phytoremediation involves the use of various green plant species to clean up, remove, or detoxify environmental contaminants or to render them harmless [31–33]. Phytoremediation is potentially the best practice for removing pollutants, is very promising as an environmental technology, and can be employed at a lower cost than conventional or alternative methods. Phytoremediation technologies are quite successful in their ability to clean up waste solutions. The phytoremediation approach exploits the ability of various plant species to remove heavy metals from the environment and then accumulate a large amount of toxic metals. The green plant species required to be effective in phytoremediation typically needs to grow rapidly, produce large quantities of biomass, have deep roots and easily harvested shoots, and have the potential to accumulate high concentrations of contaminants in these shoots. The advantages of this method

Table 1: Organisms that remove heavy metal from waste (selection).

Element	Waste from ...	Organisms	Mechanism
Copper [28]	Electronic waste	Leaf extract weed *Lantana camara*	
Copper [28]	Electronic waste	*Fusarium* and *Pseudomonas*	
Arsenic	Water	*Lactobacillus acidophilus*	Bind and remove
Chromium (IV) [29]	Aqueous solution	Guar gum	Nanozinc oxide biocomposite
Chromium (IV) [30]	Aqueous solution	Seaweed biomass *Acanthophora spicifera*	Biosorption
Cadmium (Cd)	Food environment	Yeast *Zygosaccharomyces rouxii* and *Saccharomyces cerevisiae*	Intracellular cross

compared to the existing remediation techniques are that they involve minimal site destruction and destabilization, have a low environmental impact, and are aesthetically favorable [19].

One important characteristic of phytoremediation is phytoextraction. Phytoextraction technology involves the reduction of metal concentration in the soil through the cultivation of plants that have a high capacity for metal accumulation in the shoots or that are capable of uptaking the metal from the contaminated soil via the plant root. Phytoextraction technology is a plant-based technology that cleans heavy metal from the soil through the process of hyperaccumulation [34]. This technology is used to achieve better environmental protection with a sustainable metal source and is based on the hyperaccumulation of metals into the whole plants [35]. Two categories of plants can be used for phytoextraction: small plants that have high foliar metal concentration but slow growth rates that do not provide a high annual biomass (such as *Thlaspi caerulescens*) and high biomass crops which have a large biomass production but take up lower metal concentrations (such as *Brassica juncea*). Gupta and coworkers [36] used *Phaseolus vulgaris* var. T55 for the phytoextraction of heavy metals from flash ash (by-product of combustion of coal). The capability of the plants to reduce the amount of heavy metals present in contaminated soils depends on plant biomass production and their metal bioaccumulation factor. The bioaccumulation factor is the ratio of metal concentration present in the shoot tissue of the roots to the one of the soil. It can be determined by the ability and capacity of the roots to take up metals and transfer them to the xylem through the mass flow in xylem by transpiration and their ability to accumulate, store, and detoxify metals while maintaining metabolism, growth, and biomass production [37].

2.2. Characterization of Metal Biosorption Mechanisms. The biological interaction between biological cells and metal ions has potential in the production of metal nanoparticles or metal compounds. These processes are very popular in the bioremediation of soil and water sources that have been contaminated by heavy metal effluent [7]. The detailed features of the metal nanoparticles were obtained and the performance of the process depends on the respective type of biological cells and metal ions [12]. The interaction processes that are involved include biosorption, accumulation, and bioreduction [7, 12].

The mechanism for binding metals to the walls of bacterial cells consists of three steps: (i) ion exchange reactions with peptidoglycan and teichoic acid, (ii) precipitation through nucleation reactions, and (iii) complexation with nitrogen and oxygen ligands [38, 39].

The bioaccumulation process is the use of metabolic activity of a living organism to remove heavy metal from a given environment [12, 40].

The biosorption process involves the extracellular passive binding of a metal to a nonliving biomass in an aqueous solution. Two types of approaches commonly used are biosorption without enzyme (a.k.a. protein capping) and biosorption with capping of enzyme. Biosorption has already been investigated for the decontamination of heavy metal pollution solutions [41]. Biosorption technology provides one potential biological approach to cleaning heavy metal industrial wastewater [10]. A number of review papers have discussed the use of biosorption technology in the bioremediation process.

The biosorption process always depends on a number of mechanisms such as complexation, ion exchange, coordination, adsorption, desorption, chelation, and microprecipitation [42, 43]. In general, desorption is one of the most common mechanisms that are employed in the biosorption process [44]. This process is the reverse of sorption (adsorption and absorption). The importance of desorption lies in its potential to actually reuse certain biomass as well as recover sorbents [16, 44]. Through the use of this biosorption-desorption process, low-cost heavy metal nanoparticles could be biologically synthesized during the bioremediation process. As far as the literature reviewed for the purposes of this paper, bioabsorption is typically regarded as a passive and metabolically independent process that involves passive biological materials such as biomass [44]. The use of biomass with industrial microbial or agricultural wastes for synthesizing metal nanoparticles contained within wastewater represents an effective, innovative, and sustainable method of waste management.

Bioreduction is very important in both biosorption and bioaccumulation processes. It enhances ion metal biotransformation activity by reducing microorganisms; for example, Chromium (VI) can be reduced to nontoxic Chromium (III) using *Shewanella alga, Ochrobactrum, Bacillus*, and others [45]. Various researchers have assessed the use of microorganisms to transform Chromium (IV) to Chromium (III) [46–49].

Beside living and dead biomass, cell-free extracts are also used as bioreduction agents to produce metal [50]. Cell-free extract is used to give an enzyme and protein molecules capping to the metal salts to reduce them to metal nanoparticles. The cell-free extract from dead biomass produces a higher number of nanoparticles than living cells, dead biomass, and cell-free living cells [51]. The metabolically independent production process yields better morphology of nanoparticles than the metabolism dependent production [52]. This makes it possible to control the size and shape of nanoparticles by adjusting the amount of metal salt and the nonmetabolic bioreduction agents [53] and by controlling the pH of the aqueous solution [54]. The rate of bioreduction varies according to temperature; the higher the temperature, the higher the rate of bioreduction [55].

Even though the biosorption process is limited, especially in its ability to alter the metal valence state, there are some arguments on the selection of biomass, as reviewed by Nguyen et al. [16]. Beside the availability and cost effectiveness of biomass, selection also depends on the binding capacity of the biomass and selectivity for heavy metals. This will allow the development of a full-scale biosorption process.

