pollutants

Review

Nano-Phytoremediation of Heavy Metals from Soil: A Critical Review

Priyanka Prakash and Smitha Chandran S *

Department of Chemistry, Amrita Vishwa Vidyapeetham, Amritapuri Campus, Kollam 690525, Kerala, India
* Correspondence: smithachandran@am.amrita.edu

Abstract: Heavy metal pollution is one of the major global issues arising from various anthropogenic activities. The natural habitat and human health may be at peril from heavy metal exposure since they are tenacious, bio-accumulative, and non-biodegradable. Therefore, eradicating heavy metals from the soil ecosystem is a crucial responsibility to create a secure, viable, and zero-waste ecosystem. There are numerous techniques for eliminating heavy metals from the environment, but each has its own benefits and drawbacks. When a biological agent is used to degrade pollutants, this process is called bioremediation. Nano-phytoremediation, an emerging bioremediation approach in the field of nanotechnology, uses biosynthesized nanoparticles and plant species for the removal of toxic heavy metals from the environment. It is an efficient, economical, and environmentally friendly technique. The adverse consequences of metal exposure on different plant species have been discovered to be greatly reduced by engineered nanomaterials. Because of their tiny dimensions and huge surface area, nanomaterials have an attraction towards metals and can thus quickly enter the contaminated zone of ecosystems that are metal-challenged. The current review provides an overview of various aspects of nano-phytoremediation for heavy metal remediation.

Keywords: phytoremediation; nano-phytoremediation; heavy metals

check for updates

Citation: Prakash, P.; S, S.C. Nano-Phytoremediation of Heavy Metals from Soil: A Critical Review. *Pollutants* **2023**, *3*, 360–380. https://doi.org/10.3390/pollutants3030025

Academic Editor: Ali Elkamel

Received: 8 November 2022
Revised: 27 February 2023
Accepted: 26 May 2023
Published: 1 August 2023

Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Due to its great potential toxicity, heavy metal poisoning of soil is currently an important world-wide issue. The ecosystem and human health may both be greatly damaged by soil contamination caused by hazardous heavy metals. Heavy metal contamination has become a serious threat to the ecosystem and food security due to the accelerated growth of agriculture sectors and industries. Along with this, disruption of the natural habitat brought on by the enormous rise in the world's population has also increased heavy metal contamination on earth [1]. The prevention and management of heavy metal pollution are among the more influential areas of environmental research [2,3]. Because of their lengthy persistence and lack of degradability, they bioaccumulate and bio-magnify all along the food web, eventually leading to harmful consequences on human health [4]. A significant number of heavy metals frequently end up in the bodies of species at the upper levels of the food chain owing to their age, well-being, and dietary habits. The root system and performance characteristics of plants will also be destroyed by heavy metals in the soil [5].

Heavy metals are chemically defined as metals and metalloids with atomic numbers beyond 20 and specific gravities more than 5 g cm^{-3} [6]. Presence of heavy metals can cause toxicological changes in the soil-dwelling organisms on the surface of the earth, which may have an adverse effect on both their viability and functionality [7]. The main heavy metals consist of arsenic (As), lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), nickel (Ni), copper (Cu), and zinc (Zn) [8]. Heavy metals can be categorized into four main groups according to their use and toxicity: heavy metals that are essential (such as Cr, Cu, Mn, Zn, and Fe) and non-essential (Li, Ba, Zr, etc.), and highly toxic (Hg, As, Cd, etc.) and less toxic (Sn, Al, etc.) metals [9]. The term "micronutrient" also refers to essential heavy metals. These are necessary for proper health, growth, reproduction, and disease resistance of human beings. However, consuming more than what is allowed can be harmful and harm the organisms [10]. Even at smaller concentrations, highly toxic metals are generally known to be extremely harmful [11].

Biological, physical, and chemical techniques have been applied to remove these heavy metals from the environment over the years. Physical and chemical remediation techniques are high cost, destroy the soil microbial community and adversely affect the soil texture. Utilizing several methods, including plants, animals, and microorganisms, bioremediation removes toxins without harming the environment. Phytoremediation is a fruitful, environmentally friendly, and cost-efficient method of bioremediation. This method is increasingly utilized to clean up heavy metal and hazardous organic compound contaminated locations. This method is also used to remove radioactive contaminants from groundwater and agricultural lands. Phytoremediation is a low-cost method that works best when contaminants are present in the plant's root zones. Flax (*Linum usitatissimum*) is a viable target for the phytoremediation of Cu because it can remove significant amounts of Cu from soils and can be developed to produce flax seed [12]. The removal of heavy metal contamination can be accomplished by different phytoremediation techniques, including phytostabilization, rhizofiltration, phytoextraction, and phytovolatilization. Along with plants, the rhizospheric bacteria are crucial in the process of purifying contaminated areas. To reduce organic and inorganic pollutants, both plants and microbes use the same phytoremediation principles that nature uses [13].

It has been found that using engineered nanomaterials can significantly lessen the adverse effects of heavy metals on plants [14,15]. Because of their enormous surface area and high reactivity compared with their bulk form, nanomaterials are helpful for the remediation method and may rapidly penetrate contaminated locations. Thus, the application of nanotechnology in the area of phytoremediation has a high potential for removing contaminants from both soil and water. Both technologies are complementary to each other. Nano-phytoremediation has a more cumulative effect than the impact of an individual technology. Many researchers are interested in using plants and nanomaterials together to manage the environment since some nanomaterials can enhance the growth of plants and improve the absorption of major heavy metals by plants, increasing the effectiveness of phytoremediation in heavy-metal-contaminated soil. A study by A.G. Khan et al. (2020) suggests that, these days, the most promising technologies are phytotechnology and nanobiotechnology [16]. The current review focuses on the various aspects of nano-phytoremediation of heavy metals. It also discusses the conventional methods used for heavy metal remediation and how nano-phytoremediation is more beneficial.

2. Heavy Metals

2.1. Heavy Metal Sources and Their Global Status

Heavy metals enter ecosystems through both natural and man-made processes. Rain, snow, volcanic eruption, and wildfires are a few examples of natural sources of heavy metals, while man-made sources include fertilizers, combustion of fuels, mining, construction works, deforestation, and various industrial activities [11,17]. Different natural sources of major heavy metals are showed in Table 1.

Table 1. Major heavy metals present in nature and their sources.

Heavy Metals	Sources	References
Chromium	Chemical manufacturing industry, cement production, sewage sludge, electroplating, air conditioning cooling towers, combustion of petroleum products, leather industry, and textile industry.	[9]
Lead	Lead-based paints, other petrol-based materials, pesticides, and batteries.	[9]
Cadmium	Volcanoes, refining of petroleum products, paint, pigment stabilization, Ni–Cd batteries, pesticides, electroplating, and poly vinyl chloride manufacturing.	[9]
Arsenic	Industrial dust, mining activities, smelting activities, combustion of fossil fuels, arsenic pesticides, automobile exhaust, wood preservatives, and dyes.	[9,18]

Arsenic is one of the common elements that surround us. It ranks as the 12th most prevalent element in humans, the 20th most prevalent element in the crust of the earth, and the 14th most prevalent element in the ocean [19]. A total of 41% of the world's 1.4 million arsenic-polluted sites are in the United States, and the USEPA has stated that Australia has an arsenic (As) concentration of more than ten thousand milligrams per kilogram [20]. Pakistan has many shallow reservoirs and bore wells that are polluted by arsenic and it also exceeds the USEPA's suggested guidelines for arsenic concentration of ten parts per billion [21]. In several nations around the world, groundwater has been discovered to be contaminated with arsenic [22]. Groundwater toxicity in Asia, particularly in South Asia, is concerning. It has been observed in Vietnam's Red River Delta and the Mekong Basin of Cambodia and Vietnam, Nepal's Terai Belt, and the Bengal Basin of India, Bangladesh, and Pakistan. As a result, at least 100 million people in these countries are in peril of developing different As-related diseases such as cancer. Pentavalent arsenic is easier to dispose of than trivalent arsenic. Hence, the latter must be oxidized before being removed [23]. More than 200 enzymes can be rendered inactive by arsenite by it interacting with the thiol groups present on the proteins, and arsenate can take the place of phosphate in numerous metabolic pathways [24].

According to estimates, the total Cr output worldwide since the dawn of the industrial age is 105.4 million tonnes, which is a huge rise from the 1950s [25] Unlike other heavy metals, Cr pollution has received less attention since it is absorbed poorly and transferred by plants, which makes it uncommon for Cr phytotoxicity and build-up within the food chain to occur under field settings. Chromium (VI) compounds are far more serious for employees and the general population in terms of toxicity and carcinogenicity than trivalent and other valence states of chromium compounds. By influencing soil microbes and altering the ecosystem of these enzyme-rich soil microbes, chromium may influence the activity of various soil enzymes [26,27]

Due to its harmful effects on living beings, cadmium is a heavy metal that poses an alarming situation for the environment. It is more mobile than zinc at pH 4.5 and 5.5, but when the pH range is over 7.5, it becomes stationary. Over the past 130 years, a steady hike in the Cd concentration of soils in the United Kingdom has been documented, with the last 20 years seeing the biggest increase [28]. In Japan, where many people consume rice that has been cultivated in cadmium-polluted irrigation water, environmental exposure to cadmium has proven to be particularly troublesome (http://www.kanazawa-med.ac.jp/~pubhealt/cadmium2/itaiitai-e/itai01.html, accessed on: 27 August 1997). The quantity of cadmium that may be emitted into the air from disposal sites and incinerators is restricted by several state and federal rules in the United States, ensuring that properly managed sites remain safe. Cadmium can prevent the function of enzymes and prevent DNA-mediated transformation in microbes present in the soil [29].

Lead is a dangerous environmental pollutant that is highly poisonous to numerous body organs. Lead-based paint is found in many houses constructed before 1978. The US federal government outlawed lead-based paint in residential structures in 1978. (http://www.epa.gov/lead, accessed on: 30 January 2013). The Restriction of Hazardous Substances Directive, adopted by the European Union in 2003, also restricted the use of lead (https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:174:0088:0110:en:PDF, accessed on 1 January 2020). In 1993, lead shot was made illegal nationally for use in sport shooting and hunting, and thus lead deposition in the Netherlands significantly decreased, from 230 tonnes in 1990 to 47.5 tonnes in 1995. It has a variety of adverse effects on living creatures at different levels because of its high immobility, concentration in the top 8 inches of the ground, and high consistency in soil [30–32].

Various biological, chemical, and physical techniques have been used over time to remove various heavy metals from the ecosystem. Most of the existing heavy metal remediation techniques rely on different physicochemical methods. Physical remediation techniques generally necessitate a significant amount of manpower and material resources, whereas chemical approaches require a higher cost percentage for chemicals or reagents [33]. In addition, the microbial community in the soil is destroyed by physical and chemical remediation techniques, which are also expensive and have negative effects on the soil's texture.

2.2. Conventional Techniques for Heavy Metal Remediation

In recent times, various approaches and technologies have been employed in the remediation of heavy metals in polluted environments such as soil and water. These techniques include physicochemical and biological methods, which are further subdivided into in situ and ex situ bioremediation.

2.2.1. Physicochemical Method

This remediation could be accomplished through physical and chemical methods such as precipitation, ion exchange, filtration, ultrafiltration, reverse osmosis, evaporative recovery, solvent extraction, solvent extraction, electrochemical treatment, electrodialysis, electrokinetics, land filling, chemical oxidation, chemical leaching, chemical reduction, and mechanical separation of metals [34–37]. Some disadvantages of these techniques include incomplete metal removal, high solvent requirements, and the generation of toxic waste products. They also have an adverse environmental impact and are usually soil-disturbing. In addition to this, they are labor intensive, expensive, and have high energy requirements [38].

2.2.2. Bioremediation

Bioremediation can be further classified as in situ or ex situ bioremediation. Methods of in situ bioremediation treat pollutants at the site without attempting to remove soil. They include mechanisms for removing specific contaminants from the natural habitat using the metabolic potential of the microbial system without extraction of polluted samples [39]. Ex situ bioremediation is the process of excavating and treating soil prior to returning it to its original state [40]. Ex situ remediation techniques are more costly than in situ remediation techniques.

