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Phytogenic Nanoparticle Engineering: Emerging Trends in Sustainable Biosynthesis and Functional Applications

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Abstract: Recent years have seen tremendous progress in the area of bio-nanotechnology, especially in the production and use of bio-nanoparticles (BNPs). The green synthesis of BNPs utilizing biological organisms including algae, fungus, bacteria, and plants is the main topic of this paper. Using these organisms to synthesize nanoparticles provides a sustainable and environmentally benign substitute for traditional chemical and physical processes, which often need hazardous chemicals and a lot of energy. The synthesis of nanoparticles with a variety of shapes and sizes is facilitated by phytochemicals found in plant extracts, distinct metabolic pathways, biomolecules in bacteria and fungus, and the complex biochemical makeup of algae. The broad range of uses of BNPs in industries such as wastewater treatment, fuel cells, energy production, and medicines is further examined in this paper. BNPs have shown effectiveness in antibacterial, anti-inflammatory, antioxidant, and anticancer properties in treatments. In order to increase sustainability and efficiency, BNPs are being incorporated into fuel cells and other energy generating systems, such as bio-diesel, in the energy industry. These devices' performance is improved by their high surface area and catalytic qualities. BNPs are used in wastewater treatment, another crucial sector, to remove organic pollutants, microbiological contaminants, and heavy metals, providing an economical and sustainable approach to water purification. The potential of bio-nanoparticles produced using environmentally friendly techniques is highlighted in this thorough analysis. It draws attention to the need of further study in order to improve synthesis procedures, comprehend mechanisms of action, and broaden the range of applications. By addressing the benefits and some of the most urgent issues in energy, environmental sustainability, and medical, BNPs may open the door for creative and long-lasting technological breakthroughs in the future.

Keywords: bio-nanoparticles; green synthesis; therapeutic properties; fuel cells; energy generation; wastewater treatment; characterization

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1. Introduction

Nanotechnology research and studies have advanced rapidly worldwide, and the applications of nanoparticles (NPs) in various fields, including biomedical applications, In recent years, major research topics have included cell labeling, medication delivery, plant tissue culture, biomarkers, the automotive industry, and the energy sector [1–3]. NPs of different sizes and shapes may be generated using a variety of synthesis techniques. While physical and chemical procedures are often used, biological methods are becoming more and more popular as an alternative [4]. Chemical methods [5–9] frequently employ chemical agents like sodium hydroxide, sodium borohydride, potassium hydroxide, and hydrazine for reduction purposes, while physical methods [10–17] for NP synthesis commonly employ condensation, laser ablation, laser pyrolysis, evaporation lithography, and ball milling. Because it makes use of renewable and biodegradable materials, the synthesis of bionanoparticles is a sustainable solution in the field of nanotechnology (Figure 1).

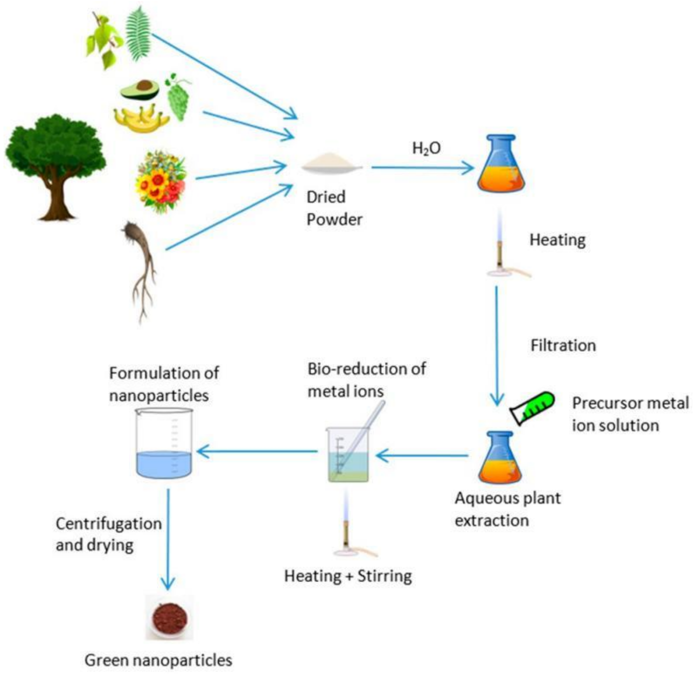

Figure 1. Green synthesis of bio-nanoparticles from plants.