Several characterization methods can be used to confirm the presence of metallic nanoparticles. These include transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), field emission scanning electron microscopy (FESEM), energy dispersive X-ray fluorescence spectrometry (EDXRF), and vibrating sample magnetometry (VSM) [56]. The crystallinity of nanoparticles can be investigated by numerous methods such as by XRD, for example, of iron oxide nanoparticles (Fe_3O_4 NPs) [56] and Silver nanoparticles (AgNPs) [57].

Important features that lead to the production of optimum nanoparticles are their optical properties, surface plasmon resonance (SPR) [58], and effective scattering phenomena [50]. SPR can be characterized by UV-Vis spectroscopy, while surface enhanced Raman scattering can be used to characterize scattering features. A number of groups have presented the ideal characteristics for Gold nanoparticles, where the UV-Vis spectrometer indicates the peak around 450 to 560 nm [50, 51, 59].

The biosynthesis process promises a green, safe, cost effective, and sustainable method of producing nanoparticles. The demands for heavy metal industrial activity have led to continuous bioremediation processes, which may lead to the depletion of both microorganisms and dead biomass. In order to reduce costs, it is important that we identify a method of recycling both dead and living microorganisms through the use of immobilization and desorption techniques [12]. The implementation of these techniques has enhanced bioremediation technology through the generation of recycled metal nanoparticles for further application.

The biological approaches used for bioremediation applications are always related to geomicrobiological process [4]. The metal-accumulating mechanisms involved in nanoparticle formation create metal-mineral-microbe interactions.

2.3. Metal Recovery from Heavy Metal Industry Effluent. Metal resources are nonrenewable; as such, the recovery of metal from industrial waste water could provide a means of maintaining the supply of heavy metals [10]. Scientists currently predict that a number of critical metal elements, such as Zinc, Silver, and Gold, will be depleted within the next 50 years if the current rate of consumption is maintained [60]. As a result of the rapid growth of the world economy, the consumption rate of these critical elements is increasing. As discussed in Section 2.1, several conventional remediation methods offer the potential to recover some of these metals from waste products, for example, chemical precipitation, membrane filtration, electrochemical treatment, bioleaching, and adsorption processes.

The use of a bioremediation process that employs a biosorption-desorption mechanism using natural biomass may represent one viable form of environmentally friendly bottom-up nanoparticles synthesis that could help to avoid a metal source depletion crisis [4, 61]. The definition of biosorption-desorption is discussed in Section 2.3. The quality of the recovered metals or nanoparticles depends on various aspects, such as types of biosorbents, type of metals, ion, pH, and temperature. The synthesis of high quality metal nanoparticles is a field of research that is generally discussed by groups outside bioremediation research. See Sections 2.3 and 2.4 for a comprehensive discussion of nanoparticle biosynthesis.

Various researchers have proposed the use of bioremediation to recover raw materials from waste [4, 61, 62]. In their review of heavy metal removal, Purkayastha et al. [63] compared Cd(II) recovery efficiency between conventional and contemporary methods. The contemporary method of biosorption is widely trusted and is the most popular and frequently used method of heavy metal removal and recovery. It also has the potential to be both a low-cost and environmentally friendly bioremediation process. From [63], a Cd(II) recovery of nearly 100% efficiency was demonstrated through the use of sulfide precipitation and biosorption processes. The conventional method of sulfide precipitation has the capability to recover Cd(II) up to 99.9% from its initial concentration [64]. Similar capability in Cd(II) recovery could also be obtained via a biosorption-leaching method, up to 98.89% from the initial concentration by using blackgram husk with 0.1 M HCl as a leaching agent [65]; the use of sawdusk obtained from mulberry wood with 1.5 M HCl has achieved Cd(II) recovery capability up to 92.79% [66], while Cd(II) recovery of up to 98.7% was obtained by using an *Annona squamosa*-based absorbent with 0.1 M HCl [67]. A Cd(II) recovery of up to 82% was obtained by using the biomass of *Pseudomonas aeruginosa* with 0.1 M HCl [68]. The recovery of Cu(II) of 100% was obtained by using volcanic rock matrix-immobilized *Pseudomonas putida* cells with surface-displayed cyanobacterial metallothioneins at pH 2.35 [69]. 100% recovery of Cu(II) was also obtained by using the activated sludge at pH 1 [70]. Over 90% recovery of Cu and Pb was obtained at pH ≤ 2 through the use of an indigenous isolate *Enterobacter* sp.J1 [71]. Liu et al. [72] compared the recovery efficiency between biosorption-leaching and biosorption-pyrolysis technology when recovering Pb from an aqueous solution. A Pb recovery of up to 94.9% was achieved in HCl solution, while 98.2% was achieved via the fast pyrolysis process.

Heavy metals can also be removed and recovered through bioleaching, which utilizes microorganisms as reduction agents [62]. The efficiency of the recovery process depends on the ability of the microorganisms to transform the solid compound within the contaminated soil into a soluble substance that can be extracted and recovered.

Several methods can be applied to achieve physical synthesis of metallic nanoparticles. These include attrition and pyrolysis. However, the process involves a significant conversion of energy to maintain the high pressure and temperature required during the synthesis process [73]. Top-down synthesis in the physical approach involves methods such as thermal decomposition, diffusion, irradiation, and arc discharge.

Chemical procedures are generally low-cost and can process high volumes; however, they typically involve the use of toxic solvents and generate hazardous byproducts. Examples of a bottom-up synthesis using a chemical approach include the seeded growth method, the polyol synthesis method, electrochemical synthesis, and chemical reduction. Scientists have successfully used a chemical reduction method to reduce a metal particle to nanoparticles using chemical agents such as Sodium borohydride or Sodium citrate.

Biological methods in the synthesis of metallic nanoparticles are becoming increasingly popular as they are low-cost, nontoxic, and environmentally benign. Synthesis using biological methods, especially those involving plants, can actively reduce metal ions in a biocompatible way where they can secrete functional biomolecules. The biological agents that are used in the biological approach to the synthesis of nanoparticles involve a variety of microbes [58, 74] including bacteria [73], fungi [75, 76], yeast, and plants [77].

2.4. Biosynthesis as an Approach to Producing Nanoparticles during a Bioremediation Process. Various review papers deal with the relationship between the bioremediation process and the production of metal nanoparticles [4, 61]. The main process that is used for both bioremediation and biosynthesis of nanoparticles is biosorption [8, 11]. Nanoparticle biosynthesis can be mediated by the biomass of plants and microorganisms (bacteria, algae, fungi, and yeast) through biosorption.