Major in situ bioremediation techniques include:

Bioaugmentation: Certain sites in bioaugmentation necessitate microorganisms to extract pollutants. They can also surpass indigenous microorganisms so that they can clean up the site quickly. In practice, mixed cultures containing a wide range of microorganisms are employed for bioaugmentation [41]. A *Bacillus* sp. strain and a *Streptomyces* sp. strain bioaugmented a cadmium-enriched soil environment, and a consortium of filamentous fungi used bioaugmentation to remove heavy metals such as Ni, Pb, and Zn [42]. In a study, bioaugmentation and bioaugmentation-assisted phytoremediation were both used to treat soil contaminated with heavy metals such as Zn, Cr (III), Cr (VI), and Al. A significant reduction in the bioavailability of all heavy metals was observed in bioaugmentation experiments where cyanobacteria inoculation was combined with an increase in the biochar dose (from 0 to 5%). The results of bioaugmentation-assisted phytoremediation using Portulaca oleracea, biochar, and cyanobacteria revealed a significant decrease in the bioavailability of all heavy metals, particularly at a 5% dose of biochar [43]. There have been numerous drawbacks reported for this technique. For example, it has been noticed that the population of exogenous microorganisms decreases after their introduction to a contaminated environment due to various factors, which occur as a result of a lack of growth nutrients, temperature changes, and pH, as well as competition between introduced and indigenous microorganisms [44,45].

Bioventing: Microbial conversion of pollutants to a nontoxic state occurs in bioventing through the introduction of nutrients and moisture [46]. To release pollutants into the atmosphere via biodegradation, bioventing necessitates a restricted flow of air and reduced oxygen rates. Its main disadvantage is its incapability to provide oxygen to polluted soil and the inadequate ventilation of narrow contamination [47].

Bioattenuation: The process depends on converting pollutants into less dangerous forms or immobilized forms [48]. By using proteobacteria-mediated bioattenuation, metals such as As, Ni, and Al were successfully eliminated, according to a 2017 study by Fauziah et al. (2015) [49]. Acinetobacteria were discovered to participate in the bioattenuation process for the natural elimination of metals such as U, Al, Cd, Co, Cu, Mn, and Ni [50]. Even though this method is frequently viewed as the "do nothing" approach, it necessitates proper surveillance of polluted soil [51].

Biosparging: This method involves injecting air into the subsurface of soil to speed up the rate at which naturally occurring bacteria break down contaminants biologically [52]. Biosparging focuses mainly on saturated polluted areas with respect to groundwater remediation [53].

Biostimulation: By providing soil microorganisms with the ideal environment, biodegradation can be stimulated [51]. For bioremediation to be effective, a number of soil physiochemical components, such as moisture, redox conditions, temperature, pH, organic matter, and nutrients (C, N and P), are required. These components also affect the microbial activity and chemical diffusion in the soil [54]. Kanmani et al. (2012) used clusters of bacteria isolated from polluted areas in their biostimulation study for removing Cr [55]. Fulekar et al. (2012) used aerobic bacteria cultured from isolated heavy metals in their biostimulation study for eliminating Fe, Cu, and Cd.

Bioslurping: By simultaneously using vacuum-enhanced recovery, soil vapor extraction, and bioventing, soil and groundwater remediation is accomplished by indirectly incorporating oxygen and promoting pollutant biodegradation [56]. The main issue with this specific "in situ" technique is the creation of a vacuum on a deep, permeable site with a fluctuating water table because it results in saturated soil lenses that are challenging to aerate.

Major ex situ bioremediation techniques include:

Bioreactor: This is a vessel constructed for the removal of pollutants from pumped groundwater or wastewater using microbes. To attain a high output of bioremediation, the system could include the tissues, microorganisms, and animal, plant, and enzyme cells. Since this target environment in bioreactor systems is simpler to manage, control, and predict than in other systems, biodegradation occurs at a higher rate overall than in other systems. Despite the benefits of reactor systems, it is discovered that the polluted environment needs the pollutants to be physically removed from the soil before being treated by a bioreactor. This method is not cost-effective because treating a high quantity of polluted soils or other substances and transferring pollutants to the site of treatment requires more labor, money, and safety precautions. With so many bioprocess variables in a bioreactor, if any variable is not regulated properly it turns into a limiting factor and lowers microbial activity, making the technique less effective. It is also crucial to have the best design available because pollutants react differently to different bioreactors [46,52]

Land farming: Land farming is a simple and direct process that involves excavating polluted soil over a prepared site with regular tilling until pollutants are degraded via microorganisms, with the practice being restricted to the treatment of a small part of the soil [57]. Due to the release of volatile organic compounds (VOCs), land farming causes air pollution issues and health risks for workers. These issues can be mitigated by wrapping the space with a greenhouse arrangement to reduce the dust. The method is simple and very effective, especially when applied to soil that has been polluted with petroleum. The method can only treat a small area of the upper soil, though. It is limited in some more ways. It necessitates a sizable operating area, extra expense because of excavation, a decrease in microbial activity because of unfavorable environmental conditions, and a decreased efficacy in inorganic pollutant removal [58,59].

Biopile: Composting and land farming are combined or hybridized in biopiles. For various microorganisms, biopiles create enriched environments. As it is more effective than land farming and composting at transferring water, nutrients, and air in large quantities, the biopile is regarded as a better pollutant removal strategy. Heavy metal removal from soil can be accomplished using this method [60]. One of its drawbacks is that it is challenging to accomplish a decline in the constituent concentration of more than 95% and 0.1 ppm (ppm).

3. Nanomaterials and Phytoremediation

There are benefits and drawbacks to each of the above-said ex situ and in situ bioremediation methods. Phytoremediation is a successful, environmentally responsible, and economically advantageous form of bioremediation. The term "phytoremediation," which combines the Greek words "phyton" for plants and "remediare" for "to remediate," describes a process in which specific plants and soil microbes work together to transform toxins into safe and frequently lucrative forms. The idea to utilize plants to eliminate hazardous metals from polluted soils was inspired by the discovery of a variety of wild plants, many of which are indigenous to naturally mineralized soils and collect considerable levels of metals in their leaves [61,62]. Plants have demonstrated the ability to survive comparatively high levels of xenobiotic chemicals without experiencing toxic effects, and, in some circumstances, they can quickly absorb chemicals and transform them into less toxic metabolites [63–66]. Heavy metal hyper-enriched plants, also known as hyperaccumulator plants, are those that take up many heavy metals and remove them from the environment [67]. This technique is used increasingly to clean up areas that have been contaminated with heavy metals and dangerous organic compounds. The effectiveness of phytoremediation, a low-cost technique, depends on the presence of contaminants in the plant's root zones. Phytoextraction, phytodegradation, phytostabilization, phytovolatilization, and rhizofiltration are the major mechanisms used by plants for remediation.

Phytoextraction: This process is also referred to as "phytoaccumulation." In this mechanism, the root system of the plants absorbs the pollutants and transports them to the plant parts located above the ground level. The main purpose of phytoextraction is to treat polluted soils. This technique makes use of plants to draw harmful metals from contaminated soils, concentrate them, and then precipitate them into the biomass above ground. The ability of plants to absorb metals from contaminated soil has been revealed by the identification of metal hyperaccumulator species. When compared with more conventional mechanisms, phytoextraction has the benefit of being relatively affordable. The fact that the contamination is eliminated from the soil is an additional advantage. In some circumstances, the pollutant is recovered from the biomass of the contaminated plant, which also significantly reduces the amount of waste that must be discarded. Because of their slow development, low yield of biomass, and poor root systems, hyperaccumulator species are not widely used. The biomass of plants must also be appropriately gathered and carried out in compliance with regulations. Some of the parameters limiting the degree of phytoextraction of metals include metals' bioavailability in the rhizosphere, speed of accumulation of metals by roots, the amount of metal present in the roots, the pace of xylem loading to shoots, and cellular resistance to hazardous metals [68–70]. The presence of nanoparticles enhances the phytoextraction mechanism. Liang et al. (2017) investigated the effects of nano-hydroxyapatite on Pb phytoextraction using ryegrass. After 1.5 months, the addition of 0.2% nano-hydroxyapatite substantially enhanced the concentration of Pb in the overground part of the plant [71]. Several nanomaterials have been shown to boost Cd phytoextraction in soil [72].

Phytodegradation: Phytodegradation is the term used to describe the metabolic breakdown of organic contaminants by enzymes. In plant sediments and soils, enzymes such as nitroreductase, dehalogenase, nitrilase, laccase, and peroxidase have been found. Phytodegradation may take place in soil environment where biodegradation is not possible. One of the drawbacks of this mechanism is that it generates hazardous intermediates or degradation products [68,73–75]

Phytostabilization: This process is also known as in-place inactivation. It is commonly used for sediment and sludge remediation. Certain plant species are used to absorb and accumulate toxins in the soil. This procedure adsorbs chemicals to roots or precipitates contaminants within the plant's root zone. It lessens the contaminant's mobility, avoids migration to the groundwater, and lowers the metal's bioavailability to the food web. Sorption, complexation, or precipitation can result in phytostabilization. This method has several benefits, such as not requiring the handling of waste materials or biomass and being particularly successful when quick immobilization is necessary to protect ground and surface waterways. However, this clean-up technology has several significant drawbacks, including the fact that contaminants remain in the soil, that extensive fertilization or soil amendments must be applied, that mandatory monitoring is necessary, and the possibility that the stabilization of the pollutants may be primarily attributable to the soil amendments [69]. According to Vitkova et al. (2018), the concentration levels of heavy metals Cd, Pb, Zn, and As in both shoots and roots were reduced by 50–60% by using nano-zero-valent iron (nZVI) for phytostabilization [76].

Phytovolatilization: In this method, plants absorb pollutants from the soil, convert them into volatile forms, and then release these into the environment through transpiration. Contaminants are also ingested by plants by phytovolatilization; however, the contaminants, a volatile form of them, or a volatile breakdown product are then transpired with water vapor from leaves. Phytovolatilization is common for the elimination of pollutants present in the sediment, water, or soil. Arsenic and mercury are frequently investigated heavy metals in phytovolatilization as they exist in volatile forms and can be biologically converted into gaseous species by plants. The benefit of this procedure is the possibility of changing the pollutant into a less harmful chemical. This has the drawback of repeating the anaerobic bacteria's creation of methylmercury by releasing mercury into the atmosphere, which is subsequently recycled by precipitation and deposited again into lakes and oceans [68,77]

Rhizofiltration: Rhizofiltration is frequently used to remove metals or other inorganic compounds from wastewater, surface water, or groundwater. Rhizofiltration is identical to phytoextraction, except the focus is on treating contaminated groundwater as compared to soil. In greenhouses, the plants that will be used for clean-up are grown with growing roots under water instead of dirt. Once a substantial root system has been established, it is necessary to acclimatize the plants by providing them with contaminated water from a waste site in place of their natural source of water. Then, the plants are placed in the polluted region, where their root system absorbs both the toxins and the water. The roots are harvested as they become saturated with pollutants. The benefits of rhizofiltration include the use of both terrestrial and aquatic plants for in situ and ex situ uses. The fact that pollutants do not need to be transferred to the shoots is an additional benefit. The utilization of species apart from hyperaccumulators is thus possible. Because their roots are longer and more fibrous, the roots of terrestrial plants have a larger surface area, and they are preferred for this process. The consistent need to adjust pH is one drawback, as is the requirement for plant growth in a greenhouse or nursery. Other drawbacks include the requirement for periodic plant harvesting and disposal, the need for a well-engineered tank design, and the requirement for a thorough understanding of chemical speciation and interactions [68].

Summary of all the major mechanisms used by plants for remediation is given in Table 2

Numerous benefits come with phytoremediation, such as habitat restoration, lower installation and maintenance costs, and the ability to clean up pollutants locally rather than having to move the issue to another location. With phytoremediation, the addition of organic matter could increase soil fertility [78].

Nanomaterials are useful for the remediation process because they can quickly enter contaminated areas and have a large surface area relative to their bulk form [79,80]. Nanotechnology improves the effectiveness of phytoremediation, and nanoparticles can be used to clean up soils and water contaminated with heavy metal, organic, and inorganic pollutants [81]. Since some nanomaterials can boost plant growth and significant heavy metal absorption by plants, enhancing the efficacy of phytoremediation in heavy-metal-contaminated soil, many researchers are interested in combining plants with nanomaterials to manage the environment. Jiamjitrpanich et al. (2013) assert that the remediation of TNT from the soil is more successful when nanotechnology and phytotechnology are combined. The current study covers topics regarding nano-phytoremediation in the removal of heavy metals from soil [82].