[18] claims that the precise process behind the phytosynthesis of metallic nanoparticles has not yet been established. According to [19], it is still difficult to pinpoint the exact biochemical processes that go into the environmentally friendly creation of metallic nanoparticles. The typical process for producing plant-based nanoparticles is as follows: a plant and a certain portion of it are chosen, crushed, and the plant extract is then produced. To get rid of any contaminants, the plant extract is treated. The plant extract is then combined with the precursor, which is usually a metallic solution, to create nanoparticles. Effectively facilitating the process requires maintaining the right pH, temperature, and constant stirring, which guarantees the formation of equally sized nanoparticles. In some nanoparticles, like Ag and Au, a change in color in the plant extract might be interpreted as a sign of nanoparticle creation because of surface plasmon resonance (SPR) [20–22]. The production of nanoparticles is indicated by the color shift that is seen during the reaction process. This shift is brought about via SPR, in which light interacts with the nanoparticles to alter their hue in relation to the bulk material. The color fluctuation seen during the fabrication of metallic nanoparticles is caused by both SPR and the quantum confinement effect [23, 24]. While plants contain a variety of secondary metabolites, including phenols, terpenes, and alcohols, microorganisms create a variety of important enzymes. These enzymes as well as

Metabolites have the ability to function as reducing agents, which makes the production of nanoparticles easier. Furthermore, plant extracts have the ability to stabilize solutions without the requirement for supplementary stabilizing chemicals [20,21,25]. According to Ref. [26], Tithonia diversifolia contains phytochemicals such triterpenes, flavonoids, saponins, and steroids. In a similar vein, [22] verified that the stabilizing and reduction processes involved in the creation of nanoparticles are aided by the presence of functional groups of carbon (C) and oxygen (O). Additionally, plant extracts may stabilize nanoparticles during synthesis by acting as capping agents. The participation of different carbon (C), hydrogen (H), and oxygen (O) bonds in plant extracts that aid in the capping process has been verified by FTIR analysis [22,27,28]. Polyphenols are very reactive in chemical reactions because they have many hydroxyl (-OH) groups linked to aromatic rings. For instance, nearby hydroxyl groups in polyphenols (usually in the ortho position) bond with gold ions during the production of gold nanoparticles to create a stable five-membered chelate ring. Gold ions are reduced (gain electrons) to neutral gold atoms (Au0), whereas ortho-dihydroxyl groups (two -OH groups on neighboring carbons) are oxidized forming quinones (C=O groups). Gold's strong redox potential is the cause of this reduction [19,20]. Furthermore, [19] noted that proteins provide carbonyl (-C=O) groups, which serve as stabilizing agents. By encircling the nanoparticles, these amino acid residues maintain stability and stop aggregation. This stabilizing process has been supported by FTIR studies [24]. The solution's silver ions (Ag+) are reduced to neutral silver atoms (Ag) when the hydrogen radical contributes its unpaired electron to them. Silver nanoparticles (Ag NPs) are created when these silver atoms group together. The remaining eugenol molecule, which now has a phenoxy radical on its oxygen atom, goes through resonance stabilization after this reduction step. The radical becomes less reactive and more stable as a result of the unpaired electron on the oxygen atom delocalizing throughout the benzene ring and its double bonds. Both stabilization and nanoparticle production are facilitated by these stabilized radicals, which stay dissolved in the solution [19, 29]. According to Ref. [30], nearby hydroxyl groups in polyphenolic compounds combine to create a five-membered chelate ring. Due to the extremely high oxidation-reduction potential of Au3+, the chelated ortho-dihydroxy groups are oxidized to quinones, while Au3+ is simultaneously reduced to Au. The formation of Au NPs occurs through the aggregation of nearby Au atoms, and quinones and polypheno- lic compounds subsequently stabilize these nanoparticles. However, there exists several research areas for further development; for example, the efficiency of various natural re- sources for the green synthesis of nanomaterials has not been fully studied. Importantly, the negative impacts of those nanomaterials are also not sufficiently understood. Therefore, it is mandatory to focus on risk management throughout production, processing, preservation, and discharge [31,32]. Furthermore, the green synthesis of NPs using biological materials and their properties are summarized in Table 1.