Biosynthesis is a bottom-up approach that uses biological molecular size entities to form nanoparticles [78]. Various biosynthetic methods are used to produce stable metal nanoparticles [79]. The biosynthesis of Gold, Silver, Gold-Silver, Platinum, Palladium, silica, alloy, Titanium, zirconia, Selenium, and Tellurium nanoparticles has already been reported [58]. Organisms, both unicellular and multicellular, have demonstrated unique potential in the environmentally friendly production and the accumulation of nanoparticles of different shapes and sizes that can be utilized for different commercial applications. Biosynthesis approaches for the production of metallic nanoparticles were reviewed by various groups [79]. Kulkarni and Muddapur [56] published a review on single-step biosynthesis mechanism of metal and metal oxide nanoparticles through the use of plants and microorganisms. The biomolecules present in plant extracts can be used to reduce metal or metal oxide ions to nanoparticles. This approach is low-cost, nontoxic, and environmentally benign and it allows the size of the nanoparticles to be controlled. The methods of nanoparticle characterization are used to understand the mechanism of particle formation and determine its future application [79]. In the biosynthesis of nanoparticles, different major factors, such as pH, temperature, concentration of metal ions, and concentration of extracts, influence the process of reducing metal ions to metal nanoparticles [57, 80].

2.4.1. Plant-Mediated Biosynthesis of Nanoparticles. Plants have demonstrated a better ability to mediate nanoparticle synthesis than other methods and they offer a number of further advantages [78]. During the biosynthesis process, plants as biological agents act as reducing and capping agents [57]. Every part of the plant can be used for nanoparticles including leaves, flower, seeds, stems, fruits, latex, and calli. Furthermore, biomass from dead and dried plants can also be used for the synthesis of nanoparticles [81].

Research in plant-mediated biosynthesis of nanoparticles that has been conducted over the past 10 years (2003–2012) was reviewed extensively by Mittal et al. [74]. Over 50 different types of plant extracts have been used to synthesize metal nanoparticles and these have mostly been employed to produce Silver and Gold nanoparticles and alloys of different sizes and shapes [74]. A review of Iron, Zinc oxide, Selenium, Silver, and Gold nanoparticles that were mediated by plants, marine plants, and some microorganisms was published by Kulkarni and Muddappur [56]. Table 2 displays the results of a recent project which was not reviewed by Mittal et al. [74] and Kulkarni and Muddappur [56] in their review papers.

Of the reviewed projects (which were all conducted in the last 10 years before 2014), the majority of the plant extracts employed were derived from the leaf part of the plant. In order to create a sustainable method of recycling metal industrial effluent through the use of bioremediation technology, green and low-cost bioreduction agents from food industrial waste biomass should be used. Fruit peel, tea leaves, seeds, and flowers are among large-scale food industrial waste products and agricultural waste that should be reused to obtain a sustainable resource that can have a nanotechnology application.

The development of Gold and Silver nanoparticles is highly attractive to researchers due to the nobility of these metals and their wide range of applications, especially in biomedical and biochemistry fields. Remediating the waste produced by the Gold and Silver mining industry and its leachates through the use of food industrial waste not only will clean the water or soil of metal waste, but also could reduce the cost of the process.

2.4.2. Microorganism-Mediated Biosynthesis of Nanoparticles

(1) Bacteria-Mediated Biosynthesis of Nanoparticles. The strong relationship between bioremediation technologies and the bacteria-mediated biosynthesis of nanoparticles through the application of biosorption was discussed by

Table 2: Plant extract-based biosynthesis of metal or metal-based ion nanoparticles.

Plant/plant part extract	Scientific name	Metal NPs	NPs size (nm)	Reference
Leaf	Lemon	Se	60–80	[82]
Leaf	Green tea	Fe ion		[83]
Leaf	*Ecliptaprostrata*	TiO	36–68	[84]
Leaf	*Cinnamomum tamala*	Au/TiO_2	8–20	[85]
Plant	*Cacumen platycladi*	Pt	2.4 ± 0.8	[86]
Leaf	*Ocimum tenuiflorum* (Tulasi)	Ag	7–15	[87]
Leaf	*Chenopodium murale*	Ag	30–50	[88]
Gum olibanum	*Boswellia serrata*	Ag	7.5 ± 3.8	[89]
Leaf	*Cissus quadrangularis* Linn	Ag	15–23	[90]
Leaf	Aloe	Ag	20	[91]
Fruit	*Tribulus terrestris*	Ag	16–28	[92]
Leaves	*Stevia rebaudiana*	Ag	2–50	[93]
Leaf	*Artemisia nilagirica*	Ag	70–90	[94]
Root	*Morinda citrifolia*	Ag	30–55	[95]
Leave	*Rhizophora apiculata*	Ag	19–42	[96]
Leaf	*Prosopis juliflora*	Ag	35–60	[97]
Leaf	*Olive*	Ag	20–25	[98]
Fruit	*Terminalia chebula*	Ag	25	[99]
Coir	*Cocos nucifera*	Ag	23 ± 2	[100]
Leaf	*Malva parviflora*	Ag	19–25	[101]
Leaf	*Mangifera indica*	Ag	20	[102]
Peel	*Mangifera indica* Linn (Mango)	Ag	7–77	[103]
Leaf	*Origanum vulgare*	Ag	136 ± 10.09	[104]
Leaf	*Pepper*	Ag	5–60	[105]
Leaf	*Coccinia grandis*	Ag	20–30	[106]
Leaf	*Catharanthus roseus* Linn G. Donn	Ag	27–32	[107]
Peel	*Citrus unshiu*	Ag	5–20	[108]
Plant	*Scutellaria barbata* D. Don	Au	5–30	[59]
Seed	*Benincasa hispida*	Au	10–30	[55]
Pod	*Gymnocladus assamicus*	Au	4.57 ± 0.23–22.57 ± 1.24	[109]
Leaf	*Piper betle*	Au	50 (mean size)	[110]
Pulp	*Beta vulgaris*	Au	Nanorod (25 nm) Nanowire (30 nm)	[111]
Leaf, stem, root	*Ipomoea carnea*	Au	3–100	[112]
Marine plant	*Sargassum muticum*	Au		[113]
Glucan of mushroom	*Pleurotus florida*	Au	5.33–18	[114]
Plant	*Zingiber officinale*	Au	5–15	[115]
	Crocus sativus	Au	11–20	[116]
Leaf	*Hibiscus rosasinensis*	Au		[117]
Leaf	Green tea	Au	20	[118]
Flower	*Rosa damascena*	Au, Ag	10–30	[119]

various researchers [120, 121]. Kulkarni and Muddappur [56] reviewed recent research on the biosynthesis of metal nanoparticles through the use of bacteria as reduction agents. Table 3 lists the types of bacteria that synthesize metal nanoparticles. Most such syntheses are extracellular binding metal nanoparticles to bacterial biomass. The bacterial biomass, such as *Pseudomonas aeruginosa* and *Aeromonas hydrophila*, is obtained at low cost from waste from bacterial synthesis in the plastic industry, polyhydroxyalkanoates [122]. Due to the biodegradability of these materials, polyhydroxyalkanoates are desirable and will offer continuous production on a large scale [123]. Thus, the production of both *P. aeruginosa* and *A. hydrophila* biomass will continuously be available and offer access to low-cost Gold and Zinc

Table 3: Bacteria-mediated biosynthesis of nanoparticles.

