



Bioremediation of Hazardous Wastes Using Green Synthesis of Nanoparticles

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Abstract: Advanced agronomic methods, urbanisation, and industrial expansion contaminate air, water and soil, globally. Agricultural and industrial activities threaten living biota, causing biodiversity loss and serious diseases. Strategies such as bioremediation and physiochemical remediation have not been effectively beneficial at treating pollutants. Metal-based nanoparticles (NPs) such as copper, zinc, silver, gold, etc., in various nanoformulations and nanocomposites are used more and more as they effectively resist the uptake of toxic compounds via plants by facilitating their immobilisation. According to studies, bio-based NP synthesis is a recent and agroecologically friendly approach for remediating environmental waste, which is effective against carcinogens, heavy metal contamination, treating marine water polluted with excessive concentrations of phosphorus, nitrogen and harmful algae, and hazardous dye- and pesticide-contaminated water. Biogenic resources such as bacteria, fungi, algae and plants are extensively used for the biosynthesis of NPs, particularly metallic NPs. Strategies involving green synthesis of NPs are nontoxic and could be employed for commercial scale production. Here, the focus is on the green synthesis of NPs for reduction of hazardous wastes to help with the clean-up process.

Keywords: green technology; metal-based nanoparticles; pollutant; toxic dyes; heavy metals

1. Introduction

The combination of two sciences, i.e., nanotechnology and biotechnology, is gradually expanding its roots in almost all the sectors involving biology, engineering, cosmetics, remediation, biomedical, agriculture, food, etc. Numerous nanoscale (below 100 nm) materials show remarkable features in contrast to their bulk elements and components. With progressive studies, researchers have developed nano-based composites and materials, and found their effective application in almost every field including waste remediation, solar applications, and nano-sensors [1–3].

Economic development and accelerated industrial growth have overall resulted in higher environmental pollution through more energy expenditure, release of hazardous wastes, emission of toxic gases [4], and exhaust emissions from the automobile industry [5]. Hazardous wastes include various dyes (Azure-B, Disperse orange I, Disperse Red I, Crystal Violet, Basic Red 9, Sudan I) eluted from textile industries [6], toxic heavy metals [7,8], pesticides [9,10], and polyaromatic hydrocarbons (chrysene, pyrene, fluoranthene, anthracene, naphthalene etc.) [11], which all are carcinogenic and mutagenic in nature [12].

Metallic nanoparticles (NPs) have been used in the past few years, as many metals such as copper (Cu), silver (Ag), gold (Au), platinum (Pt), zinc (Zn) and titanium (Ti) show promising results once utilised in nanosized composites compared to bulk materials [3]. Metallic NPs have various exceptional properties such as magnetic, electronic,



Citation: Singh, A.; Tyagi, P.; Ranjan, R.; Sushkova, S.N.; Minkina, T.; Burachevskaya, M.; Rajput, V.D. Bioremediation of Hazardous Wastes Using Green Synthesis of Nanoparticles. *Processes* **2023**, *11*, 141. https://doi.org/10.3390/pr11010141

Academic Editor: Raluca Maria Hlihor

Received: 9 November 2022 Revised: 26 December 2022 Accepted: 28 December 2022 Published: 3 January 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/). optical, catalysing, anti-cancer, and antimicrobial activities in contrast with their respective elements. Conventionally, metal NPs have been synthesised using physicochemical procedures [13]. These various synthesis procedures include chemical vapor deposition, microemulsion synthesis, thermal decomposition, sol-gel method, hydrothermal process, stream transport synthesis, mechanochemical process, spray pyrolysis, co-precipitation, spark discharge method, liquid infiltration, inert gas condensation and biological synthesis [14,15].

Due to drawbacks such as the use of extreme conditions and hazardous reagents, the synthesis procedures have shifted towards eco-friendly approaches involving living entities, either using unicellular or multicellular organisms. Biological constituents, as depicted in Figure 1, serve to be a great platform for their non-toxic and economic synthesis [16], which not only include various microorganisms and plants but also their products and components such as extracts, isolates, enzymes, etc. These have been effectively utilised in polymer preparation, catalysis, sensor technology, disease management, and labelling of optoelectronic recorded media [13].



Figure 1. Various biological resources used for nanoparticle synthesis via green approach.