Biological Material

Table 1. Green synthesis of NPs using biological materials.

	Name	**Morphology**	**Nanoparticle Size (nm)**	Nanoparticle	Reference
Plant	*Abutilon indicum* leaves	Hexagonal	16	CuO	[33]
	Aloe vera leaves	Spherical	15–50	Ag	[34]
	Bergenia ciliata Rhizome	Spherical	20	CuO	[35]
	Capparis spinosa tissues	Spherical and semispherical	15–30	Ag	[36]
	Catharanthus roseus leaves	Hexagonal	35	ZnO	[37]
	Coriandrum sativum leaves	Spherical	15–50	Ag	[34]
	Corymbia citriodora leaves	Needle	21–28	Mn	[38]

Biological Material

Table 1. *Cont.*

	Name	**Morphology**	**Nanoparticle Size (nm)**	Nanoparticle	Reference
	Cuminum cyminum seeds	Crystalline	15	TiO_2	[39]
	Cymbopogon citratus leaves	Spherical	15–50	Ag	[34]
	Cymbopogon olivieri	Spherical	28	ZnO	[40]
	Eucalyptus robusta leaves	Spherical	16–23	Mn	[38]
	Euphorbia helioscopia leaves	Crystalline	30–100	Ag	[41]
	Euphorbia pulcherrima flowers	Cubical	16–54	CuO	[42]
	Fragaria ananassa fruits	Spherical	10–30	Cu	[43]
	Hypericum perforatum leaves	Spherical	20–50	MnO_2	[44]
	Lemna minor tissues	Spherical	10–20	ZnO	[45]

	Melia azedarach leaves	Crystalline and spherical	50–71	TiO_2	[46]
	Mentha arvensis leaves	Spherical	15–50	Ag	[34]
	Nerium oleander leaves	Spherical	26	Cu	[47]
	Ocimum sanctum leaf	Granular	-	CuO	[48]
	Paullinia cupana Kunth leaf extract	Spherical morphology	39–126	Ag	[49]
	Phoenix dactylifera L leaves	Cubic to spherical	12–97	Ag	[50]
	Phyllanthus emblica fruit	Large, irregularly shaped flakes	-	Cr_2O_3	[51]
	Saccharum officinarum stem	Spherical, square, cube, plate, rectangular	29–60	CuO	[52]
	Triticum aestivum seed	Spherical	21–42	CuO	[53]
Bacteria	*Aquaspirillum magnetotacticum*	Octahedral prism	40–50	Fe_2O_3	[54]
	Arthrobacter gangotriensis	Spherical	5–6	Ag	[55]
	Arthrobacter kerguelensis	Spherical	5	Ag	[55]
	Bacillus cecembensis	Spherical	7	Ag	[55]
	Bacillus cereus	Spherical	20–40	Ag	[56]
	Bacillus indicus	-	4–6	Ag	[55]
	Bacillus megaterium D01	Spherical	2.5	Au	[57]
	Bacillus subtilis 168	Hexagonal-octahedral	5–50	Au	[58]
	Escherichia coli	Wurtzite structure	2–5	CdS	[59]
	Escherichia coli DH 5α	Spherical	8–25	Au	[60]
	Klebsiella aerogenes	-	20–200	CdS	[61]
	Lactobacillus casei	Spherical	20–50	Ag	[62]
	Magnetospirillum magnetotacticum	Chain	47	Fe_3O_4	[63]
Biological Material	*Plectonemaboryanum UTEX* 485	Cubic, octahedral	10–25	Au	[64]
	Pseudomonas antarctica	Spherical	11–12	Ag	[55]
	Pseudomonas meridiana	Spherical	5–6	Ag	[55]
	Pseudomonas proteolytica	Spherical	7	Ag	[55]
	Rhodopseudomonas capsulate	Spherical	10–20	Au	[65]
	Serratia sp. (ZTB29)	Polydisperse, spherical	20–40	CuO	[66]
	Shewanella oneidensis	-	1–5	UO_2	[67]
	Shewanella alga	Triangular	10–20	Au	[68]