Table 2. Summary of different phytoremediation techniques.

Phytotechnology	Mechanism	Pollutants
Phytoextraction	Hyperaccumulation in different parts of plants that are harvestable	Inorganic: Pb, Zn, Au, Co, Cr, Ni, Hg, Mo, Ag, Cd Radionuclides: Pb, Sr, U, Cs
Rhizofiltration	Rhizosphere accumulation through precipitation, sorption, and concentration precipitation	Inorganics or organics: metals such as Cr, Cd, Cu, Ni, radionuclides
Phytovolatilization	Pollutant eradication	Organic compounds, phenols, chlorinated solvents, munitions herbicides
Phytostabilization	Sorption, precipitation, and complexation	Inorganic: Cu, As, Cr, Zn Cd, Pb

3.1. Nanoparticles: Advantages and Synthesis

Because of the nanoscale structure of the nanoparticle, its higher surface area to volume ratio, its reactivity, etc., nanoparticle chemical and physical characteristics differ from those of their original bulk particle [79,80]. Nanoparticles can be used to eliminate metal ions from soil ecosystems in a very efficient manner. However, several studies support both the beneficial and detrimental effects that these nanomaterials have on plants [14,83–85]. TiO_2 nanomaterials increase the photosynthetic rate and reduce oxidative stress generated by UV-B in spinach [86,87]. nZVI raises plant biomass while lowering the absorption rate of heavy metals in the soil [88].

There are numerous synthesis processes for nanoparticles, but the most common are top-down or bottom-up approaches. Bottom-up techniques are commonly used for regulated size, shape, and chemical composition [89–93]. Biosynthesis is an example of the bottom-up method. Biosynthesis of nanoparticles has many benefits in terms of eco-friendliness and suitability for pharma and other biomedical applications because harmful chemicals are not employed in the synthesis process [94]. The main chemical reaction taking place during the biosynthesis of nanoparticles is either oxidation or reduction [95]. The advancement of phytonanotechnology has paved a novel way to produce nanoparticles, and the technique is relatively easy, scalable rapid, environmentally benign, biocompatible, and economical [96]. In-depth research has been done on the reduction of metal nanoparticles by mixtures of biomolecules found in plant extracts, such as polysaccharides, proteins, enzymes, vitamins, and amino acids usually obtained by contacting a broth of plant leaves with metal salts [97]. Materials derived from plants tend to be the best options among all the reagents used in biosynthesis, and they are suitable for the large-scale production of nanoparticles. Similar to methods involving plant-based materials, microorganisms can also be used to produce nanoparticles, but their rate of synthesis is slower and they are only capable of a small range of sizes and shapes [98].

3.1.1. Synthesis of Nanoparticles from Microbes

Microbes have been discovered as an excellent constituent for the biosynthetic pathways of nano-sized particles, with the significant promise of being an ecologically benign and economical technique, eliminating hazardous, hard chemical substances and avoiding high energy demand for physiochemical synthesis methods. Because of various reductase enzymes present in them, microorganisms are good at the absorption and detoxification of heavy metals, and they can convert metal from its salt form to zero-valent metal nanomaterials with small size distributions and hence less polydispersity. Over the last few years, microorganisms such as bacteria, yeast, and fungi have widely been studied for the creation of nanoparticles. Most fungi with considerable metabolites with increased bioaccumulation potential are suitable for culture used for efficient, low-cost formation of nanoparticles.

Furthermore, fungi have better tolerating and absorption abilities for nanoparticle synthesis than other microbes, notably in regard to their high binding capacity of fungi with metal ions for increased nanoparticle production. In recent times, the eco-friendly production of ZnO nanoparticles using *Cochliobolus geniculatus* fungi was investigated. The ZnO nanoparticles formed were discovered to be detoxing, distinct, and spherical structures in the size range of 2 nm to 6 nm, and they exhibited an energy gap of 3.28 eV [99]. Copper oxide nanoparticles mediated by green have been created utilizing the fungus strain Trichoderma. Cu $(NO_3)_2 3H_2O$ was introduced to a mycelial-free water extract and mixed overnight in the absence of light at 40 °C, followed by 3 h of heating at 75–80 °C. The color of the solution altered showing the presence of copper oxide nanoparticles.

It is found that the major mechanism of bacterial nanoparticle production is based primarily on enzymes. Bacteria such as Streptomyces anulatus, Pseudomonas deceptionensis, Bacillus amyloliquefaciens, Bacillus subtilis, Bacillus methylotrophicus, Bacillus licheniformis, Listeria monocytogenes, Weissella oryzae, Rhodobacter sphaeroides, and Brevibacterium frigoritolerans have recently been studied for metal nanoparticles synthesis. Five psychrophilic bacteria, Arthrobacter gangotriensis, Arthrobacter kerguelensis, Pseudomonas proteolytica, Pseudomonas antarctica, and Pseudomonas meridiana, and two mesophilic bacteria, Bacillus cecembensis, and Bacillus indicus, were used to make very stable nanoparticles of silver. The mean dimension of the produced nanoparticles of silver ranged from 6 nm to 13 nm [100]. Kirthi et al. (2011) used the bacterium Bacillus subtilis to create titanium dioxide nanoparticles [101]. Jha et al. (2009) described Lactobacillus-sp.-mediated production of TiO_2 nanoparticles as a low-cost green biosynthetic technique [102]. The mean particle size was determined to be around 30 nm.

3.1.2. Synthesis of Nanoparticles from Plants

Scalability and biocompatibility are the two main benefits of producing nanoparticles from plants. Ag nanoparticles are the most popular nanomaterials created via the biosynthetic approach owing to the antimicrobial qualities of Ag nanoparticles, and the ease with which silver salts can be reduced to zero-valent silver, etc. Shikuo Li et al. (2007) created nano-sized silver from the extract of the plant species *Capsicum annuum* [103]. The synthesis process was uncomplicated, with nanoparticles forming as many crystalline parts converting to a single crystal in the process and the mean size of nanoparticles increasing as the reaction continued. *Brassica juncea* seedlings were used in the in vitro synthesis of silver nanoparticles by Shekhawat and Arya (2009) [104]. In vitro grown *B. juncea* seedlings and plants that were 14 days old were placed in a nutrient solution with the addition of $AgNO_3$, and they were then grown in a hydroponic atmosphere for seven days. The plants that emerged from this process were then collected and examined using TEM and a UV-VIS spectrophotometer, which demonstrated the existence of tiny Ag nanoparticles. The possibility of using the dried plant materials from the *Ocimum sanctum* plant in the production of silver nanoparticles has been explored. The method was easy and performed at normal temperature, with the extract of plants serving as the reducing agent in the process [105]. *Cinnamon zeylanicum* powder and extract from the plant's bark were used to develop Ag nanoparticles. The number of Ag nanoparticles prepared was greater in the bark extract than in the powder due to the abundance of reducing agents in it [106]. The leaf extract of *Pelargonium graveolens* was also studied to produce Ag particles on a nanometer scale. Nano-sized Ag particles have been synthesized due to the fast reduction of the Ag^+ ions in the solution [107]. According to reports, the sustainable production of nano-sized silver particles using leaf extract *Psidium guajava* as the reduction and capping agent is very easy and expensive. This plant was chosen for the experiment due to its proven medicinal benefits, and it is conveniently available everywhere in all seasons of the year [108]. Abhirami et al. (2020) presented an uncomplicated and inexpensive method for the green production of Ag nanoparticles utilizing onion peel extract, a common household waste, under normal pressure and temperature settings [109]. Nonetheless, silver nanoparticles in plants are largely explored since silver not only creates nanoparticles in plants but also has stronger catalytic characteristics due to its high electrochemical reduction potential and several other relevant qualities. An easy biological method for the production of gold nanoparticles utilizing *Cassia auriculata* extract (leaf) was also investigated [110]. The production of TiO_2 nanoparticles utilizing *Jatropha curcas* was researched and evaluated [111]. Abisharani et al. (2019) utilized Cucurbita pepo seeds extract to form titanium dioxide nanoparticles from titanium trichloride solution in a greener pathway [112]. K. Ganapathi Rao et al. (2015) employed a green synthesis method to create TiO_2 nanoparticles from aloe vera plant leaf extract [113]. The production of ZnO nanoparticles in a single-pot biological process employing leaf extract of *Barbadensis Miller* was explored. This method is preferable as it does not require the use of high temperatures, pressure, energy, and dangerous compounds in nanoparticle formation [114]. Inexpensive starting materials such as zinc nitrate and plant ingredients such as *Azadirachta indica* were utilized in a simple biological synthesis of ZnO nanoparticles. Natural products have components of phenol and flavonoid, which are soluble in water and play an essential function in the reduction [115]. *Punica granatum* peel extract was utilized to make copper oxide nanoparticles. The extracts made from the peel were introduced into a copper salt solution (copper acetate monohydrate) and stirred for 10 min at normal temperature. The fluid changed its color from green to brown, showing the formation of copper oxide nanoparticles.

4. Nano-Phytoremediation for Heavy Metal Elimination

The rising utilization of heavy metals across a wide range of sectors has led to a major ecotoxicological issue that can affect the entire globe. Phytoremediation, a low-cost and ecologically sustainable substitute to conventional physicochemical clean-up methods, has developed to resist contamination due to heavy metals. The removal of these harmful metals/metalloids from ecosystems can be enhanced using nanomaterials along with phytoremediation. According to data from various research, the utilization of nanoparticles could enhance the phytoremediation of soil polluted with chromium, cadmium, zinc, nickel, and lead [14,71,72,76,116]. Mitigating heavy metal stress in plants using nanoparticles is one of the biggest issues the modern industrial world is currently dealing with [14]. The presence of certain nanoparticles can improve the antioxidant status of plants, enhancing their capacity to withstand harsh conditions. On the other hand, certain plant species may experience oxidative stress when exposed to the same or different types of nanoparticles, which can interfere with the activity of certain enzymes. [86,117].

4.1. Uptake of Heavy Metals and Its Tolerance

The mechanism governing heavy metal tolerance in plant cells includes the following steps: the roots of plants absorb heavy metals from the soil ecosystem, binding of heavy metals to cell walls, active ion transport into the vacuole, chelation via activation of peptides that aid metal-binding, and synthesis of metal complexes [118,119]. The root plasma membrane's unique transporters, also known as channel proteins, are responsible for absorbing heavy metal ions [120,121]. Heavy metal exposure can result in the production of the oligopeptide ligands phytochelatin and metallothionein in plant tissues. Phytochelatins are formed using glutathione and are subsequently transformed into peptides. The main prerequisite for phytoremediation to work effectively is heavy metal tolerance. Plants have numerous techniques for heavy metal elimination and tolerance. They each have their own special qualities and contribute in varying amounts to detoxify various heavy metals. Plants employ their techniques to keep the concentrations of heavy metals in their cells below the severity boundary levels [122,123]. By producing organic acids, several plants have the capacity to detoxify the heavy metals inside the rhizosphere and decrease their accessibility. Another method of heavy metal detoxification is the immobilization of heavy metals in the root system by linking them to pectins present in cell walls and the cytoplasm–membrane interfaces that are negatively charged because of their significant electrochemical potential. By producing redox enzymes, which allow hazardous metals to be changed into less hazardous ones, some plants can lower the valence of heavy metals.

Selecting the right plant species relies on various factors, including its ability to cope with the specific metal, achieve restorative characteristics, and adapt to other site-specific aspects [124]. Additionally, the chosen plants should have traits such as high plant biomass, a highly branching root system, good growth and production, being able to withstand pollutants, susceptible to genetic modification, and easy to harvest. In order to be used in phytoremediation, nanoparticles must not be harmful to plants. The use of specific nanoparticles has greatly enhanced plant development, and nano-augmentation has raised the capacity for phytoremediation, resulting in higher removal of pollutants from the soil ecosystem. Due to their ability to support plant development hormones and improve plant species' ability to absorb contaminants, many nanoparticles have been recognized as the catalyst for growing plants.