Pollution and contamination of the environment is a big issue to tackle. Numerous solutions have been identified and worked upon, and the use of nanotechnology is one of them. Nanoformulations such as nanomembranes, nanotubes, nanopolymers, graphene-based NPs, and metal-, carbon-, and silicon-based NPs have been extensively used in the remediation of environmental toxic elements [17]. As they are obtained from natural sources, NPs have been found to be effective in reducing pollutants in the environment with negligible effects on ecosystems. The green approach of NP synthesis is eco-friendly and does not interfere with other living organisms [1]. Their phyto- and cytotoxic effects are notably low, indicating that they are safe to use for broader practices [18].

The current review focuses on various research activities with reference to the green biosynthesis of metal-based NPs, their reducing sources, and mechanisms of action. It discusses various biological sources of NPs and their contribution to the remediation process for mitigating hazardous wastes from environment.

2. Nanoparticles and Approaches to Green Synthesis

Based on nature, size, morphology, and chemical characteristics, NPs have been briefly categorised in five groups as stated below and depicted in Figure 2 [19–23].

- 1. Natural carbon-containing NPs: Fullerene, chitosan NPs etc.;
- 2. Anthropogenic carbon-containing NPs: Carbon nanotubes/nanofibers, graphene NPs etc.;
- 3. Natural inorganic NPs: Iron oxide/sulfides, silver, gold, manganese, aluminosilicates NPs etc.;
- 4. Anthropogenic inorganic NPs: Quantum dots, titanium dioxide, silicon dioxide, ceramics NPs etc.;
- 5. Peptide- and DNA-based NPs: Gelatine, albumin, silk sericin NPs etc.



Figure 2. Brief categorisation of nanoparticles.

The methods involved in the synthesis of NPs are categorised into two classes, namely the top-down approach and bottom-up approach, based on differences in the starting materials, as depicted in Figure 3.



Figure 3. Biological, chemical, and physical methods of NP synthesis are categorized as bottom-up and top-down approaches.

2.1. Top-Down Approach

The base material is exploited in bulk to reduce the size to nanoscale in top-down approaches, which can be achieved by both physical and chemical techniques [23]. These methods include photochemical and chemical reduction as well as electrochemical changes using various techniques such as laser and thermal ablation and mechanical milling, which yield stabilised NPs. These are easier to implement but might induce changes in properties and surface chemistry of the prepared NPs [3].

Laser ablation involves the application of high-powered lasers onto metal plates, yielding ablated NPs in the liquid medium. This method is suitable for NP fabrication and is affected by ablation time, wavelength and energy of the laser, and absorption by the liquid medium. This technique has been used for the synthesis of Cu, Au, and Ag NPs [24]. Mechanical milling involves the reduction of coarse particles into the desired smaller size. It is achieved by using an agitator at the speed of 75–500 rpm as per the requirements. The size of the vial in which the operation is carried out, the speed, time, temperature, and environment (dry or wet) of milling, and the usage of inert or reactive gases affect the particle size and homogeneity of the prepared NPs [25].

2.2. Bottom-Up Approach

On the other hand, bottom-up approaches involve the assembly of atoms or molecules to form nanostructured building units which eventually form the desired NPs. It can be achieved via both chemical and biological techniques. Studies have clearly shown that biological methods for NP synthesis have the fewest drawbacks compared with the other methods. Physical methods have high expenditures in time, energy and cost, as well as low production rate. Chemical synthesis is attained by involvement of toxic chemicals and solvents and results in noxious derivatives and byproducts [23].

In contrast with various alternatives, the solid-state method of NP synthesis is cost effective and convenient to use. The stages involved are milling, calcination, and sintering [26]. Particles produced using this method are unlikely to aggregate and are highly stable. Secondly, the preparation process involves the removal of solvents, which facilitates simpler handling and large-scale synthesis of the NPs, for example, AgNPs [27]. One of the liquid-state methods, i.e., synthesis via sol-gel technique, provides economic production of metal-oxide NPs with various other advantages. In addition to being a simple and fast technique, the method is suitable for the synthesis of high quality and complex nanocomposites with low processing temperature and higher purity. Various metal-oxide NPs such as zinc oxide (ZnO), tungsten oxide (WO₃), tin oxide (SnO₂), and titanium dioxide (TiO₂) have been prepared using this method [28]. This chemical technique involves the formation of a gel-like phase which comprises both a solid and liquid phase. The organic solvents used in the procedure might be toxic for human beings, which is a major drawback of this process [5].