Table 1. *Cont.*

Fungi	*Alternata alternate*	Spherical	20–60	Ag	[69]
			Size (nm)		
	Aspergillus flavus	-	1–8	Ag	[70]
	Aspergillus flavus TFR7	Spherical	12–15	TiO_2	[71]
	Aspergillus fumigates	Spherical	5–25	Ag	[72]
	Aspergillus niger	Spherical	20	Ag	[73]
	Aspergillus terreus	Spherical	8	ZnO	[74]
	Cariolus versicolor	Spherical	25–75	Ag	[75]
	Cladosporium cladosporioides	Spherical	10–100	Ag	[76]
	Fusarium oxysporum	Spherical	8–14	Au-Ag alloy	[77]
	Fusarium semitectum	Crystalline spherical	10–60	Ag	[78]
	Fusarium solani	Spherical	5–35	Ag	[79]
	Penicillium brecompactum	Crystalline spherical	23–105	Ag	[80]
	Penicillium fellutanum	Spherical	5–25	Ag	[81]
	Phanerochaete chrysosporium	Pyramidal	50–200	Ag	[82]
	Phoma glomerata	Spherical	60–80	Ag	[83]
	Rhizopus nigricans	Round	35–40	Ag	[84]

Name **Morphology** **Nanoparticle**
Nanoparticle Reference

Rhizopus stolonifer	Spherical	25–30, 1–5	Ag Au

					[85]
	Saccharimyces cerevisae broth	Spherical	4–15	Ag, Au	[86]
	Trichoderma viride	Spherical	5–40	Ag	[87]
	Trichothecium sp.	Spherical, rod-like, triangular	10–25	Au	[88]
	Verticillium	Spherical	21–25	Ag	[89]
	Verticillium luteoalbum	Triangular, hexagonal	10	Au	[90]
Algae	*Bifurcaria bifurcate*	Crystalline	5–45	CuO	[91]
	Caulerpa racemosa	Spherical and triangular	5–25	Ag	[92]
	Chaetomorpha linum	Nano-clusters	3–44	Ag	[93]
	Chlamydomonas reinhardtii	Round/rectangular	5–35	Ag	[94]
	Chlorella vulgaris	Crystalline	2–10	Au	[95]
	Colpmenia sinusa	Spherical	20	Ag	[96]
	Cystophora moniliformis	Spherical	50–100	Ag	[97]
	Ecklonia cava	Spherical and triangular	30	Au	[98]
	Enteromorpha flexuosa	Spherical	2–32	Ag	[99]
	Enteromorpha flexuosa	Spherical	2–32	Ag	[99]
	Gracilaria gracilis	Crystalline	25–50	ZnO	[100]
	Jania rubins	Spherical	12	Ag	[96]
	Lemanea fluviatilis	Spherical	5–15	Au	[101]
	Padina gymnospora	Spherical	53–67	Au	[102]
	Prasiola crispa	Spherical	5–25	Au	[103]
	Pterocladia capillacae	Spherical	7	Ag	[96]
	Sargassum muticum	Cubic	18	Fe_3O_4	[104]
	Sargassum muticum	Hexagonal wurtzite	30–57	ZnO	[105]
	Sargassum muticum	Spherical	5.4	Au	[106]
	Tetraselmis kochinensis	Spherical and triangular	5–35	Au	[107]
	Ulva faciata	Spherical	7	Ag	[96]