The function of TiO_2 nanoparticles in plants has been explored the most thoroughly among the nanoparticle types. Under both typical and stressed circumstances, TiO_2 nanoparticle application resulted in improved plant productivity in terms of growth, physiology, and yield [125]. Other nanoparticles have also shown promise in applications against metal stress in addition to TiO_2 nanoparticles. It may be possible to reduce Cd toxicity in mustard by using nanoscale hydroxyapatite [126]. In addition to TiO_2 nanoparticles and nanoscale hydroxyapatite, other nanoparticles such as nZVI, salicylic acid nanoparticles, fullerene nanoparticles, silicon nanoparticles, ZnO nanoparticles, silver nanoparticles, etc., are also widely used in nano-phytoremediation of different heavy metals.

4.2. Elimination of Arsenic

Arsenic (As, atomic number 33) is a metalloid that can be found either as a pure element or in numerous minerals along with sulphur and other metals [127]. Due to arsenic's high carcinogenicity and toxicity, there is growing concern over soil pollution brought on by the extensive use of pesticides, herbicides, and fertilizers that include arsenic [128]. Phytoextraction and phytostabilization are indeed the two key phytoremediation mechanisms used to lower soil arsenic contamination. Arsenic can be absorbed by plants through three different mechanisms: direct movement to the plant vascular system through cells; absorption from lower concentration to higher concentration via the symplast; and absorption from higher concentration regions to lower concentration regions via the apoplast [129]. TiO_2 nanocomposites have been shown to have a greater attraction for both inorganic forms of arsenic due to their high surface area-to-volume ratio, corrosion resistance, and stability [130]. According to reports, rice seedlings' bioaccumulation of arsenic can be reduced by a sorption technique using nano-TiO_2 with anatase and rutile structures by roughly 40–90% without compromising the plants' growth [131]. According to Souri et al. (2017), employing nanostructured salicylic acid could enhance the phytoextraction of arsenic by *Isatis cappadocica* [132]. Salicylic acid has vital roles in plant development and arsenic tolerance, so the authors added nanostructured salicylic acid to the system for phytoextraction of the heavy metal. Salicylic acid nanoparticles significantly boosted both phytoremediation efficiency and plant growth. Due to its ability to absorb substances and serve as a nutrient, Yan and colleagues (2021) used nano-zinc oxide in agricultural output [133]. To investigate how ZnO nanoparticles affect the toxicity and accumulation of arsenic in rice, an investigation was carried out. The result of the experiment showed that zinc nanoparticles had an important effect on the growth of rice seedlings while also preventing the build-up of xenobiotics in this food. According to a study conducted by Vtkova et al. (2018), using nano-zero-valent iron (nZVI) particles had a favorable impact on the stability of arsenic in the sunflower rhizosphere [76]. It was observed that the quantity of arsenic concentration in the plant roots and shoots decreased after the five-week growth period, while the concentrations of arsenic in soil pore water dropped by more than 80%. According to studies, the best immobilization effect occurs when nZVI concentrations are 10% because, at that level, As availability is relatively low, fostering the development of *Hordeum vulgare* L. plants and lowering As absorption [134]. The ability of nZVI and graphene oxide nanoparticles (nGOx) to increase or decrease the availability of As and metals in polluted soils was compared. No matter the kind of soil used, As availability noticeably decreased with the application of nZVI and increased with the application of nGOx [135].

4.3. Elimination of Chromium

Chromium (Cr), a heavy metal that occurs naturally in salt water and the crust of the earth, is used in various industrial operations [24]. The two primary chemically stable states of Cr include trivalent and hexavalent, with Cr(VI) causing the biggest threat due to its propensity for malignancy [136]. By applying nZVI at the greatest rate to contaminated locations, heavy metals such as chromium are efficiently eliminated [137]. The effectiveness of immobilizing Cr^{6+} from the soil grew by 100% after 15 days of employing the nZVI in a pot experiment [138]. It was discovered that nanosized TiO_2, MgO, and ZnO were effective adsorbents for the removal of Cr ions from soil treated with leather manufacturing waste [139]. The nZVI revealed a much-improved immobilization of Cr in Chinese cabbage and edible rapeseed (*Brassica napus*). The availability and biomagnification of Cr in both plants were reduced as a result of the usage of nanoparticles [140]. For the in situ remediation of soil contaminated with hexavalent chromium, a nanoscale zero-valent iron supported with biochar (nZVI@BC) was used. nZVI@BC remediation considerably decreased Cr's capacity for upward translocation in the soil environment and was advantageous for plant growth [141].

4.4. Elimination of Cadmium

One of the dangerous heavy metals, cadmium is regularly liberated into the soil by several industrial operations. There is proof that certain nanomaterials can enhance cadmium phytoextraction from the soil. Researchers showed that TiO_2 nanoparticles in soybean plants increased cadmium deposits by 1.9, 2.1, and 2.6 times in the shoots and by 2.5, 2.6, and 3.3 times in the roots, respectively. These researchers' results demonstrated that the inclusion of TiO_2 nanoparticles increased Cd uptake, and they postulated a potential method through which the tiny TiO_2 nanoparticles could penetrate chloroplasts of the leaf and enhance light adaptation and electron transfer [72]. The introduction of TiO_2 nanoparticles to spinach reduces oxidative stress by lowering the levels of H_2O_2, superoxide radicals, and malonyldialdehyde, according to studies by Lei et al. (2008) [86]. Additionally, it was discovered that the utilization of TiO_2 nanoparticles increases the activity of antioxidant enzymes such as guaiacol and ascorbate peroxidases, superoxide dismutase, and catalase. The introduction of nZVI nanoparticles enhances the cadmium collection in the stems, leaves, and roots. It has been established that the presence of nZVI in Ramie [*Boehmeria nivea* (L.) *Gaudich*] led to an increase in Cd concentrations of 31 to 73%, 29 to 52%, and 16 to 50% in the leaves, stems, and roots, respectively [142]. Nasiri et al. (2013) used the liquid phase process to develop carboxymethyl-cellulose-coated iron nanoparticles that were uncoated [143]. The results demonstrated that iron nanoparticles can be utilized as effective adsorbents for removing cadmium from soil and water resources. Rice seeds and leaves accumulate considerably less Cd when nZVI is applied to the soil with elevated Cd levels [144]. Due to the decreased bioavailability, the adsorption of cadmium on the surface of nanoparticles aids in lowering Cd toxicity. Houben and Sonnet (2010) reported that the application of finely ground Fe nanoparticles lowers soil Cd concentrations [145]. When silver nanoparticles were introduced to maize, Cd concentrations rose from 0.65% to 0.73% mg/kg DW in the plant shoot [116]. Carbon nanotubes' impact on Cd build-up in smooth cordgrass was studied by Chai et al. in 2013 [146]. Their experimental findings indicated that, while carbon nanotubes did not produce phytotoxicity at low Cd concentrations, they did protect plants from inhibitory effects at high Cd concentrations. Through a number of studies, Chand et al. (2015) concluded that sweet basil is a hyperaccumulator of Cd [147]. The ability of the amorphous nanoscale MnO to clean up Cd-polluted soils was also assessed [148,149]. Yu et al. (2019) assesed the phytoextraction ability of five major Cd accumulators, including *Sedum spectabile Boreau*, *Phytolacca acinosa Roxb.*, *Celosia argentea* L., and *Amaranthus hypochondriacus* L., in order to choose the best plants for phytoextraction of Cd-contaminated soils [150]. It is found that *C. argentea* could be a viable option for Cd remediation. Additionally, using malic acid effectively can boost *C. argentea's* phytoextraction efficiency.

4.5. Elimination of Lead

Lead is a common metal that is used in a variety of products, including storage batteries and petroleum products. Severe lead pollutants in soils can have a negative impact on the environment in several ways, such as the loss of natural habitat, water pollution, and toxic effects of lead in plants, animals, and human beings [151–153]. The commonly used phytoremediation method for eliminating lead from polluted soil is phytoextraction. Since ryegrass grows quickly, has a high tolerance to lead, and is inexpensive, it is frequently utilized to phytoextract the heavy metal lead from contaminated soils. The effect of utilizing nano-hydroxyapatite on ryegrass's capacity to eliminate lead from the environment was investigated by Liang et al. (2017) [71]. After 1.5 months, the introduction of 0.2 percent (w/w) nano-hydroxyapatite considerably boosted the lead deposit in the plant's shoot, according to the study results. The removal rate of lead was increased when 5 g/kg nano-hydroxyapatite was added to lead-contaminated soil [154]. In research conducted by Huang et al. (2018), different concentrations of nZVI particles were added to the ryegrass to aid in the removal of lead [155]. The researchers discovered that, over the course of a 45-day treatment period, small amounts of nZVI could boost Pb accumulation in ryegrass. Yuan-Yuan Gao et al. (2013) found that *Impatiens balsamina* had a high Pb accumulation and tolerance capacity [156]. Based on this discovery, they investigated the effect of NZVI associated with *Impatiens balsamina* on the phytoremediation of polychlorinated biphenyl–lead (PCB–Pb) co-polluted soils. The findings demonstrated that nZVI could promote plant growth in both clean soil and soil with high levels of pollution. This may be attributed to nZVI's ability to enhance soil quality and adjust soil pH. Particularly, all the treatments that included nZVI had significantly higher PCB concentration efficiencies than those that did not, indicating that nZVI-phytoremediation would be a very promising technique in the future. For the in situ immobilization of lead (Pb^{2+}) in soils, Liu et al. (2007) utilized sodium carboxymethyl cellulose (CMC) and CMC-stabilized iron nanoparticles [157]. The results revealed that it can significantly lower the leachability of Pb^{2+} in the soil. According to research by Huang et al. (2018), the use of nZVI in combination with phytoremediation can lower the amount of lead that is acid soluble, which results in a decrease in the toxicity of heavy metals in sediments [155]. According to research by Fajardo et al. (2019), 5% nanometer zero-valent iron (nZVI) is more efficient at cleaning up soil that has been contaminated with lead and cadmium [158]. nZVI has a brief reaction time, and its long-term efficacy is unclear. Using sweet sorghum, Cheng et al. (2021) examined the individual and combined effects of the arbuscular mycorrhizal (AM) fungus and nZVI (S-nZVI and B-nZVI) on the phytoremediation of an acidic environment with pollution [159]. Both S-nZVI and B-nZVI demonstrated no phytotoxicity to sweet sorghum at any of the test concentrations (50–1000 mg/kg), and they improved the phytoextraction of lead and the immobilization of heavy metals on their surface. Despite the fungitoxicity of nZVI, AM inoculation successfully colonized plant roots. Overall, the merged use of AM inoculation and low concentrations of nZVI resulted in a harmonious effect on heavy metal immobilization. According to a study by Fazal Hussain et al. (2021), 15 mg L^{-1} ZnO nanoparticles significantly increased Pb concentration and accumulation in P. hydropiper seedlings [160]. The ability of the amorphous nanoscale MnO to clean up Pb-polluted soils was also assessed [148,149].

5. Environmental Concern

Because of their increasing use, many people are concerned about the environmental consequences of intentional nanoparticles emissions. The use of nanoparticles to eliminate pollutants in the soil increases the number of nanoparticles in the soil and surrounding environment. According to recent research, the increased use of nanoparticles in agricultural activities has had negative consequences. Klaine (2008) proposed that, despite the presence of many natural nanoparticles in the environment, artificial nanoparticles may behave differently [161]. These materials are engineered to exhibit surface qualities and chemistries that are unlikely to be found in natural particles. It has been studied that the intentional application of nanoparticles may cause their accumulation or a rise in the level of their parts in the soil, thereby changing the soil's characteristics [162]. Nanoparticles may endanger priceless soil microbe communities if they are introduced into the environment. The effect of nanoparticles on microbial activity could be assessed by measuring soil respiration and enzymatic activity [163]. According to reports, the presence of nanoparticles in soils alters the pH of the soil, one of the most important factors affecting various properties such as the accessibility of nutrients in the soil, the health of the total soil ecosystem, microbial dynamics, and the development and growth of plants [164]. In addition, reduced dehydrogenase activity is associated with higher nanoparticle concentrations, which upsets the balance of soil quality and nutrition [165,166]. It is very likely that persistent nanoparticle release into the surroundings will lead to their ubiquity, with nanoparticles invading the food web at different trophic levels and having toxicological impacts on a variety of living things [167,168]. Therefore, before utilizing nanoparticles for bioremediation, these environmental issues should be prioritized, and nanoparticles should be developed in a sustainable way. The main issues with phytoremediation are poor remediation effectiveness and improper handling of polluted biomass. The effectiveness of phytoremediation still needs to be improved, despite the use of several different techniques [169].