The gas-phase method of synthesis involves magnetron-sputtering using gas-phase condensation and inert-gas cooling which provides high cluster yield under the controlling parameters including temperature, pressure, and vapor concentration [20]. The technique offers an advantage in yielding NPs of desired size and is controlled by the flow rate of the inert gas, which could be argon or helium. Another approach called biological synthesis or green synthesis is subsequently gaining attention as it involves exploitation of microorganisms for the synthesis of NPs [14], which will be specifically discussed in detail in the following sections.

3. Green Synthesis of Nanoparticles

Formation of NPs using green synthesis is currently growing as an emerging approach combining both biotechnology and nanotechnology. This technique involves production of NPs using biological resources, which effectively overcomes the drawbacks imposed by physical and chemical methods [29]. A few examples include Cu NPs from seeds of *Illicium vercium* (star anise) and *Mysristica fragrans* (nutmeg) [30], Ag NPs from agricultural

wastes [31] and extracts of red currant and bilberry wastes [32]. Being eco-friendly, this approach does not require the involvement of noxious chemicals and extreme conditions. It is cost effective and could be useful for large-scale production [29,33]. The green synthesis approach serves various advantages of being simple, reproducible, biocompatible, eco-friendly, and economic. Different biological agents have their own mechanisms to acknowledge metal ions for the synthesis of respective NPs. Major advantages of using biological resources over non-biological means is obtained via biomolecules present in the biological system which maintains the properties of NPs and therefore stabilizing or capping agents are not required [13].

Extraction from plants includes drying and downsizing of the plant component, leading to increased surface area [34]. Green synthesis involves heating and boiling for preparation of plant extracts. Powdered peels of *Punica granatum* (pomegranate) for copper oxide (CuO) NPs [35], Cucurbita pepo (pumpkin) seeds for TiO₂ NPs [36], Chromolaena odorata roots for smart nanocomposites [37], and Basella alba leaves for Ag NPs [38] were boiled in distilled water for 30 min at 55 °C, 2 h at 90 °C, 2 h at 85 °C, 20 min at 60 °C, respectively. Nepeta leucophylla roots were boiled in methanol for 8 h to synthesize Ag NPs [39]. Alternatively, various other methods such as sonication, maceration, autoclaving etc., have also been employed. Ground kernels of Caesalpina bonducella were sonicated for 30 min [40], fruits of Solanum mammosum [41] and Crateagus pentagyna [42] were macerated, roots of Scutellaria biacalensis [43] were autoclaved at 100 °C for 30 min for green synthesis of CuO, Ag, (Fe/Si/Cu-Ag), and ZnO NPs, respectively. Another technique called coprecipitation has been used to synthesize ferric sulfate (Fe₂SO₃) NPs from marine alga (Turbinaria ornate) [44]. Cube-shaped ferroso ferric oxide (Fe₃SO₄) NPs were synthesised using Fenton process from extracts of Rhamnidium elaeocarpum and therefore could be regarded as a green chemical approach [45]. In another study, the biogenic deposition precipitation approach has been used for biogenic preparation of Ag-ZnO nanocomposites via extracts of fennel seeds, which were found to degrade chlorpyrifos pesticide and rhodamine dye [46].

Cyanobacteria, regarded as 'cell factories', are the most appropriate biological resource for synthesis of metal-based NPs. In one study [47], they employed *Haloleptolyngbya alcalis* KR2005/106 cyanobacterial extract as a reducing agent acting upon silver ions to yield Ag NPs of size < 50 nm when exposed to photosynthetically active radiation (PAR). The synthesised Ag NPs were shown to possess ammonia-sensing properties which could be used to monitor water quality. In another study, Ag NPs were biologically synthesised using *Bacillus brevis* (NCIM 2533). The prepared NPs showed potential antibacterial activity against various pathogenic bacteria such as *Staphylococcus aureus* and *Salmonella typhi* which could further be used in disease management [48]. Another advantage of green synthesised NPs includes generation of no by-products in the process. Additionally, various phytochemicals and natural compounds present in biological extracts stabilize and enhance various physico-chemical properties of the NPs without needing any other external agent [49].