Metal/metal oxide	Microorganisms		Nanoparticle size (nm)
Au	*Geobacillus* sp. [125]		5–50
	Klebsiella pneumoneae [126]		
	Escherichia coli [127, 128]	Extracellular	17–32, 5–70 (uniform at 2.2)
	Magnetospirillum gryphiswaldense MSR-1 [54]	Extracellular	10–40
	Pseudomonas aeruginosa [129]	Extracellular	15–30
	Rhodopseudomonas capsulate [130]	Extracellular	10–20
	Micrococcus luteus [131]	Extracellular	6 nm and 50 nm
	Stenotrophomonas [132]	Extracellular *marine source*	10–50
Ag	*E.coli* [133]		
	Lactobacillus sp. [134]		10–25,
	Bacillus licheniformis [135]		2–100
	Streptomyces hygroscopicus (BDUS 49) [136]	*Live cells from sewage*	20–30
	Corynebacterium glutamicum (0) [120]		5–50
	Streptomyces sp. BDUKAS10 [137]	Extracellular	21–48
	Bacillus cereus [138]		4-5
	Bacillus amyloliquefaciens LSSE-62 [139]	Intracellular	14.6
	Stenotrophomonas [132]		40–60
Se	*Klebsiella pneumoneae* [9, 133]		100–550
	Zooglea ramigera [140]	Extracellular	30–150
	Bacillus subtilis [141]	Extracellular	50–400
Ag_2O	*Lactobacillus mindensis* [142]		2–20
Ti	*Lactobacillus* sp. [134]		10–70
TiO_2	*Bacillus subtilis* [143]		66–77, 10–30
Cu_2S	*Streptomyces* sp. [144]		100–150
	Desulfovibrio desulfuricans [121]		20–30
Zinc nitrate	*Streptomyces* sp. [144]		100–150
ZnO	*Calotropis gigantean* [145]		
	Lactobacillus sporogenes [146]		5–15
	Lactobacillus plantarum VITES07 [147]		7–19
	Aeromonas hydrophila [148]		57.72
CdS	*Rhodopseudomonas* [149]	Intracellular	8.01 ± 0.25

oxide nanoparticle biosynthesis, respectively, especially with intention to recover these metals from the industrial effluent produced by the metals industry. The Selenium and Titanium oxide nanoparticle biosynthesis could also be continuously obtained, since *Bacillus subtilis* biomass is available on a continuous basis. *Bacillus subtilis*-based enzymes are in high demand in a number of consumer chemical production industries such as those that produce cleaning products, paper and textiles, food, and pesticides [124].

Many other forms of bacteria biomass could be obtained from industrial waste and subsequently be used for the low-cost, environmentally friendly, and sustainable bioremediation of metal industrial effluents.

(2) Fungi-Mediated Biosynthesis of Nanoparticles. The fungi-mediated biosynthesis of Silver nanoparticles was reported by Duran et al. [79]. Uniformity in terms of size and shape of the Gold nanoparticles formed through the use of *Aspergillus oryzae* var. *viridis* (waste industrial fungal biomass from industry) ranged between 10 and 60 nm [51]. Mishra et al. [52] reported the potential of an industrially important fungus, *Penicillium rugulosum*, for the synthesis of Gold nanoparticles. Reduction of Silver nitrate to Silver metallic nanoparticles is currently an established routine in laboratories worldwide. Vigneshwaran et al. [150] investigated the use of white rot fungus *Phaenerochaete chrysosporium* for the extracellular synthesis of Silver nanoparticles. The mycelium of *P. chrysosporium* was found to reduce Silver nitrate to metallic silver nanoparticles. Utilization of *Coriolus versicolor* to reduce Silver nitrate to Silver metallic nanoparticles was reported by Sanghi and Verma [151]. The formation of Silver nanoparticles through an extracellular cell wall reduction

Table 4: Fungi-mediated biosynthesis of metal nanoparticles.

NPs	Name	Binding location	Size of NPs (nm)
Ag	*Phaenerochaete chrysosporium* [150]	Extracellular	50–200
Ag	*Aspergillus flavus* [152]	Extracellular	8.92 ± 1.61
Ag	*Coriolus versicolor* [151]	Intra-/extracellular	
Ag	*Penicillium brevicompactum* WA2315 [154]	Extracellular	23–105
Ag	*Cladosporium cladosporioides* [155]	Extracellular	10–100
Ag	*Candida albicans* [50]		5–30
Ag	*Neurospora crassa* [156]	Intra-/extracellular	11
Ag	*Fusarium oxysporum* [157]	Extracellular	5–15
Pt	*Fusarium oxysporum* [158]	Extracellular	5–30
TiO_2	*Aspergillus flavus* [159]	Extracellular	62–74
TiO_2	*Humicola sp.*[160]		
ZnO	*Candida albicans* [161]		
Au	*Aspergillus oryzae* var.*viridis* [51]		30–400
Au	*Sclerotium rolfsii* [53]		25
Au	*Penicillium rugulosum*[52]		20–80
Au	*Cylindrocladinum* [162]		5–35
Au	*Candida albicans* [50]		5–30
Au	*Neurospora crassa* [156]	Intra-/extracellular	32

process of Silver nitrate by using *Aspergillus flavus* was successfully performed by Vigneshwaran et al. [152]. Silver nanoparticles with a size of 8.92 ± 1.61 nm were obtained in this study. Silver metallic nanoparticles that were 5–25 nm in size were obtained through extracellular biosynthesis by using *Aspergillus fumigatus* [153]. Table 4 shows the fungi-mediated biosynthesis of metals nanoparticles for noble metals.