6. Conclusions and a Look toward the Future

The field of nano-phytoremediation is a relatively new technique for detoxifying the environment. There is much evidence in the literature to support the idea that nanoparticles are absorbed by plants and that nanoparticles cause different physiological changes in different agricultural plants. The use of nanoparticles in phytoremediation has shown a strong promise for improving remediation performance during the past couple of years. The current study covers topics related to soil remediation for various heavy metals using nano-phytoremediation. Using nanomaterials to aid the phytoremediation of polluted soil can be a beneficial method, even though it is still in the research and testing stage. Extensive laboratory research is still needed to develop phytoremediation approaches for effective pollution removal. Future research needs to be carried out to determine whether nanoparticles have any toxicological effects on plants or the ecosystem, and it is also necessary to study the mechanism underlying their transit into the environment. For the high-resolution clean-up method, it is also necessary to choose the right species of plants and nanoparticles for toxin absorption.

Author Contributions: Literature survey, P.P.; Resources, P.P. and S.C.S.; Validation, P.P. and S.C.S.; Visualization, P.P. and S.C.S.; Supervision, S.C.S. Writing—original draft, P.P.; Writing—review & editing, P.P. and S.C.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors have no conflict of interest to declare that are relevant to the content of this manuscript.

References

1. Sarwar, N.; Imran, M.; Shaheen, M.R.; Ishaque, W.; Kamran, M.A.; Matloob, A.; Rehim, A.; Hussain, S. Phytoremediation strategies for soils contaminated with heavy metals: Modifications and future perspectives. *Chemosphere* **2016**, *171*, 710–721. [CrossRef] [PubMed]
2. Li, Z.; Deblon, J.; Zu, Y.; Colinet, G.; Li, B.; He, Y. Geochemical baseline values determination and evaluation of heavy metal contamination in soils of lanping mining valley (Yunnan Province, China). *Int. J. Environ. Res. Public Health* **2019**, *16*, 4686. [CrossRef] [PubMed]

3. Yang, L.; Ren, Q.; Ge, S.; Jiao, Z.; Zhan, W.; Hou, R.; Ruan, X.; Pan, Y.; Wang, Y. Metal (loid) s spatial distribution, accumulation, and potential health risk assessment in soil-wheat systems near a Pb/Zn smelter in Henan province, central China. *Int. J. Environ. Res. Public Health* **2022**, *19*, 2527. [CrossRef] [PubMed]
4. Kankia, H.I.; Abdulhamid, Y. Determination of accumulated heavy metals in benthic invertebrates found in Ajiwa Dam, Katsina State, Northern Nigeria. *Arch. Appl. Sci. Res.* **2014**, *6*, 80–87.
5. Shi, Y.N.; Zhan, C.; Zhang, Z.J.; Wu, W.H.; Yang, W. Solidification and stabilization treatment of polluted sludge and planting performance test. Prog. Water Conserv. *Hydropower Sci. Technol.* **2021**, *41*, 89–94.
6. Ali, H.; Khan, E. What are heavy metals? Long-standing controversy over the scientific use of the term' heavy metals'—Proposal of a comprehensive definition. *Toxicol. Environ. Chem.* **2018**, *100*, 6–19. [CrossRef]
7. Khan, S.; Hesham, A.E.; Qiao, M.; Rehman, S.; He, J.Z. Effects of Cd and Pb on soil microbial community structure and activities. *Environ. Sci. Pollut. Res.* **2010**, *17*, 288–296. [CrossRef]
8. Rascio, N.; Navariizzo, F. Heavy metal hyperaccumulating plants: How and why do they do it, and what makes them so interesting. *Plant Sci.* **2011**, *18*, 169–181. [CrossRef]
9. Mahamood, Q.; Rashid, A.; Ahmad, S.S.; Azim, M.R.; Bilal, M. Current Status of Toxic Metals Addition to Environment and Its Consequences. In *The Plant Family Brassicaceae: Contribution towards Phytoremediation*; Springer: Dordrecht, The Netherlands, 2012; pp. 35–69. [CrossRef]
10. Aelion, C.M.; Davis, H.T.; McDermott, S.; Lawson, A.B. Metal concentrations in rural topsoil in South Carolina: Potential for human health impact. *Sci. Total Environ.* **2008**, *402*, 149–156. [CrossRef]
11. Mukesh, K.R.; Kumar, P.; Singh, M.; Singh, A. Toxic effect of heavy metals in livestock health. *Vet. World* **2008**, *1*, 28–30.
12. Saleem, M.H.; Fahad, S.; Khan, S.U.; Din, M.; Ullah, A.; EL Sabagh, A.; Hossain, A.; Llanes, A.; Liu, L. Copper-induced oxidative stress, initiation of antioxidants and phytoremediation potential of flax (*Linum usitatissimum* L.) seedlings grown under the mixing of two different soils of China. *Environ. Sci. Pollut. Res.* **2020**, *27*, 5211–5221. [CrossRef] [PubMed]
13. Bakshi, M.; Abhilash, P.C. Nanotechnology for soil remediation: Revitalizing the tarnished resource. In *Nano-Materials as Photocatalysts for Degradation of Environmental Pollutants*; Elsevier: Varanasi, India, 2020; pp. 345–370. [CrossRef]
14. Tripathi, D.K.; Singh, V.P.; Prasad, S.M.; Chauhan, D.K.; Dubey, N.K. Silicon nanoparticles (SiNp) alleviate chromium (VI) phytotoxicity in *Pisum sativum* (L.) seedlings. *Plant Physiol. Biochem.* **2015**, *96*, 189–198. [CrossRef] [PubMed]
15. Tripathi, D.K.; Singh, V.P.; Prasad, S.M.; Chauhan, D.K.; Dubey, N.K.; Rai, A.K. Silicon-mediated alleviation of Cr(VI) toxicity in wheat seedlings as evidenced by chlorophyll florescence, laser induced breakdown spectroscopy and anatomical changes. *Ecotoxicol. Environ. Saf.* **2015**, *113*, 133–144. [CrossRef] [PubMed]
16. Khan, A.C. Promises and potential of in situ nano-phytoremediation strategy to mycorrhizo-remediate heavy metal contaminated soils using non-food bioenergy crops (*Vetiver zizinoides* & *Cannabis sativa*). *Int. J. Phytoremediat.* **2020**, *22*, 900–915.
17. Licata, P.; Trombetta, D.; Cristani, M.; Giofre, F.; Martino, D.; Calo, M.; Naccari, F. Levels of "toxic" and "essential" metals in samples of bovine milk from various dairy farms in Calabria, Italy. *Environ. Res.* **2004**, *30*, 1–6. [CrossRef]
18. Genchi, G.; Lauria, G.; Catalano, A.; Carocci, A.; Sinicropi, M.S. Arsenic: A Review on a Great Health Issue Worldwide. *Appl. Sci.* **2022**, *12*, 6184. [CrossRef]
19. Jomova, K.; Jenisova, Z.; Feszterova, M.; Baros, S.; Liska, J.; Hudecova, D.; Rhodes, C.J.; Valko, M. Arsenic: Toxicity, oxidative stress and human disease. *J. Appl. Toxicol.* **2011**, *31*, 95–107. [CrossRef]
20. Smith, E.; Juhasz, A.L.; Weber, J. Arsenic uptake and speciation in vegetables grown under greenhouse conditions. *Environ. Geochem. Health* **2009**, *31*, 125–132. [CrossRef]
21. Malik, A.H.; Khan, Z.M.; Mahmood, Q.; Nasreen, S.; Bhatti, Z.A. Perspectives of low cost arsenic remediation of drinking water in Pakistan and other countries. *J. Hazard. Mater.* **2009**, *168*, 1–12. [CrossRef]
22. Bhattacharya, P.; Alan, H.W.; Kenneth, G.S.; Mike, J.M.; Bundschuh, J.; Panaullah, G. Arsenic in the environment: Biology and chemistry. *Sci. Total Environ.* **2007**, *379*, 109–120. [CrossRef]
23. Bissen, M.; Frimmel, F.H. Arsenic—A review. Part II: Oxidation of arsenic and its removal in water treatment. *Acta Hydrochim. Hydrobiol.* **2003**, *31*, 97–107. [CrossRef]
24. Tchounwou, P.B.; Yedjou, C.G.; Patlolla, A.K.; Sutton, D.J. Heavy metal toxicity and the environment. *Exp. Suppl.* **2012**, *101*, 133–164. [CrossRef] [PubMed]
25. Han, F.; Sridhar, B.B.M.; Monts, D.L.; Su, Y. Phytoavailability and toxicity of trivalent and hexavalent chromium to *Brassica juncea*. *N. Phytol.* **2004**, *162*, 489–499. [CrossRef]
26. Babich, H.; Stotzky, G.; Schiffenbauer, M. Comparative toxicity of trivalent and hexavalent chromium to fungi. *Bull. Environ. Contam. Toxicol.* **1982**, *28*, 452. [CrossRef] [PubMed]
27. Voleksy, B.; Holan, Z.R. Biosorption of heavy metals. *Biotechnol. Prog.* **1995**, *11*, 235.
28. Jensen, A.; Bro-Rasmussen, F. Environmental contamination in Europe. *Rev. Environ. Contam. Toxicol.* **1992**, *125*, 101–181.
29. Henao, S.G.; Ghneim-Herrera, T. Heavy Metals in Soils and the Remediation Potential of Bacteria Associated with the Plant Microbiome. *Front. Environ. Sci.* **2021**, *9*, 604216. [CrossRef]
30. Zeng, L.S.; Liao, M.; Chen, C.L.; Huang, C.Y. Effects of lead contamination on soil enzymatic activities, microbial biomass, and rice physiological indices in soil-lead-rice (*Oryza sativa* L.) system. *Ecotoxicol. Environ. Saf.* **2007**, *67*, 67–74. [CrossRef]
31. Pourrut, B.; Shahid, M.; Dumat, C.; Winterton, P.; Pinelli, E. Lead uptake, toxicity, and detoxification in plants. *Rev. Environ. Contam. Toxicol.* **2011**, *213*, 113–136. [CrossRef]