4. Mechanisms Involved in Green Synthesis

The mechanism in biosynthesis simply involves the reduction of metal ions into the respective NPs. Ref. [50] synthesised Ag/TiO₂ nanocomposites (NCs) of sizes ranging from 25–50 nm using leaf extract of *Origanum majorana*, serving as reducing agent, under ultrasound irradiation. Ref. [51] employed *Cleistocalyx operculatus* extract as reductant to synthesize Ag/TiO₂ NCs of size ranging from 20–40 nm, which was found to be 91.4% efficient in photocatalytic degradation of Rhodamine B dye. The basic procedure makes use of biological resources which might be carried out both intra- and extracellularly as depicted in Figure 4. This can be done using cell free extracts, supernatants of bacterial cultures, and bacterial biomass. The complex down-streaming process in intra-cellular synthesis is the reason that an extracellular process is preferred [13].



Figure 4. Mechanism of nanoparticle synthesis via reduction of metal ions.

The ion transport system present in microbial cells facilitates intracellular production. Positively charged metal ions are attracted to the negatively charged bacterial cell wall where they are reduced by the embedded enzymes to respective metallic NPs. Reductases are secreted by the microbial cells in case of extracellular production and stabilisation where metal ions are reduced into NPs in the medium, which could be easily retrieved. As for an example, green synthesised ligninase-dependent Au NPs have been produced using fungus *Phanerochaete chrysosporium* intracellularly and was found to be highly stable [52]. Other examples with details are mentioned in Table 1.

Table 1. Various nanoparticles via different biological resources.

Name of Organism	Type of Organism	Synthesised Nanoparticles	Size (nm); Morphology of Nanoparticles	Source of Metal Ion	Mechanism of Synthesis	References
Acetobacter xylinum		Pt	6.3–9.3	K ₂ PtCl ₄	Extracellular	[53]
Bacillus cereus		Ag	18–39; spherical	AgNO ₃	Extracellular	[54]
Pseudomonas putida		Pt	8.02; spherical	H ₂ PtCl ₆ ·6H ₂ O	Extracellular	[55]
Psychrobaacter faecalis	ſ ERIA	Pt	2.49; Spherical	H ₂ PtCl ₆ ·6H ₂ O	Extracellular	[55]
Rhodococcus spp.	BACT	Au	5–15; spherical	HAuCl ₄	Intracellular	[56]
Shewanella oneidensis		Pd-Pt	3–40; spherical	Mixed salt solution of Pd(II) and Pt(IV)	Both extra- and intracellular	[57]
Vibrio fischeri		Pt	3.84; Spherical	$H_2PtCl_6 \cdot 6H_2O$	Extracellular	[55]
Agaricus bisporus		Cu	10; spherical	Cu(NO ₃) ₂	Extracellular	[58]
Hypocrea lixii	G	NiO	3.8; spherical	NiCl ₂ ·6H ₂ O	Extracellular	[59]
Hypocrea lixii	ND	NiO	1.25; spherical	NiCl ₂ ·6H ₂ O	Intracellular	[59]
Lentinula edoded	н	Au	72; triangular, spherical, hexagonal, irregular	HAuCl ₄	Extracellular	[60]

Name of Organism	Type of Organism	Synthesised Nanoparticles	Size (nm); Morphology of Nanoparticles	Source of Metal Ion	Mechanism of Synthesis	References	
Caulerpa racemosa		Ag	5–25; triangular and spherical	AgNO ₃	Extracellular	[61]	
Chlorella vulgaris	- - -	Au	2–10	HAuCl ₄	Extracellular	[62]	
Desmodesmus spp.		spp.		15–30; Spherical	AgNO ₃	Intracellular	[63]
Ecklonia cava	ALG	Au	30; triangular and spherical	HAuCl ₄	Extracellular	[64]	
Rhizoclonium fontinale		Au	16; spherical	HAuCl ₄	Extracellular	[65]	
Tetraselmis lochinensis		Au	5–35; triangular and spherical	HAuCl ₄	Intracellular	[66]	
Arabidopsis thaliana		Au	20–50; triangular and spherical	KAuCl ₄	Intracellular	[67,68]	
Arabidopsis spp. (WT)	T	p. (WT)		32; spherical	$\begin{array}{c} Pd(C_2H_3O_2)_2,\\ K_2PdCl_4 \end{array}$	Intracellular	[69]
Arachis hypogaea		Ag 30–100; mostly spherical		30–100; mostly spherical	AgNO ₃	Extracellular	[70]
Tephrosia apollinea	Ц	Ag	Cubical and spherical	AgNO ₃	Extracellular	[71]	
Vigna unguiculata		Au	20–50; spherical	HAuCl ₄	Extracellular	[72]	

Table 1. Cont.