(3) Algae-Mediated Biosynthesis of Nanoparticles. Abdel-Aziz et al. [88] successfully obtained Gold nanoparticles that were 3.85–77.13 nm in size through the use of an extract of the *Galaxaura elongata* algae. The use of *G. elongata* to obtain the nanosize Gold nanoparticles demonstrated the high effectiveness of this method compared to the use of *E. coli* and *K. pneumonia*, which yielded Gold nanoparticles of size 13.5 and 13 nm, respectively. Arockiya et al. [163] obtained Gold nanoparticles of a size ranging between 18.7 and 93.7 nm through the use of *Stoechospermum marginatum*. The obtained nanoparticles demonstrated potential to be used as antibacterial agents.

(4) Yeast-Mediated Biosynthesis of Nanoparticles. Au nanoparticles have been obtained through the use of the *Saccharomyces cerevisiae* AP22 yeast and CCFY-100 through accumulation processes inside the cells [164], while Ag nanoparticles with an average size of 19 ± 9 nm were obtained through the use of the *Saccharomyces cerevisiae* BU-MBT-CY1 yeast [165].

2.5. Hyperaccumulation of Metals for Phytomining Applications. Accumulation of metal by plant species for soil remediation was first used as early as 1983, and it advanced to an accepted metal mining technology in recent years [34]. Metal accumulating species can be used for phytoremediation (removal of contaminants from soils) (as discussed in Section 2.4) or for phytomining, which involves growing plants to harvest metals (this will be discussed in this section). In addition, many of the metals that can be hyperaccumulated also provide essential nutrients; food fortification and phytoremediation might be considered two sides of the same coin [166]. Many heavy metals are essential or beneficial as micronutrients for the growth and metabolism of microorganisms, plants, and animals but are dangerous if found in high concentrations. These include Cobalt (Co), Copper (Cu), Iron (Fe), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), and Zinc (Zn). On the other hand, some heavy metals do not seem to be essential because there is no demonstrated biological or physiological function (yet). These include Lead (Pb), Arsenic (As), Cadmium (Cd), and Mercury (Hg). Several reasons and hypotheses exist concerning why some plants hyperaccumulate metals. The first is that the metals [166] provide the plants with a physiological strategy that protects them from herbivore attack through feeding deterrence and from pathogen attack through their toxicity [34, 166]. Sagner and coworkers [167] observed the repellent effect that plant sap had on the fruit fly *Drosophila melanogaster*, indicating that, in hyperaccumulating plants, Nickel serves as an agent to prevent predation. Furthermore, the defensive enhancement increases with increasing metal concentration [168]. Hyperaccumulator species are distributed across a wide range of distantly related families, showing that the hyperaccumulation trait has evolved independently more than once under the spur of selective ecological factors. The ability of plant species to accumulate heavy metals is of interest in multidisciplinary fields as it holds potential for the development of technologies that are of human and environmental concern.

2.5.1. Hyperaccumulation of Metal by Plants. Plants have the ability to accumulate metals from the soil in their tissue during growth and development. The hyperaccumulation process offers a new, environmentally friendly method of producing metal nanoparticles [34]. The term "hyperaccumulator" describes plants that have the ability to grow on metalliferous soils and to accumulate extraordinarily high amounts of heavy metals that are far in excess of the levels found in the majority of species in their aerial organs, without suffering phytotoxic effects [169]. Chaney [170] proposed the idea of using plants that hyperaccumulate metals to selectively remove and recycle excessive metals in soil. Hyperaccumulator plants have been defined as those that accumulate metal in concentrations that are 10–100 times more than those found in normal plants [170]. According to Reeves [171], there are 440 hyperaccumulator plant species, of which 75% are Nickel hyperaccumulators. Other plant species accumulate metals like Cadmium, Arsenic, Manganese, Sodium, Thallium, and Zinc. When metal ions have been taken up and are concentrated in the tissue of the hyperaccumulator plants, the biomass may be harvested, dried, and burnt to ash for recycling as a bio-ore [172, 173] or stored for later use.

Wei and coworkers [174] summarized the main characteristics of hyperaccumulator plants as follows:

(i) accumulation property, that is, the minimum concentration in the shoots of a hyperaccumulator; for As, Pb, Cu, Ni, and Co, it should be greater than 1000 mg kg^{-1} dry mass, for Zn and Mn 10,000 mg kg^{-1}, for Au 1 mg kg^{-1} and Cd 100 mg kg^{-1}, respectively [175];

(ii) translocation property; that is, elemental concentrations in the shoots of a plant should be higher than those in the roots [176, 177];

(iii) enrichment property; that is, enrichment factor EF (concentration ratio of plant to media) in shoots of plants should be higher than those in roots [178];

(iv) tolerance property; that is, a hyperaccumulator should have high tolerance to heavy metals [178]. The tolerance mechanism in plants that hyperaccumulate Cd was explored from root morphology by Wei and coworkers [174].

Hyperaccumulation by plants includes the uptake of heavy metal through "root-to-shoot." The majority of the heavy metal is absorbed from the soil by the root and then detoxified by chelation in the cytoplasm or stored in vacuoles. Hyperaccumulators rapidly and efficiently translocate the element to the shoot via the xylem. Rascio and Navari-Izzo [166] described three basic characteristics by which hyperaccumulator plants can be distinguished from nonaccumulation plant species:

(1) a much greater capability to extract heavy metals from the soils,

(2) a faster and effective root-to-shoot translocation of metals, and

(3) a much greater ability to detoxify and sequester huge amounts of heavy metals in the leaves.

Plants Species in Hyperaccumulation. Many species of plant can hyperaccumulate heavy metals. These include *Asteraceae, Brassicaceae, Caryophyllaceae, Cyperaceae, Cunouniaceae, Fabaceae, Flacourtiaceae, Lamiaceae, Poaceae, Violaceae, Sapotaceae*, and *Euphobiaceae*. The *Brassicaceae* family has the largest number of taxa, consisting of about 11 genera and 87 species. Members of the family *Bracecaceaeaare* are well known as hyperaccumulators of Nickel (genera *Thalaspi* and *Alyssum*), Cadmium, and Zinc (*Thalaspi caerulescens, T. praecox, T. geosingese*, and *Arabidopsis halleri*). According to research performed by Sagner et al. [167] and Jaffre et al. [179], the highest concentration of Nickel in latex has been recorded in different parts (latex, leaves, trunk bark, twig bark, fruits, and wood) of the *Sebertia acuminata* (Sapotaceae) tree from New Caledonia. More taxa of plants species are accumulators of Nickel (more than 75%) than of any other metal, and only five species accumulate Cadmium [166]. Several heavy metal hyperaccumulating species that belong to the *Thlaspi* genus have been studied, among them *Thlaspi caerulescens* hyperaccumulating Zn/Cd [180], *Thlaspi rotundifolium* ssp. *cepaeifolium* hyperaccumulating Pb [173], and *T. praecox* Wulf hyperaccumulating Zn [181]. The hyperaccumulator plant *Alyssum murale* can accumulate Ni up to 20,000 mg kg^{-1} dry weight, and a biomass of 10,000 kg/ha can be harvested per year [182]. Serpentine soils contain Ni at concentrations between 1000 and 7000 mg kg^{-1}. These concentrations are well below the exploitation threshold required by traditional mining (30,000 mg kg^{-1}) but are sufficient to allow hyperaccumulating plants to extract and accumulate Ni [175]. A selection of hyperaccumulator plant species and their threshold concentrations is given in Table 5.