32. Tangahu, B.V.; Sheikh Abdullah, S.R.; Basri, H.; Idris, M.; Anuar, N.; Mukhlisin, M. A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. *Int. J. Chem. Eng.* **2011**, *2011*, 1687–1806. [CrossRef]
33. Gong, Y.; Zhao, D.; Wang, Q. An overview of field-scale studies on remediation of soil contaminated with heavy metals and metalloids: Technical progress over the last decade. *Water Res.* **2018**, *147*, 440–460. [CrossRef] [PubMed]
34. Lajayer, B.A.; Ghorbanpour, M.; Nikabadi, S. Heavy metals in contaminated environment: Destiny of secondary metabolite biosynthesis, oxidative status and phytoextraction in medicinal plants. *Ecotoxicol. Environ. Saf.* **2017**, *145*, 377–390. [CrossRef] [PubMed]
35. Lasat, M. Phytoextraction of metals from contaminated soil: A review of plant/soil/metal interaction and assessment of pertinent agronomic issues. *J. Hazard. Subst. Res.* **1999**, *2*, 5. [CrossRef]
36. Tang, C.Y.; Fu, Q.S.; Criddle, C.S.; Leckie, J.O. Effect of flux (transmembrane pressure) and membrane properties on fouling and rejection of reverse osmosis and nanofiltration membranes treating perfluorooctane sulfonate containing wastewater. *Environ. Sci. Technol.* **2007**, *41*, 2008–2014. [CrossRef] [PubMed]
37. Xia, Y.; Liyuan, C. Study of gelatinous supports for immobilizing inactivated cells of *Rhizopus oligosporus* to prepare biosorbent for lead ions. *Int. J. Environ. Stud.* **2002**, *5*, 1–6.
38. Gardeatorresdey, J.; Peraltavidea, J.; Delarosa, G.; Parsons, J. Phytoremediation of heavy metals and study of the metal coordination by X-ray absorption spectroscopy. *Coord. Chem. Rev.* **2005**, *249*, 1797–1810. [CrossRef]
39. Fruchter, R.; Demian, P. CoMem: Designing an interaction experience for reuse of rich contextual knowledge from a corporate memory. *AI EDAM* **2002**, *16*, 127–147. [CrossRef]
40. Carberry, B.J.; Wik, J. Comparison of ex situ and 'in situ' bioremediation of unsaturated soils contaminated by petroleum. *J. Environ. Sci. Health Part A* **2001**, *36*, 1491–1503. [CrossRef]
41. Di Toro, S.; Zanaroli, G.; Fava, F. Intensification of the aerobic bioremediation of an actual site soil historically contaminated by polychlorinated biphenyls (PCBs) through bioaugmentation with a non acclimated, complex source of microorganisms. *Microb. Cell Factories* **2006**, *5*, 11. [CrossRef]
42. Lebeau, T.; Jézéquel, K. Performance of bioaugmentation-assisted phytoextraction applied to metal contaminated soils: A review. *Environ. Pollut.* **2008**, *153*, 497–522. [CrossRef]
43. Zanganeh, F.; Heidari, A.; Sepehr, A.; Rohani, A. Bioaugmentation and Bioaugmentation—Assisted Phytoremediation of Heavy Metals Contaminated Soil by a Synergistic Effect of Cyanobacteria Inoculation, Biochar, and *Purtolaca oleracea*. *Environ. Sci. Pollut. Res.* **2022**, *29*, 6040–6059. [CrossRef] [PubMed]
44. Stroo, H.F.; Leeson, A.; Ward, C.H. (Eds.) *Bioaugmentation for Groundwater Remediation*; Springer: New York, NY, USA, 2013.
45. Bouchez, T.; Patureau, D.; Dabert, P.; Juretschko, S.; Dore, J.; Delgenes, P.; Moletta, R.; Wagner, M. Ecological study of a bioaugmentation failure. *Environ. Microbiol.* **2000**, *2*, 179–190. [CrossRef] [PubMed]
46. Philp, J.C.; Atlas, R.M. Bioremediation of contaminated soils and aquifers. In *Bioremediation: Applied Microbial Solutions for Real-World Environmental Cleanup*, 1st ed.; American Society for Microbiology: Washington, DC, USA, 2005; Chapter 5.
47. Azubuike, C.C.; Chikere, C.; Okpokwasili, G.C. Bioremediation techniques–classification based on site of application: Principles, advantages, limitations and prospects. *World J. Microbiol. Biotechnol.* **2016**, *32*, 180. [CrossRef] [PubMed]
48. Smets, B.F.; Pritchard, P.H. Elucidating the microbial component of natural attenuation. *Curr. Opin. Biotechnol.* **2003**, *14*, 283. [CrossRef] [PubMed]
49. Fauziah, S.H.; Jayanthi, B.; Emenike, C.U.; Agamuthu, C. Remediation of heavy metal contaminated soil using potential microbes isolated from a closed disposal site. *Int. J. Biosci. Biochem. Bioinform.* **2015**, *7*, 230–237. [CrossRef]
50. Schmidt, A.; Haferburg, G.; Sineriz, M.; Merten, D.; Büchel, G.; Kothe, E. Heavy metal resistance mechanisms in actinobacteria for survival in AMD contaminated soils. *Geocheminstry* **2005**, *65*, 131–144. [CrossRef]
51. Ying, G.G. Remediation and Mitigation Strategies Integrated Analytical Approaches for Pesticide Management. *Integr. Anal. Approaches Pestic. Manag.* **2018**, 207–217. [CrossRef]
52. Vidali, M. Bioremediation. An overview. *Pure Appl. Chem.* **2001**, *73*, 1163–1172. [CrossRef]
53. Johnson, P.C.; Johnson, R.L.; Bruce, C.L.; Leeson, A. Advances in In Situ Air Sparging/Biosparging. *Bioremediat. J.* **2001**, *5*, 251–266. [CrossRef]
54. Hussain, S.; Siddique, T.; Arshad, M.; Saleem, M. Bioremediation and phytoremediation of pesticides: Recent advances. *Crit. Rev. Environ. Sci. Technol.* **2009**, *39*, 843–907. [CrossRef]
55. Kanmani, P.; Aravind, J.; Preston, D. Remediation of chromium contaminants using bacteria. *Int. J. Environ. Sci. Technol.* **2012**, *9*, 183–193. [CrossRef]
56. Gidarakos, E.; Aivalioti, M. Large scale and long term application of bioslurping: The case of a Greek petroleum refinery site. *J. Hazard. Mater.* **2007**, *149*, 574–581. [CrossRef] [PubMed]
57. Sivakumar, D.; Kandaswamy, A.; Gomathi, V.; Rajeshwaran, R.; Murugan, N. Bioremediation studies on reduction of heavy metals toxicity. *Pollut. Res.* **2014**, *33*, 553–558.
58. Khan, F.I.; Tahir, H.; Ramzi, H. An overview and analysis of site remediation technologies. *J. Environ. Manag.* **2004**, *71*, 95–122. [CrossRef] [PubMed]
59. Maila, M.P.; Cloete, T.E. Bioremediation of petroleum hydrocarbons through landfarming: Are simplicity and cost-effectiveness the only advantages? *Rev. Environ. Sci. Bio/Technol.* **2004**, *3*, 349–360. [CrossRef]

60. Tampouris, S.; Papassiopi, N.; Paspaliaris, I. Removal of contaminant metals from fine grained soils, using agglomeration, chloride solutions and pile leaching techniques. *J. Hazard. Mater.* **2001**, *84*, 297–319. [CrossRef]
61. Baker, A.J.M. Metal Tolerance. *New Phytol.* **1987**, *106*, 93–111. [CrossRef]
62. Raskin, I.; Smith, R.D.; Salt, D.E. Phytoremediation of metals: Using plants to remove pollutants from the environment. *Curr. Opin. Biotechnol.* **1997**, *8*, 221–226. [CrossRef]
63. Burken, J.G.; Schnoor, J.L. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. *Environ. Sci. Technol.* **1998**, *32*, 3379–3385. [CrossRef]
64. Briggs, G.G.; Bromilow, R.H.; Evans, A.A. Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. *Pestic. Sci.* **1982**, *13*, 495–504. [CrossRef]
65. Newman, L.A.; Strand, S.E.; Choe, N.; Duffy, J.; Ekuan, G.; Ruszaj, M.; Shurtleff, B.B.; Wilmoth, J.; Heilman, P.; Gordon, M.P. Uptake and biotransformation of trichloroethylene by hybrid poplars. *Environ. Sci. Technol.* **1997**, *31*, 1062–1067. [CrossRef]
66. Ohkawa, H.; Imaishi, H.; Shiota, N.; Yamada, T.; Inui, H. Cytochrome P450s and other xenobiotic metabolizing enzymes in plants. In *Pesticide Chemistry and Bioscience: The Food-Environment Challenge*; Special Publication 233; Brooks, G.T., Roberts, T.R., Eds.; The Royal Society of Chemistry: Cambridge, UK, 1999; pp. 259–264.
67. He, L.; Zhong, H.; Liu, G.; Dai, Z.; Brookes, P.C.; Xu, J. Remediation of heavy metal contaminated soils by biochar: Mechanisms, potential risks and applications in China. *Environ. Pollut.* **2019**, *252*, 846–855. [CrossRef] [PubMed]
68. United States Environmental Protection Agency (USEPA). *Introduction to Phytoremediation; EPA 600/R-99/107, (Mechanism of Nano Phytoremediation)*; U.S. Environmental Protection Agency, Office of Research and Development: Cincinnati, OH, USA, 2000.
69. Blaylock, M.J.; Huang, J.W. Phytoextraction of metals. In *Phytoremediation of Toxic Metals: Using Plants to Clean up the Environment*; Raskin, I., Ensley, B.D., Eds.; John Wiley and Sons: New York, NY, USA, 2000; pp. 53–70.
70. McGrath, S.P. Phytoextraction for soil remediation. In *Plants That Hyperaccumulate Heavy Metals*; Brooks, R.R., Ed.; CAB International: New York, NY, USA, 1998; pp. 109–128.
71. Ding, L.; Li, J.; Liu, W.; Zuo, Q.; Liang, S.-X. Influence of nano-hydroxyapatite on the metal bioavailability, plant metal accumulation and root exudates of ryegrass for phytoremediation in lead-polluted soil. *Int. J. Environ. Res. Public Health* **2017**, *14*, 532. [CrossRef] [PubMed]
72. Singh, J.; Lee, B.K. Influence of nano-TiO_2 particles on the bioaccumulation of Cd in soybean plants (Glycine max): A possible mechanism for the removal of Cd from Critical reviews in environmental science and technology of the contaminated soil. *J. Environ. Manag.* **2016**, *170*, 88–96. [CrossRef]
73. Susarla, S.; Medina, V.F.; McCutcheon, S.C. Phytoremediation: An ecological solution to organic chemical contamination. *Ecol. Eng.* **2002**, *18*, 647–658. [CrossRef]
74. Dec, J.; Bollag, J.M. Use of plant material for the decontamination of water polluted with phenols. *Biotechnol. Bioeng.* **1994**, *44*, 1132–1139. [CrossRef]
75. Strand, S.E.; Newman, L.; Ruszaj, M.; Wilmoth, J.; Shurtleff, B.; Brandt, M.; Choe, N.; Ekuan, G.; Duffy, J.; Massman, J.W.; et al. Removal of trichloroethylene from aquifers using trees. In *Innovative Technologies for Site Remediation and Hazardous Waste Management, Proceedings of the National Conference of the Environmental Engineering, Pittsburgh, PA, USA, 23–26 July 1995*; Vidic, R.D., Pohland, F.G., Eds.; Division of the American Society of Civil Engineers: New York, NY, USA, 1995.
76. Vitkova, M.; Puschenreiter, M.; Komarek, M. Effect of nano zero-valent iron application on As, Cd, Pb, and Zn availability in the rhizosphere of metal(loid) contaminated soils. *Chemosphere* **2018**, *200*, 217–226. [CrossRef]
77. Sakakibara, M.; Watanabe, A.; Inoue, M.; Sano, S.; Kaise, T. Phytoextraction and phytovolatilization of arsenic from As-contaminated soils by *Pteris vittata*. In Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy, Amherst, MA, USA, 18–21 October 2010; Volume 12. Available online: https://scholarworks.umass.edu/soilsproceedings/vol12/iss1/26 (accessed on 7 November 2022).
78. Mench, M.; Schwitzguébel, J.-P.; Schroeder, P.; Bert, V.; Gawronski, S.; Gupta, S. Assessment of successful experiments and limitations of phytotechnologies: Contaminant uptake, detoxification and sequestration, and consequences for food safety. *Environ. Sci. Pollut. Res.* **2009**, *16*, 876–900. [CrossRef]
79. Watlington, K. *Emerging Nanotechnologies for Site Remediation and Wastewater Treatment*; National Network for Environmental Management Studies Fellow North Carolina State University, U.S. Environmental Protection Agency Office of Solid Waste and Emergency Response Office of Superfund Remediation and Technology Innovation Technology Innovation and Field Services Division: Washington, DC, USA, 2005. Available online: www.epa.govwww.clu-in.org (accessed on 7 November 2022).
80. Ahmad, B.; Zaid, A.; Jaleel, H.; Khan, M.M.A.; Ghorbanpour, M. *Nanotechnology for Phytoremediation of Heavy Metals: Mechanisms of Nanomaterial-Mediated Alleviation of Toxic Metals Advances in Phytonanotechnology*; Elsevier: Amsterdam, The Netherlands, 2019; Chapter 13. [CrossRef]
81. Srivastav, A.; Yadav, K.K.; Yadav, S.; Gupta, N.; Singh, J.K.; Katiyar, R.; Kumar, V. Nano-phytoremediation of Pollutants from Contaminated Soil Environment: Current Scenario and Future Prospects. In *Phytoremediation*; Ansari, A., Gill, S., Gill, R., Lanza, G.R., Newman, L., Eds.; Springer Nature: Cham, Switzerland, 2018. [CrossRef]
82. Jiamjitrpanich, W.; Parkpian, P.; Polprasert, C.; Kosanlavit, R. Trinitrotoluene and its metabolites in shoots and roots of *Panicum maximum* in nano-phytoremediation. *Int. J. Environ. Sci. Dev.* **2013**, *4*, 7. [CrossRef]