Besides enzymes, various cofactors such as NADH, compounds such as quinones and glutathione [13] and biomolecules such as vitamins, tannins, steroids, flavonoids, amino acids and peptides, and carboxylic acids are also responsible for the reduction of the metal ions [73]. Other compounds such as phytochemicals and secondary metabolites found in medicinal plants such as saponins, alkaloids, terpenes, phenols, alcohols and extracellular enzymes and metabolites such as hemicellulose, acetyl xylem asterase, glucosidase, paracelsin, and cell wall lytic enzymes are excreted by several fungal species and aid in the reduction of metal ions [74]. Comprehensively, the overall mechanism and the biomolecules used in NP synthesis are summarized in Figure 5.



Figure 5. Brief mechanisms of nanoparticle synthesis.

5. Green Synthesised Nanoparticles in Remediation for Degrading Toxic Substances

Remediation processes involving the exploitation of biological resources, or their components and extracts, are referred to as 'bioremediation', which is achieved by the breakdown of toxic components into less toxic ones [75] as shown in Figure 6.



Figure 6. Concept of bioremediation using green nanoparticles.

Nanoformulations are great alternatives to get rid of contaminants present in the environment. They are actively used in remediation processes for treating and eliminating hazardous wastes. Heavy metals and dye contaminants cause serious issues for both land and aquatic biota by restraining uptake and consumption of dissolved oxygen and diminishing photosynthetic capability. Fe-based NPs possess properties required not only to disinfect water but also for removal of heavy metals from soil [1].

5.1. Bacterial Nanoparticles in Remediation

Bacterial cells are suitable options for the production of NPs as they contain biomolecules required for the reduction of metal ions, and NPs can be synthesised both intra- and extracellularly in the medium and display a large number of applications [15] such as green synthesised ZnO nanoflower from *Bacillus licheniformis* MTCC 9555 [76], which possesses the capability of photocatalytic degradation of pollutant dye methylene blue ($C_{16}H_{18}N_3SCl$). Bacterial cells secrete stabilising enzymes that prevent the agglomeration of NPs. Photocatalysis is a helpful technology, regarded as an advanced oxidation process, which requires direct application of solar energy for elimination of numerous organic pollutants [77]. ZnO NPs are most extensively studied as photocatalysts in remediating aquatic wastewater [78]. Various other studies have been cited in Table 2.

5.2. Fungal Nanoparticles in Remediation

Mycosynthesised NPs have gained tremendous importance as they are cost effective and their yield is relatively good. Among other biological agents, fungi are considered to be the most suitable because they possess a large number of mycelia and fruiting bodies [79], and contain an ample amount of biomolecules required for NP synthesis [80,81]. Therefore, the amount of mycosynthesised NPs are sufficient and quick as compared with other biological agents [82]. Numerous fungal species have been exploited for biosynthesis of NPs employed for remediation. In one study, the waste substrate of *Lentinula edodes* was used to synthesise ferroferric oxide NPs which were found to be effective in the reduction of pollutants such as Cr, NH₄-N, Pb, Ni, and Cu [83]. Various studies have been cited and elaborated on in Table 2.