Lin and coworkers [190] examined the different concentrations of Copper sulphate in the growth and accumulation of Cu^{2+} in different parts, such as in the root, hypocotyl, cotyledon, and leaf, of the sunflower (*Helianthus annuus* L.) plant. They found that the concentration of Cu^{2+} was higher in the roots than it was in other parts of the *Helianthus annuus* and concluded that these plants have the potential ability to accumulate Copper. Copper is a catalytic cofactor of enzymes and is necessary in the normal growth and development of many plants species. Juárez-Santillán and coworkers [197] carried out an experiment that aimed to identify Manganese accumulation in the plants growing in the mining zone of Hidalgo, Mexico. They used eight species of accumulator plants and found a Mn content in the substrate ranging from 11,637 to 106,104 mg kg^{-1} dry weight, with the concentrations being between 2 and 21 times higher than the phototoxic level of 5,000 mg kg^{-1} dry weight according to Alloway [198]. Jiang and coworkers [191] investigated the effects of Cadmium chloride concentration, uptake, and accumulation of Cd^{2+} using the hyperaccumulator garlic *Allium sativum* L. Their results showed that the concentration of Cadmium was higher in the roots than it was in the shoot and bulb.

Types of Hyperaccumulation. There are two types of hyperaccumulation, natural (using plants) and induced (adding chemicals). Natural hyperaccumulation occurs when plant species use their physiological ability to accumulate the state

Table 5: Hyperaccumulators in phytomining. Source: van der Ent et al. [183] with modifications, together with the metal concentration in selected hyperaccumulators.

Metal	Number of hyperaccumulator species recorded	Hyperaccumulation threshold (mg kg^{-1})	Selected hyperaccumulator species	Concentration of metals (mg/kg d.w.)
Nickel	450	1000	*Sebertia acuminate* [167, 179]	
			Streptanthus polygaloides [184, 185]	
			Alyssum bertolonii [186, 187]	13400
			Berkheya coddii [187]	17000
			Thlaspi geosingense [188]	
			Alyssum tenium [19]	
			Alyssum troodii [19]	
Cobalt	30	300	*Haumaniastrum robertii* [189]	10200
Copper	32	300	*Helianthus annuus* L. [190]	
			Haumaniastrum katangense [169]	8356
Zinc	12	3000	*Thlaspi calaminare* [181]	10000
Zinc and Cadmium			*Thlaspi caerulescens*	
			Sedum alfredii	
			Polycarpaea longiflora [19]	
Cadmium	2	100	*Allium sativum* L. [191]	
			Thlaspi caerulescens [19]	3000
			Solanum nigrum [192]	
			Rorippa globosa [174]	
Gold (induced hyperaccumulation)		1	*Brassica juncea* *Barkley coddii* [193, 194]	10
Manganese	12	10000	*Macadamia neurophylla* [195]	55000
Lead	14	1000	*Thlaspi rotundifolium* subsp. [181]	8200
Thallium	2	100	*Biscutella laevigata* *Iberis intermedia* [193, 196]	4055

of heavy metals as a normal function of their growth, while induced hyperaccumulation is performed by adding chemicals to the soil in order to manipulate the soil-plant environment. Several pieces of research have covered hyperaccumulation [34]. The majority of the discussion in the existing reports concentrates on natural hyperaccumulation. Anderson and coworkers [193] attempted to induce plants to hyperaccumulate Au by adding ammonium thiocyanate to substrate, and their results revealed that Indian mustard (*Brassica juncea*) accumulated up to 57 mg kg^{-1}. In this research, the hyperaccumulation of Gold was defined as accumulation greater than 1 mg kg^{-1} based on normal concentration in plants of 0.01 mg kg^{-1} [199, 200].

2.5.2. Hyperaccumulation of Metal by Others. Aquatic macrophytes, such as *Eleocharis acicularis*, hold great potential for phytoremediation of water contaminated with multiple heavy metals from mine tailings, mine drainage, and water [201, 202]. Ha and coworkers [203] completed a laboratory investigation in which they studied the ability of dwarf hair grass (*Eleocharis acicularis*) to accumulate Indium, Silver, Copper, Cadmium, Lead, and Zinc and assessed phytoremediation and phytomining. Their results indicated that *Eleocharis acicularis* does have the ability to accumulate metals; the concentrations of metals in the roots of the plant were as follows: Indium 477 mg kg^{-1}, Silver 326 mg kg^{-1}, Copper 575 mg kg^{-1}, Cadmium 195 mg kg^{-1}, Lead 1120 mg kg^{-1}, and Zinc 213 mg kg^{-1} dry weight after 15 days exposure, and they concluded that there was the potential to extract Indium and Silver from these plants and that they can be used for phytomining.

2.5.3. How Organisms Accumulate Heavy Metals. As discussed above, bioaccumulation involves the accumulation of metal from the soil or water and is always performed by living microorganisms such as bacteria, fungi, algae, and yeast [8, 10]. The microorganisms take up the metal into the cell across the cell membrane [11]. Understanding the mechanism of biosorption and the structure of the cell wall or cell membrane is important to identify an appropriate method of removing metals from polluted water or soil. Microbes, including eukaryotes and prokaryotes, interact with metals and minerals in natural and symbiotic association with each other and other organisms. They can alter the physical and chemical condition and have an impact on the growth, activity, and survival of microbials [4]. Chmielewská and Medved [204] confirmed the high Ni^{2+} bioaccumulation ability of *Cladophora glomerata*. Furthermore, *Microspora* also might have potential to be useful in bioremediation. The mechanisms by which metal is bound to microbial biomass are divided into three types:

(i) intracellular accumulation, where the process requires live cells,

(ii) sorption or complex formation on the cell surface for both living and dead cells, and

(iii) extracellular accumulation or precipitation where the process may require viable cells [205, 206].