83. Tripathi, D.K.; Singh, S.; Singh, V.P.; Prasad, S.M.; Chauhan, D.K.; Dubey, N.K. Silicon nanoparticles more efficiently alleviate arsenate toxicity than silicon in maize cultivar and hybrid differing in arsenate tolerance. *Front. Environ. Sci.* **2016**, *4*, 46. [CrossRef]
84. Tripathi, D.K.; Singh, S.; Singh, S.; Pandey, R.; Singh, V.P.; Sharma, N.C.; Prasad, S.M.; Dubey, N.K.; Chauhan, D.K. An overview on manufactured nanoparticles in plants: Uptake, translocation, accumulation and phytotoxicity. *Plant Physiol. Biochem.* **2017**, *110*, 2–12. [CrossRef] [PubMed]
85. Cox, A.; Venkatachalam, P.; Sahi, S.; Sharma, N. Silver and titanium dioxide nanoparticle toxicity in plants: A review of current research. *Plant Physiol. Biochem.* **2016**, *107*, 147–163. [CrossRef]
86. Lei, Z.; Mingyu, S.; Xiao, W.; Chao, L.; Chunxiang, Q.; Liang, C.; Hao, H.; Xiaoqing, L.; Fashui, H. Antioxidant stress is promoted by nano-anatase in spinach chloroplasts under UV-B radiation. *Biol. Trace Elem. Res.* **2008**, *21*, 69–79. [CrossRef] [PubMed]
87. Hong, F.S.; Yang, P.; Gao, F.Q.; Liu, C.; Zheng, L.; Zhou, J. Effect of nano-anatase TiO_2 on spectral characterization of photosystem II particles from spinach. *Chem. Res. Chin. Univ.* **2005**, *21*, 19.
88. Tafazoli, M.; Hojjati, S.M.; Biparva, P.; Kooch, Y.; Lamersdorf, N. Reduction of soil heavy metal bioavailability by nanoparticles and cellulosic wastes improved the biomass of tree seedlings. *J. Plant Nutr. Soil Sci.* **2017**, *180*, 683–693. [CrossRef]
89. Vaseghi, Z.; Nematollahzadeh, A. Nanomaterials. In *Green Synthesis of Nanomaterials for Bioenergy Applications*; Wiley: Hoboken, NJ, USA, 2020; pp. 23–82.
90. Kolahalam, L.A.; Kasi Viswanath, I.V.; Diwakar, B.S.; Govindh, B.; Reddy, V.; Murthy, Y.L.N. Review on nanomaterials: Synthesis and applications. *Mater. Today Proc.* **2019**, *18*, 2182–2190. [CrossRef]
91. Ealias, A.M.; Saravanakumar, M.P. A review on the classification, characterization, synthesis of nanoparticles and their application. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *263*, 032019. [CrossRef]
92. Ijaz, I.; Gilani, E.; Nazir, A.; Bukhari, A. Detail review on chemical, physical and green synthesis, classification, characterizations and applications of nanoparticles. *Green Chem. Lett. Rev.* **2020**, *13*, 59–81. [CrossRef]
93. Jamkhande, P.G.; Ghule, N.W.; Bamer, A.H.; Kalaskar, M.G. Metal nanoparticles synthesis: An overview on methods of preparation, advantages and disadvantages, and applications. *J. Drug Deliv. Sci. Technol.* **2019**, *53*, 101174. [CrossRef]
94. Geethalakshmi, R.; Sarada, D.V.L. Synthesis of plant-mediated silver nanoparticles using *Trianthema decandra* extract and evaluation of their antimicrobial activities. *Int. J. Eng. Sci. Technol.* **2010**, *2*, 970–975.
95. Marchiol, L. Synthesis of metal nanoparticles in living plants. *Ital. J. Agron.* **2012**, *7*, e37. [CrossRef]
96. Noruzi, M. Biosynthesis of gold nanoparticles using plant extracts. *Bioprocess Biosyst. Eng.* **2015**, *38*, 1–14. [CrossRef] [PubMed]
97. Iravani, R. Green synthesis of metal nanoparticles using plants. *Green Chem.* **2011**, *13*, 2638–2650. [CrossRef]
98. Kharissova, O.V.; Dias, H.V.R.; Kharisov, B.I.; Pérez, B.O.; Pérez, V.M.J. The greener synthesis of nanoparticles. *Trends Biotechnol.* **2013**, *31*, 240–248. [CrossRef] [PubMed]
99. Kadam, V.V.; Ettiyappan, J.P.; Balakrishnan, R.M. Mechanistic insight into the endophytic fungus mediated synthesis of protein capped ZnO nanoparticles. *Mater. Sci. Eng. B* **2019**, *243*, 214–221. [CrossRef]
100. Shivaji, S.; Madhu, S.; Singh, S. Extracellular synthesis of antibacterial silver nanoparticles using psychrophilic bacteria. *Process Biochem.* **2011**, *46*, 1800–1807. [CrossRef]
101. Kirthi, A.; Rahuman, A.; Rajakumar, G.; Marimuthu, S.; Santhoshkumar, T.; Jayaseelan, C.; Elango, G.; AbduzZahir, A.; Kamaraj, C.; Bagavan, A. Biosynthesis of titanium dioxide nanoparticles using bacterium *Bacillus subtilis*. *Mater. Lett.* **2011**, *65*, 2745. [CrossRef]
102. Jha, A.K.; Prasad, K.; Kulkarni, A.R. Synthesis of TiO_2 nanoparticles using microorganisms. *Coll. Surf. B Biointerfaces* **2009**, *71*, 226. [CrossRef]
103. Li, S.; Shen, Y.; Xie, A.; Yu, X.; Qiu, L.; Zhang, L.; Zhang, Q. Green synthesis of silver nanoparticles using *Capsicum annuum* L. extract. *Green Chem.* **2007**, *9*, 852–858. [CrossRef]
104. Shekhawat, G.S.; Arya, V. Biological synthesis of Ag nanoparticles through in vitro cultures of *Brassica juncea* C. zern. *Adv. Mater. Res.* **2009**, *67*, 295–299. [CrossRef]
105. Ahmad, N.; Sharma, S.; Alam, K.; Singh, V.; Shamsi, S.; Mehta, B.; Fatma, A. Rapid synthesis of silver nanoparticles using dried medicinal plant of basil. *Colloids Surf. B Biointerfaces* **2010**, *81*, 81–86. [CrossRef] [PubMed]
106. Sathishkumar, M.; Sneha, K.; Won, S.W.; Cho, C.-W.; Kim, S.; Yun, Y.-S. Cinnamon zeylanicum bark extract and powder mediated green synthesis of nano-crystalline silver particles and its bactericidal activity. *Colloids Surf. B Biointerfaces* **2009**, *73*, 332–338. [CrossRef] [PubMed]
107. Shankar, S.S.; Ahmad, A.; Sastry, M. Geranium leaf assisted biosynthesis of silver nanoparticles. *Biotechnol. Prog.* **2003**, *19*, 1627–1631. [CrossRef] [PubMed]
108. Bose, D.; Chatterjee, S. Biogenic synthesis of silver nanoparticles using guava (*Psidium guajava*) leaf extract and its antibacterial activity against *Pseudomonas aeruginosa*. *Appl. Nanosci.* **2016**, *6*, 895–901. [CrossRef]
109. Santhosh, A.; Theertha, V.; Prakash, P.; Chandran, S.S. From waste to a value added product: Green synthesis of silver nanoparticles from onion peels together with its diverse applications. *Mater. Today Proc.* **2021**, *46*, 4460–4463. [CrossRef]
110. Kumar, V.G.; Gokavarapu, S.D.; Rajeswari, A.; Dhas, T.S.; Karthick, V.; Kapadia, Z.; Shrestha, T.; Barathy, I.A.; Roy, A.; Sinha, S. Facile green synthesis of gold nanoparticles using leaf extract of antidiabetic potent Cassia auriculata. *Colloids Surf. B Biointerfaces* **2011**, *87*, 159–163. [CrossRef] [PubMed]

111. Goutam, S.P.; Saxena, G.; Singh, V.; Yadav, A.K.; Bharagava, R.N.; Thapa, K.B. Green synthesis of TiO_2 nanoparticles using leaf extract of *Jatropha curcas* L. for photocatalytic degradation of tannery wastewater. *Chem. Eng. J.* **2018**, *336*, 386–396. [CrossRef]
112. Abisharani, J.; Devikala, S.; Kumar, D.; Arthanareeswari, M.; Kamaraj, P. Green synthesis of TiO_2 Nanoparticles using *Cucurbita pepo* seeds extract. *Mater. Today Proc.* **2019**, *14*, 302–307. [CrossRef]
113. Rao, K.G.; Ashok, C.H.; Rao, K.V.; Chakra, C.S.; Tambur, P. Green Synthesis of TiO_2 Nanoparticles Using Aloe Vera Extract. *Int. J. Adv. Res. Phys. Sci. (IJARPS)* **2015**, *2*, 28–34.
114. Alia, K.; Dwivedi, S.; Azam, A.; Saquib, Q.; Al-Said, M.S.; Alkhedhairy, A.A.; Musarrat, J. Aloe vera extract functionalized zinc oxide nanoparticles as nanoantibiotics against multi-drug resistant clinical bacterial isolates. *J. Colloid Interface Sci.* **2016**, *472*, 145–156. [CrossRef]
115. Elumalai, K.; Velmurugan, S. Green synthesis, characterization and antimicrobial activities of zinc oxide nanoparticles from the leaf extract of *Azadirachta indica* (L.). *Appl. Surf. Sci.* **2015**, *345*, 329–336. [CrossRef]
116. Khan, N.; Bano, A. Role of plant growth promoting rhizobacteria and Ag-nano particle in the bioremediation of heavy metals and maize growth under municipal wastewater irrigation. *Int. J. Phytoremediation* **2016**, *18*, 211–221. [CrossRef]
117. Foltête, A.S.; Masfaraud, J.F.; Bigorgne, E.; Nahmani, J.; Chaurand, P.; Botta, C.; Labille, J.; Rose, J.; Férard, J.F.; Cotelle, S. Environmental impact of sunscreen nanomaterials: Ecotoxicity and genotoxicity of altered TiO_2 nanocomposites on *Vicia faba*. *Environ. Pollut.* **2011**, *159*, 2515. [CrossRef] [PubMed]
118. Mejare, M.; Bulow, L. Improving stress tolerance in plants by gene transfer. *Trends Biotechnol.* **2001**, *19*, 67–73. [PubMed]
119. Memon, A.R.; Schroder, P. Implications of metal accumulation mechanisms to phytoremediation. *Environ. Sci. Pollut. Res. Int.* **2009**, *16*, 162–175. [CrossRef]
120. Greipsson, S. Phytoremediation. *Nat. Educ. Knowl.* **2011**, *2*, 7.
121. Nguyen, T.Q.; Sesin, V.; Kisiala, A.; Emery, R.N. Phytohormonal roles in plant responses to heavy metal stress: Implications for using macrophytes in phytoremediation of aquatic ecosystems. *Environ. Toxicol. Chem.* **2021**, *40*, 7–22. [CrossRef] [PubMed]
122. Hall, J.Á. Cellular mechanisms for heavy metal detoxification and tolerance. *J. Exp. Bot.* **2002**, *53*, 1–11. [CrossRef]
123. Sharma, S.S.; Dietz, K.J. The significance of amino acids and amino acid-derived molecules in plant responses and adaptation to heavy metal stress. *J. Exp. Bot.* **2006**, *57*, 711–726. [CrossRef]
124. Cunningham, S.D.; Ow, D.W. Promises and prospects of phytoremediation. *Plant Physiol.* **1996**, *110*, 715. [CrossRef]
125. Gao, F.; Hong, F.; Liu, C.; Zheng, L.; Su, M.; Wu, X.; Yang, F.; Wu, C.; Yang, P. Mechanism of nano-anatase TiO_2 on promoting photosynthetic carbon reaction of spinach. *Biol. Trace Elem. Res.* **2006**, *111*, 239–253. [CrossRef] [PubMed]
126. Li, Z.; Huang, J. Effects of nanoparticle hydroxyapatite on growth and antioxidant system in pakchoi (*Brassica chinensis* L.) from cadmium-contaminated soil. *J. Nanomater.* **2014**, *2014*, 470962. [CrossRef]
127. Mandal, B.K.; Suzuki, K.T. Arsenic round the world: A review. *Talanta* **2002**, *58*, 201–235. [CrossRef] [PubMed]
128. Singh, R.; Singh, S.; Parihar, P.; Singh, V.P.; Prasad, S.M. Arsenic contamination, consequences and remediation techniques: A review. *Ecotoxicol. Environ. Saf.* **2015**, *112*, 247–270. [CrossRef] [PubMed]
129. Vithanage, M.; Dabrowska, B.B.; Mukherjee, A.B.; Sandhi, A.; Bhattacharya, P. Arsenic uptake by plants and possible phytoremediation applications: A brief overview. *Environ. Chem. Lett.* **2012**, *10*, 217–224. [CrossRef]
130. Ashraf, S.; Siddiqa, A.; Shahida, S.; Qaisar, S. Titanium-based nanocomposite materials for arsenic removal from water: A review. *Heliyon* **2019**, *5*, e01577. [CrossRef]
131. Wu, X.; Hu, J.; Wu, F.; Zhang, X.; Wang, B.; Yang, Y.; Shen, G.; Liu, J.; Tao, S.; Wang, X. Application of TiO_2 nanoparticles to reduce bioaccumulation of arsenic in rice seedlings (*Oryza sativa L.*): A mechanistic study. *J. Hazard. Mater.* **2021**, *405*, 124047. [CrossRef]
132. Souri, Z.; Karimi, N.; Sarmadi, M.; Rostami, E. Salicylic acid nanoparticles (SANPs) improve growth and phytoremediation efficiency of *Isatis cappadocica* Desv., under As stress. *IET Nanobiotechnology* **2017**, *11*, 650–655. [CrossRef]
133. Yan, S.; Wu, F.; Zhou, S.; Yang, J.; Tang, X.; Ye, W. Zinc oxide nanoparticles alleviate the arsenic toxicity and decrease the accumulation of arsenic in rice (*Oryza sativa* L.). *BMC Plant Biol.* **2021**, *21*, 150. [CrossRef]
134. Gil-Díaz, M.; Diez-Pascual, S.; González, A.; Alonso, J.; Rodríguez-Valdés, E.; Gallego, J.; Lobo, M. A nanoremediation strategy for the recovery of an As-polluted soil. *Chemosphere* **2016**, *149*, 137–145. [CrossRef]
135. Baragaño, D.; Forján, R.; Welte, L.; Gallego, J.L.R. Nanoremediation of As and metals polluted soils by means of graphene oxide nanoparticles. *Sci. Rep.* **2020**, *10*, 1896. [CrossRef] [PubMed]
136. Mei, B.; Puryear, J.D.; Newton, R.J. Assessment of Cr tolerance and accumulation in selected plant species. *Plant Soil* **2002**, *247*, 223–231. [CrossRef]
137. Klimkova, S.; Cernik, M.; Lacinova, L.; Filip, J.; Jancik, D.; Zboril, R. Zero-valent iron nanoparticles in treatment of acid mine water from in situ uranium leaching. *Chemosphere* **2011**, *82*, 1178–1184. [CrossRef] [PubMed]
138. Sun, T.Y.; Bornhoft, N.A.; Hungerbuhler, K.; Nowack, B. Dynamic probabilistic modeling of environmental emissions of engineered nanomaterials. *Environ. Sci. Technol.* **2016**, *50*, 4701–4711. [CrossRef]
139. Taghipour, M.; Jalali, M. Effect of clay minerals and nanoparticles on chromium fractionation in soil contaminated with leather factory waste. *J. Hazard Mater.* **2015**, *297*, 127–133. [CrossRef]
140. Wang, Y.; Fang, Z.; Kang, Y.; Tsang, E.P. Immobilization and phytotoxicity of chromium in contaminated soil remediated by CMC-stabilized nZVI. *J. Hazard. Mater.* **2014**, *275*, 230–237. [CrossRef]
141. Su, H.; Fang, Z.; Tsang, P.E.; Fang, J.; Zhao, D. Stabilisation of nanoscale zero-valent iron with biochar for enhanced transport and in-situ remediation of hexavalent chromium in soil. *Environ. Pollut.* **2016**, *214*, 94–100. [CrossRef]