5.3. Algal Nanoparticles in Remediation

Algae have been considered as 'bio-nano factories' as they actively absorb metal ions from their surroundings, resulting in their reduction and the synthesis of respective NPs in both living and dry dead form [15]. The controlled growth rate and energy of forming NPs are conventionally achieved by using suitable capping agents or surfactants. Due to being non-biodegradable in nature, these chemicals are present as remnants which are difficult to remove completely. In order to circumvent this issue, naturally occurring biomolecules found in variety of algae are employed for the stabilisation and synthesis of NPs [84] as they have a huge capacity for metal-binding. Ag NPs are the most studied and prevalent among the others. In one study, AgNO₃ was exposed to extracts of seaweed *Enteromorpha flexusa* [85] and *Chaetomorpha linum*. Reduction of metal ions was facilitated by the water-soluble components found in the extract, such as terpenoids, flavonoids, amines, and peptides, which resulted in the formation of Ag NPs [86]. Prasiola crispa, a freshwater alga, was employed for green synthesis of Au NPs carried out by reduction of aqueous solution of chloroauric acid [87]. Toxicity issues are important to consider as they must not harm living biota. Algal synthesis serves to provide no or negligible toxicity hence it is a safer and green approach. Additionally, they are considered as 'nano-reserves' and could be cultured conveniently with less effort [88].

Many algal species have been employed in remediation processes for the degradation of hazardous dyes and chemicals as earlier methods such as redox treatment, UV degradation, activated carbon sorption etc., were inefficient [84]. Ag NPs were green synthesised using seaweed *Ulva lactuca* [89] and *Hypnea musciformis* [90], which have been very efficient in degrading methyl orange dye. Green synthesised iron oxide NPs via *Spirulina* were found to be very effective in adsorbing crystal violet. NPs when treated with water containing dyes results in decolorisation of the solution, which was reaffirmed via analytical techniques hence could be used in treating wastewater [91]. Various other studies have been cited and discussed in Table 2.

5.4. Plant Nanoparticles in Remediation

Synthesis of NPs using plant extracts have been used for a long time. *Cinnamomum camphora* sun-dried leaves were employed for the biosynthesis of Ag and Au NPs of sizes ranging from 55 nm to 80 nm [92]. Utilising plant extracts is beneficial compared to microbes because they are non-pathogenic and this is a one-step process [15]. Synthetic dyes are majorly found in wastewaters, mainly via industrial effluents, inflict a serious threat to the environment, causing severe health issues and imbalances in nature [93]. CoO NPs were biosynthesised via *Vitis rotundifolia*, commonly named Jumbo Mascadine, using co-precipitation, which was found effective in degrading Acid Blue-74 (AB-74) [94].

Water treatment tools and techniques are now more refined, eco-friendly, and inexpensive. *Salvia rosmarinus* extract-mediated TiO₂ NPs were found effective in degrading Rhodamine B, Methyl orange, and Methylene blue [95]. FeO NPs were firstly biosynthesised using *Ruellia tuberosa* leaf extract and were shown to possess antimicrobial activity against various pathogenic bacteria such as *Klebsiella pneumonia, Staphylococcus aureus*, etc., and have the ability to degrade toxic dyes [96]. In one study, the synthesis of iron oxide (FeO, Fe₃O₄, and Fe₂O₃) particles was mediated by plant extracts of *Petlophorum pterocarpum*, which were found to be effective in elimination of rhodamine from wastewater [97]. Various other studies have been considered in Table 2.