Bioaccumulation via growing cells is a potential technique for removing heavy metals from a food environment. The heavy metals can be both biosorbed onto the cell surface and passed into the cell across the cell membrane through the cell metabolic cycle [207].

The uptake of metal ions by living and dead cells consists of two methods; either the metal ions bind to the surface of the cell wall and extracellular material or the metal is absorbed into the cell across the cell membrane, which is referred to as intracellular uptake, active uptake, or bioaccumulation [5]. The first method occurs in both living and dead cells in biomass, while the second method, which is dependent on the plants' metabolism, occurs only in living cells. As such, both living and dead cells are capable of metal adsorption [208]. The use of dead biomass is preferred to living matter due to the absence of toxicity limitations, growth media and nutrient requirements, and the high capacity of the binding metals. Metal uptake is also facilitated by the production of metal-binding proteins in living cells.

A less energy dependent approach for bioaccumulating Gold nanoparticles was successfully performed through the use of two different strains of yeast, *Saccharomyces cerevisiae* AP22 and CCFY-100 [164]. The ion Gold (III) is reduced to Gold (0) and the nanoparticles accumulate inside the cell nucleolus. Narayanan and Sakthivel [162] successfully synthesized nano-Gold composite by using the fungus *Cylindrocladium floridanum* via an intracellular accumulation process. This study introduced the use of microbially matrixed Gold nanoparticles as heterogeneous catalysts to control the accumulation of the nano-Gold composite.

2.5.4. Phytomining of Various Metals. Phytomining has emerged as an environmentally friendly technology that uses plants to extract heavy metals from a given substance [173, 193]. This technology involves growing and harvesting metal-accumulating plants on appropriate sites and treating the biomass to recover the metal. Phytomining describes the bio-harvesting of metals from high biomass crops grown in soil substrates, particularly those associated with subeconomic mineralization. Phytomining involves growing high-biomass plants that accumulate high metal concentrations. Phytomining technology is perhaps the most feasible, lowcost, and environmentally friendly alternative to conventional mining methods as it allows the economic exploitation of mineralized soils that are thought too metal-poor for direct mining operations. The technique of phytomining involves growing a crop of a metal-hyperaccumulating plant species, harvesting the biomass, and burning it to produce a bio-ore [193]. Pythomining has been suggested as a potential alternative to recovering metal for other applications. In this situation, several studies have attempted to recover metals, such as Nickel [189, 209, 210], from mineralized soils or waste rock. Phytomining employs hyperaccumulating plants to extract valuable metals from the substrate. Many metals, such as Nickel, Cadmium, and Manganese, occur naturally in hyperaccumulator plant species because most metals are bioavailable in the soil solution in which the plants grow [175].

Phytomining offers the possibility to exploit metals derived from low-grade ore, overburdens, mill tailings, or mineralized soil, which are uneconomic to extract by conventional methods [19]. The metal content of a bio-ore is usually much greater than that of a conventional ore and requires less storage space, despite the lower density of a bio-ore [173, 193]. Besides that, phytomining can also be used for remedial purposes to extract high concentrations of toxic metals, such as Nickel and Thallium, from mine tailings and other metal contaminated areas. Phytomining not only produces ingots of Gold but, interestingly and importantly, this technique can also be used to produce Gold nanoparticles, which is of huge potential to nanotechnology industries [211–213]. Additionally, phytomining provides a source of income from the sales of Carbon dioxide credits. Phytomining restores mined degraded land through the planting of hyperaccumulator species more quickly than natural revegetation which may take decades or even hundreds of years because it is dependent on animals and windborne seedlings. Phytomining also provides a potential energy storage that can be utilized to generate thermal energy, which is a cheap and renewable resource.

Phytomining of Nickel. Numerous studies have examined the use of Ni phytomining. The first field trials involving phytomining were carried out at the US Bureau of the Mines, Reno, Nevada, using the Ni hyperaccumulator *Streptanthus polygaloides* [184]. The findings of this initial research indicated that a yield of 100 kg/ha of sulfur-free Ni could be produced via phytomining [186, 193, 214]. Anderson and coworkers [193] tested the phytomining potential of Ni hyperaccumulator *Alyssum bertolonii* from Italy and *Berkheya coddii* from South Africa. *In situ*, an experiment for second field trials of Nickel phytomining using the Ni hyperaccumulator *Alyssum bertolonii* was performed in Tuscany, Italy [186]. In this experiment, the plants were fertilized with N + P + K combinations over a period of two years. The results indicated that the biomass of dry matter increased threefold to 9.0 t/ha and this was gained with N + P + K without dilution of unfertilized Ni concentrations. The existing research does not show a correlation between the age of a plant and Ni content. The hyperaccumulator *Alyssum bertolonii* has the potential to be used in Nickel phytomining of ultramafic soils. The hyperaccumulating plant *Alyssum murale* can accumulate up to 20,000 mg kg^{-1} dry weight, and a biomass of 10,000 kg/ha can be harvested per year [182].

Phytomining of Gold. Gold is a valuable metal that is in high demand in commercial industries. It has a potential for phytomining where the aim of the operation is to yield an economic profit and/or exploit low-grade ore or mineralized soils that are too poor for conventional mining methods [215]. Conventional technology is generally unable to economically recover residual Gold, and, as such, phytomining offers a viable alternative method of recovering these valuable Gold resources [216]. Plant species do not naturally accumulate Gold; it needs to be made soluble in soils for enhancing uptake to occur. For this purpose, hyperaccumulation is induced by adding Sodium cyanide, thiocyanate, and thiosulphates. The residual Gold can be extracted using induced hyperaccumulation if the substrate were amenable to plant growth. The Gold concentration that can be induced into a plant is dependent on the Gold concentration in the soil in which the plant is growing. Induced hyperaccumulation to uptake Gold has been reported in numerous pieces of research. Anderson and coworkers [187] showed that approximately 2 mg kg^{-1} of Gold are needed to achieve 100 mg kg^{-1} of plant dry weight in Indian mustard (*Brassica juncea*) with adding ammonium thiocyanate (NH_4SCN) at different rates of 0, 80, 160, 320, and 640 mg kg^{-1} dry substrate weight in pots containing an artificial 5 mg kg^{-1} finely disseminated Gold rich material, analogous to natural, oxidized, and nonsulphidic ores. Msuya and coworkers [194] induced hyperaccumulation in the five root crops, carrot (*Daucus carota*), red beet (*Beta vulgaris*), onion (*Allium cepa*), and two cultivars of radish (*Raphanus sativus*) with NH_4SCN and ammonium thiosulphate $[(NH_4)_2S_2O_3]$ in substrates containing 3.8 mg kg^{-1} Gold. The results showed that the roots in all five crops contained higher metal concentrations than their shoots.