142. Gong, X.; Huang, D.; Liu, Y.; Zeng, G.; Wang, R.; Wan, J.; Zhang, C.; Cheng, M.; Qin, X.; Xue, W. Stabilized nanoscale zerovalent iron mediated cadmium accumulation and oxidative damage of *Boehmeria nivea* (L.) Gaudich cultivated in cadmium contaminated sediments. *Environ. Sci. Technol.* **2017**, *51*, 11308–11316. [CrossRef]
143. Nasiri, J.; Gholami, A.; Panahpour, E. Removal of cadmium from soil resources using stabilized zero-valent iron nanoparticles. *J. Civil Eng. Urban.* **2013**, *3*, 338–341.
144. Watanabe, T.; Murata, Y.; Nakamura, T.; Sakai, Y.; Osaki, M. Effect of zero-valent iron application on cadmium uptake in rice plants grown in cadmium-contaminated soils. *J. Plant Nutr.* **2009**, *32*, 1164–1172. [CrossRef]
145. Houben, D.; Sonnet, P. Leaching and phytoavailability of zinc and cadmium in a contaminated soil treated with zero-valent iron. In Proceedings of the 19th World Congress of Soil Science, Soil Solutions for a Changing World, Brisbane, Australia, 1–6 August 2010; pp. 1–6.
146. Chai, M.; Shi, F.; Li, R.; Liu, L.; Liu, Y.; Liu, F. Interactive effects of cadmium and carbon nanotubes on the growth and metal accumulation in a halophyte *Spartina alterniflora* (Poaceae). *Plant Growth Regul.* **2013**, *71*, 171–179. [CrossRef]
147. Chand, S.; Singh, S.; Singh, V.K.; Patra, D.D. Utilization of heavy metal-rich tannery sludge for sweet basil (*Ocimum basilicum* L.) cultivation. *Environ. Sci. Pollut. Res.* **2015**, *22*, 7470–7475. [CrossRef] [PubMed]
148. Della Puppa, L.; Komárek, M.; Bordas, F.; Bollinger, J.-C.; Joussein, E. Adsorption of copper, cadmium, lead and zinc onto a synthetic manganese oxide. *J. Colloid Interface Sci.* **2013**, *399*, 99–106. [CrossRef] [PubMed]
149. Michálková, Z.; Komárek, M.; Šillerová, H.; Della Puppa, L.; Joussein, E.; Bordas, F.; Vaněk, A.; Vaněk, O.; Ettler, V. Evaluating the potential of three Fe- and Mn-(nano)oxides for the stabilization of Cd, Cu and Pb in contaminated soils. *J. Environ. Manag.* **2014**, *146*, 226–234. [CrossRef] [PubMed]
150. Yu, G.; Liu, J.; Long, Y.; Chen, Z.; Sunahara, G.I.; Jiang, P.; You, S.; Lin, H.; Xiao, H. Phytoextraction of cadmium-contaminated soils: Comparison of plant species and low molecular weight organic acids. *Int. J. Phytoremediat.* **2019**, *22*, 383–391. [CrossRef] [PubMed]
151. Buchauer, M.J. Contamination of soil and vegetation near a zinc smelter by zinc, cadmium, copper, and lead. *Environ. Sci. Technol.* **1973**, *17*, 121–123.
152. Johnson, M.S.; Eaten, J.J. Environmental Contamination Through Residual Trace Metal Dispersal from a Derelict Lead-Zinc Mine. *Environ. Qual.* **1980**, *9*, 175–179. [CrossRef]
153. Body, P.E.; Dolan, P.R.; Mulcahy, D.E. Environmental Lead: A review. *Crit. Rev. Environ. Control* **2009**, *20*, 299–310. [CrossRef]
154. Jin, Y.; Liu, W.; Li, X.-L.; Shen, S.-G.; Liang, S.-X.; Liu, C.; Shan, L. Nano-hydroxyapatite immobilized lead and enhanced plant growth of ryegrass in a contaminated soil. *Ecol. Eng.* **2016**, *95*, 25–29. [CrossRef]
155. Huang, D.; Qin, X.; Peng, Z.; Liu, Y.; Gong, X.; Zeng, G.; Huang, C.; Cheng, M.; Xue, W.; Wang, X.; et al. Nanoscale zero-valent iron assisted phytoremediation of Pb in sediment: Impacts on metal accumulation and antioxidative system of *Lolium perenne*. *Ecotoxicol. Environ. Saf.* **2018**, *153*, 229–237. [CrossRef]
156. Gao, Y.-Y.; Zhou, Q.-X. Application of nanoscale zero valent iron combined with *Impatiens balsamina* to remediation of e-waste contaminated soils. *Adv. Mater. Res.* **2013**, *790*, 73–76. [CrossRef]
157. Liu, R.; Zhao, D. Reducing leachability and bioaccessibility of lead in soils using a new class of stabilized iron phosphate nanoparticles. *Water Res.* **2007**, *41*, 2491–2502. [CrossRef]
158. Fajardo, C.; Costa, G.; Nande, M.; Martin, C.; Martín, M.; Sánchez-Fortún, S. Heavy metals immobilization capability of two iron-based nanoparticles (nZVI and Fe_3O_4): Soil and freshwater bioassays to assess ecotoxicological impact. *Sci. Total Environ.* **2019**, *656*, 421–432. [CrossRef]
159. Cheng, P.; Zhang, S.; Wang, Q.; Feng, X.; Zhang, S.; Sun, Y.; Wang, F. Contribution of nano-zero-valent iron and arbuscular mycorrhizal fungi to phytoremediation of heavy metal-contaminated soil. *Nano* **2021**, *11*, 1264. [CrossRef] [PubMed]
160. Hussain, F.; Hadi, F.; Rongliang, Q. Effects of zinc oxide nanoparticles on antioxidants, chlorophyll contents, and proline in *Persicaria hydropiper* L. and its potential for Pb phytoremediation. *Environ. Sci. Pollut. Res.* **2021**, *28*, 34697–34713. [CrossRef] [PubMed]
161. Klaine, S.J. Nanomaterials in the environment: Behavior, fate, bioavailability, and effects. *Environ. Toxicol. Chem.* **2008**, *27*, 1825–1851. [CrossRef] [PubMed]
162. Rajput, V.; Minkina, T.; Mazarji, M.; Shende, S.; Sushkova, S.; Mandzhieva, S.; Burachevskaya, M.; Chaplygin, V.; Singh, A.; Jatav, H. Accumulation of nanoparticles in the soil-plant systems and their effects on human health. *Ann. Agric. Sci.* **2020**, *65*, 137–143. [CrossRef]
163. Simonin, M.; Richaume, A. Impact of engineered nanoparticles on the activity, abundance, and diversity of soil microbial communities: A review. *Environ. Sci. Poll. Res.* **2015**, *22*, 13710–13723. [CrossRef]
164. Fernández, F.G.; Hoeft, R.G. Managing soil pH and crop nutrients. Ill. *Agron. Handb.* **2009**, *24*, 91–112.
165. Shin, Y.-J.; Kwak, J.I.; An, Y.-J. Evidence for the inhibitory effects of silver nanoparticles on the activities of soil exoenzymes. *Chemosphere* **2012**, *88*, 524–529. [CrossRef]
166. Jośko, I.; Oleszczuk, P.; Futa, B. The effect of inorganic nanoparticles (ZnO, Cr_2O_3, CuO and Ni) and their bulk counterparts on enzyme activities in different soils. *Geoderma* **2014**, *232*, 528–537. [CrossRef]
167. Rico, C.M.; Majumdar, S.; Duarte-Gardea, M.; Peralta-Videa, J.R.; Gardea-Torresdey, J.L. Interaction of nanoparticles with edible plants and their possible implications in the food chain. *J. Agric. Food Chem.* **2011**, *59*, 3485–3498. [CrossRef] [PubMed]

168. Cedervall, T.; Hansson, L.-A.; Lard, M.; Frohm, B.; Linse, S. Food chain transport of nanoparticles affects behaviour and fat metabolism in fish. *PLoS ONE* **2012**, *7*, e32254. [CrossRef] [PubMed]
169. Shen, X.; Dai, M.; Yang, J.; Sun, L.; Tan, X.; Peng, C.; Ali, I.; Naz, I. A critical review on the phytoremediation of heavy metals from environment: Performance and challenges. *Chemosphere* **2022**, *291*, 132979. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.