Biological Resource	Name of Organism	Synthesised Nanoparticles	Size of Nanoparticles (nm)	Source of Metal Ion	Applications	References
BACT ERIA	Bacillus amyloliquefaciens	Ag	20-40	AgNO ₃	Photocatalytic degradation of p-nitrophenol	[98]
	Bacillus cereus	Ag	51	AgNO ₃	Remediation of Pb and Cr	[99]
	Shewanella oneidensis	Pd-Pt	13.2	Mixed salt solution of Pd(II) and Pt(IV)	Degradation of azo dyes and nitrophenol	[57]
QCI	Saccharomyces cerevisiae	Pd	32	$C_4H_6O_4Pd$	Degradation of a textile dye named direct blue 71	[100]
	Acaulospora mellea	Nano-zero-valent iron	69.5	-	Remediation of soil contaminated with Zn, Pb and Cd	[101]
FU	Ganoderma applanatum	Au	18.70	HAuCl ₄	Reduction of methylene blue dye	[79]
	Aspergillus tamarii	Fe ₃ O ₄	16.5	FeSO₄·7H₂O and FeCl₃·6H₂O	Remediation of wastewater containing textile dyes	[102]
	Padina pavonica	Fe ₃ O ₄	23.45	FeCl ₃	Removal of Pb from wate water	[103]
	Sargassum acinarium	Fe ₃ O ₄	24.5	FeCl ₃	Removal of Pb from wate water	[103]
	Chlorella sp.	ZnO	19.44	$ZnC_4H_6O_4$	Degradation of dibenzothiophene	[104]
ALGAE	Chlorella pyrenoidosa Scenedesmus obliquus	CdSe quantum dots	6	CdCl ₂ , Cd(NO ₃) ₂ . 4H ₂ O, Na ₂ SeO ₃	Recycling of toxic cadmium metal	[105]
	Chlorella vulgaris	Ag	55.06	AgNO ₃	Degradation of methylene blue dye	[106]
	Spirulina platensis	CdS	8.4	Cd(NO ₃) ₂	Degradation of malachite green dye and detoxification Cd(II)	[107]
	Amomum longiligulare	ZnO	50	$\begin{array}{c} Zn(NO_3)_2 \cdot \\ 6H_2O \end{array}$	Degradation of malachite green and methylene blue dye	[108]
	Anthophalus cadamba	ZnO	167	$\begin{array}{c} ZnC_4H_6O_4\cdot\\ 2H_2O\end{array}$	Removal of Cr from soil	[109]
	Catharanthus roseus	Ag	58.4–97.4	AgNO ₃	Remediation of Cr and Cd	[110]
	Catunaregam spinosa	SnO ₂	47	SnCl ₂	Degradation of Congo red dye	[111]
PLANTS	Citrus reticulata	FeO	50	FeCl ₂ ·4H ₂ O, FeCl ₃	Co ⁺² heavy metal removal	[112]
	Cynometra ramiflora	Fe ₂ O ₃	58.5	FeCl ₂ , FeCl ₃	Degradation of methylene blue dye	[113]
	Eucalyptus globulus	FeO	4.17	Fe(NO ₃) ₃ . 9H ₂ O	Remediation of Cr and Cd	[114]
	Eucalyptus spp.	ZnO	20-40	$\frac{Zn(NO_3)_2}{6H_2O}$	Degradation of malachite green and Congo red dye	[115]
	Ficus benjamina	Ag	60–105	AgNO ₃	Remediation of Cd	[116]
	Jatropha curcas	TiO ₂	13	TiCl ₄	Remediation of effluent from tannery industry and Cr	[117]
	Madhuca longifolia	CuO	30	$\begin{array}{c} Cu(NO_3)_2 \cdot \\ 3H_2O \end{array}$	Degradation of methylene blue dye	[118]

 Table 2. Several biologically derived nanoparticles in environmental remediation.

Biological Resource	Name of Organism	Synthesised Nanoparticles	Size of Nanoparticles (nm)	Source of Metal Ion	Applications	References
	Ocimum tenuiflorum	Ag	32.58	AgNO ₃	Degradation of turquoise blue dye	[119]
	Parthenium	Fe	100	FeSO ₄ ·7H ₂ O	Degradation of crystal violet dye	[120]
	Phoenix dactylifera	FeS	68	FeSO ₄ ·7H ₂ O	Removal of ciprofloxacin and Cr(VI) heavy metal	[121]
	Piliostigma thonningii	Ag	50-114	AgNO ₃	Remediation of Fe, Pb, Cu, and Mg heavy metals	[122]
	Pimpinella tirupatiensis	Pd	15.4	PdCl ₂	Degradation of Congo red dye	[123]
	Plumbago zeylanica	Ag	55	AgNO ₃	Degradation of methylene blue, methyl red, phenol red dye	[124]
	Psidium guajava	Fe ₂ O ₃ -Ag	50–90	Fe(NO ₃) ₃ and AgNO ₃	Remediation of Cr(VI) heavy metal	[125]
	Sapium sebiferum	Pd	5	PdCl ₂	Degradation of methylene blue dye	[126]
	Sphagneticola trilobata	ZnO	65–80	$ZnC_4H_6O_4$	Remediation of Cr heavy metal	[127]
	Verbascum thapsus	Nano-zero-valent iron	40–50	FeCl ₃	Remediation of Cd	[128]
	Vitex agnus-castus	SnO ₂	8	SnCl ₂	Degradation of rhodamine B and Co ⁺² heavy metal removal	[129]
	Zingiber zerumbet	ZnO	10	$\frac{ZnC_4H_6O_4}{2H_2O}\cdot$	Adsorptive removal of Pb(II)	[130]

Table 2. Cont.