Phytomining of Thallium. Thallium has the biggest economic potential after Gold, Platinum, and Palladium because it is relatively naturally unavailable. Leblanc and coworkers [196] discovered unusually high hyperaccumulation of Tl by *Iberis intermedia* Guersent and *Biscutella laevigata* L. growing over Lead/Zinc mine tailings in southern France. Tailings typically contained 15,000 mg kg^{-1} Zn, 5,000 mg kg^{-1} Pb, and, locally, up to 40 mg kg^{-1} Tl. Their results indicated that the content of Thallium in *Iberis intermedia* was more than 4,000 mg kg^{-1} in the whole plant dry weight with a biomass of 10,000 kg/ha, while in the *Biscutella laevigata* the content of Thallium was over 14,000 mg kg^{-1} with a biomass of 4,000 kg/ha. *Biscutella laevigata* at 4 t/ha has less than half of the biomass of *Iberis intermedia* but three times the Thallium mean concentration (mean 10 mg kg^{-1}). These results are similar to those reported in field trials in New Zealand, where a biomass of 10,000 kg/ha was found in *Iberis intermedia* by Anderson and coworkers [193]. The hyperaccumulator plant produces about 700 kg/ha of bio-ore and 8 kg of Thallium, which was worth US$ 2400 at a world price of US$ 300/kg. A crop biomass of 10 t/ha of *Iberis intermedia* was found from field observations in France and field trials in New Zealand and this indicates that there is a potential to phytomine Thallium if sufficiently large areas of contaminated soils are available and large-scale production advantages can be acquired [193].

2.6. Biomineralization. The collective process by which organisms form minerals is called biomineralization [217]. Metal-mineral-microbe interactions are basically microbial biomineralization processes [4]. More than 70 different minerals are produced by organisms via biomineralization [218]. The preparation of biosorption is also important for estimating the operational costs associated with phytomining.

3. The Potential of Products Derived via Bioremediation from Heavy Metal Industry Effluents for High Technology Applications

3.1. Nanotechnology Applications. Metal nanoparticles, such as Gold, Silver, and Platinum, have become fundamental building blocks of nanotechnology [219]. The properties, morphology, surface area, structure, and shape of nanoparticles make them ideal for preparing nanostructured materials and devices [75, 220, 221]. Metal nanoparticles are crystalline in nature [56, 57]. To control the size, shape, and stability of nanoparticles, different synthesis conditions are applied [56].

Nanotechnology is an interdisciplinary area of science, economy, engineering, and industry, and increasing attention is being placed on the production of nanoparticles. Nanotechnologies use different metal nanoparticles in a wide range of sizes and shapes. Nanoparticles (nanocrystals, Carbon nanotubes, etc.) are microscopic particles. They are usually between 1 and 100 nm in size in each spatial dimension and are considered to be the building blocks of the next generation of optoelectronics, electronics, and various chemical and biochemical sensors. A variety of nanomaterials are at various stages of research and development, each one possessing unique functionalities that are potentially applicable to the remediation of industrial effluents, groundwater, surface water, and drinking water. Silver nanomaterials are the most interactive in the application of nanotechnology. Silver nanoparticles can be used in the development of antibacterial water filters for the treatment of waters [222]. Tran and coworkers [223] reviewed Silver nanoparticles in depth and assessed synthesis, antibacterial effects, toxicology to humans and the environment, current applications, and future prospects. Silver nanoparticles are of great interest due to their optical, electrical, and antimicrobial properties [224].

3.2. Sustainable Green Metal Mining. In recent decades, techniques for mining metals using plants—phytomining—have offered scientists the possibility to extract metals from low-grade ores, overburdens, mill tailings, or mineralized soil that would be uneconomical to mine using conventional methods [19]. Plant hyperaccumulators accumulate large amounts of metals in their roots, such as Nickel and Thallium, and hence provide a potential route for soil remediation and for the recovery and reuse of the metal [193]. Phytomining not only produces ingots of Gold but, interestingly and importantly, this technique can also be used to produce Gold nanoparticles, which are of huge potential to nanotechnology industries [211–213]. The biological systems that are used in the synthesis of nanoparticles exhibit water-soluble and biocompatible properties that are essential for many field applications, from medicine to electronics [76]. A variety of microorganisms, plants, and plant parts, including roots, stems, leaves, and bark, provide low-cost, energy efficient, and nontoxic methods of synthesizing nanoparticles. Heavy metals can be removed from contaminated soil and water via hyperaccumulation, either through phytoremediation or through phytomining, for later use as material productions in nanotechnology.

4. Conclusion

This work reviewed existing research that examines the potential of the bioremediation process for recovery of heavy metals from contaminated water and soil sources. The use of cheap and easily obtained biomass using this approach offers a low-cost and environmentally friendly solution and has the potential to be used for large-scale bioremediation. Biosorption-based bioremediation represents a low-cost and environmentally friendly method of metal recovery that may offer a means of avoiding metal depletion. The bioremediation process proposed could produce metal nanoparticles through biosorption-based biosynthesis, which also uses the biomass from plants and microorganisms. Metal nanoparticles are very important for high technology applications, such as biomedical applications, sensors, MEMS (microelectromechanical systems) and NEMS (nanoelectromechanical systems), catalysts, and antimicrobial agents. Phytomining is an environmentally friendly method of removing heavy metals from wastewaters and soil. This method is important, especially in areas in which the soil contains high levels of heavy metals.

Based on the past and present works of research in bioremediation and phytomining processes, the future of such attempts looks bright. Regarding the conversion of heavy metal effluents from waste material to a valuable resource for research, development, and industry, there is still a plenitude of basic research that needs to be performed to establish the basics, especially concerning which plants can be used on which soils with which pollutant concentration and in which environment (e.g., other plants and microbiome communities, latitude, and longitude).

The continuous implementation of both bioremediation and phytomining processes offers great benefits of green methods in various fields, such as environment, resources, economy, and human life. Comprehensive research and development for improvement of both processes promise a bright future for successful implementation of biomimetic approaches in resource management.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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