6. Factors Affecting Synthesis of Nanoparticles

Toxicity and environmental safety are crucial points to note when synthesising and using NPs in remediation. Few studies have describes health hazards imposed by NPs where the degree of severity depends upon its shape and size. Sometimes their properties are unpredictable once they are introduced to the human body [131]. Morphological characteristics and biological activities of NPs are governed by various factors involving temperature, pH, concentration of reactants, reaction time [124], the metallic precursor [132] and the type of extract utilized, and are optimized for green synthesis. Studies have depicted that larger volumes of extracts yield larger amounts of and more stabilized NPs [15].

The types and morphology of the synthesised NPs depends on the precursor and methodology used. For Cu-based NPs, CuCl₂ [133], copper nitrate [Cu(NO₃)₂] [134], Copper acetate [Cu(OAc)₂] [135], and CuSO₄ [136] have been used as precursors in various studies. Furthermore, its concentration defines the NP formation and particle size. Increased amounts of *Cuminum cyminum* (cumin) extract [137] and *Syzygium aromaticum* (clove) [138] resulted in increased size of Ag NPs. In one study, the concentration of the precursor molecule was optimized to obtain larger NP size from root extract of *Senna didymobotrya* (Popcorn Cassia) [139]. Additionally, when precursors are added in combined form, a blended nanocomposite is formed. For example, the combination of ZnO and AgNO₃ yield an Ag-ZnO nanocomposite [46] and a mixture of Fe₃SO₄, SiO₂, Cu₂O, and Ag salt yield a (Fe/Si/Cu-Ag) nanocomposite [42].

Studies have reported that plant-mediated NP synthesis is directly dependent on temperature, which ranges from 25 to 100 °C. Higher temperature facilitates increased reduction of metal ions into their respective NPs. Additionally, with the gradual increase in temperature and conversion rate, the size of NPs decreases [34]. pH values ranging from

7–9 yield maximum NPs [140] whereas acidic pH leads to inactivation of phytochemicals required for the reduction of metal ions [141]. Parameters such as temperature, pH, reactants etc., decides the reaction time and duration of the process accordingly in order to obtain maximum product [34]. Another important factor is the preparation cost of NPs. Due to cost-effectiveness, biogenic synthesis is a more adaptable approach and could be carried out on a larger scale [142].

7. Conclusions

With increases in urbanisation, population, and industrial growth, environmental issues are increasing day by day. Ecological pollution remains an unsolved issue, leading to contamination at every atmospheric level. These contaminants impose severe threats on plants, aquatic, and terrestrial lifeforms. Modern problems require modern solutions and nanobiotechnology serves to be a great platform for this. The domain has grown rapidly in the past ten years as the technologies and approaches are becoming more advanced day by day in an eco-friendly direction. There is a need to develop sustainable and pollution-free routes for NP synthesis as chemical and physical methods are harmful and, hence, green synthesis came into being. This review showed insights into remediation of hazardous wastes using NPs obtained via numerous biological resources. Nanobioremediation strategies are future solutions which are time and energy efficient and economical. Their by-products are nontoxic and biodegradable in nature, and do not impose any threat to the ecological balance as well as living biota. Many studies carried out up to now have confirmed the sustainable execution of NPs in maintaining a healthier agro-environment.

Author Contributions: All the authors actively contributed to manuscript drafting. A.S. and P.T.; wrote the manuscript, and R.R., S.N.S., T.M., V.D.R. and M.B. edited the manuscript for further refinement. 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.

Acknowledgments: A.S., P.T. and R.R. are grateful to the Director, Dayalbagh Educational Institute for providing kind support and facilities. V.D.R., S.S. and T.M. acknowledge support by the laboratory «Soil Health» of the Southern Federal University with the financial support of the Ministry of Science and Higher Education of the Russian Federation, agreement No. 075-15-2022-1122. M.B. would recognize Grant of the Ministry of Education and Science of the Russian Federation for the development of youth laboratories, within the framework of the implementation of the Tula State Lev Tolstoy Pedagogical University program "Priority 2030" under Agreement No. 073-03-2022-117/7.

Conflicts of Interest: The authors declare no conflict of interest.

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