2. Applications of Bio-Nanoparticles

Bio-nanomaterials offer significant advantages such as biocompatibility, biodegrad- ability, and enhanced biological functionality, making them ideal for several applications in energy storage, environmental remediation, and medicinal applications. However, several challenges still exist, such as synthesis complexity, stability issues, and scalability constraints that need to be addressed through advanced fabrication techniques, hy- brid material development, and computational modeling to enhance their performance and applicability.

Applications of Bio-Nanoparticles in Fuel-Cells

The fuel cell was first introduced by Sir William Grove in the 1830s. Even though the fuel cell has a long history, nowadays, many research works are being carried out that are relevant to fuel cells compared to previous decades [108,109]. The fuel cell is an effective energy converter compared to other relevant energy sources, and it only emits water and heat, making it a more environmentally friendly solution. Due to their higher energy efficiency, fuel cells are currently used in several applications in electric vehicles, alternative power sources, energy-storing methods, and space programs [110,111].

Proton exchange membrane fuel cells (PEMFs), solid-oxide fuel cells (SOFs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), direct methanol fuel cells (DMFC), and molten carbonate fuel cells (MCFCs) can be identified as the different fuel cells types that are currently at the development. These fuel cell types are used in different applications based on their power ratings and operating temperatures. Apart from conventional fuel cells, microbial fuel cells are also being developed by scientists and can also be used as fuel cells, which is an eco-friendly solution. Microbial fuel cells can generate electricity while purifying wastewater using the metabolism power of bacteria.

Apart from the anode, cathode, and electrolyte, electro-catalysts are used in fuel cells to increase the rate of reactions in the fuel cells [112]. Most of the catalysts are noble nanopar- ticles such as platinum (Pt) and platinum alloys. Currently, there is ongoing research to analyze the different extraction methods of Pt, Pt alloys, and non-precious materials. As an environmentally friendly solution, researchers are trying to develop bio-synthesized nanoparticles as nanocatalysts for fuel cells and microbial fuel cells [113–115]. Table 2 represents several recent studies that have been carried out regarding bio-synthesized nanoparticles as catalysts for conventional fuel and microbial fuel cells.

pplications of Bio-Nanoparticles in Waste Water Treatment

Due to the unique properties such as high surface area, reactivity, and functionality of bio-nanoparticles, they have emerged as highly effective agents in the wastewater treatment industry. Their properties lead to the removal of a wide range of contaminants, including heavy metals, organic pollutants, and pathogenic microorganisms. The wastewater or effluent containing non-biodegradable dyes and organic pollutants into the water reservoirs is mainly discharged from various industries, factories, and laboratories without any treatment, and it leads to a global environmental and health hazard [153]. Large quantities of dyes are used in many industrial applications such as textiles, papers, leathers, laser materials, laser printing, foodstuffs, cosmetics, xerography, gasoline, etc. And byproducts discarded from industries contain heavy metal ions and dyes, or both in most cases [154]. Furthermore, according to the estimated data, the total worldwide production of dyes is lost in their synthesis and dyeing process, which is over 15% [155]. The studies proved that most of these dyes are toxic and carcinogenic and reduce the light penetration of the aqueous systems. As a result, it causes serious concern to society due to the complex structures and non-biodegradable nature. This leads to negative effects on photosynthesis, is toxic for living organisms, is harmful to human health, and contributes significantly to the overall imbalance of the ecosystem [156].

Due to the high surface area and affinity for metal ions, carbon-based and metal- oxide nanoparticles have shown exceptional adsorption capacity on heavy metals like lead, mercury, and cadmium from wastewater [157,158]. Nanoparticles such as titanium dioxide show photocatalytic activity, and they are employed to break down organic contaminants, including pesticides, dyes, and pharmaceutical residues, converting them into less harmful substances. TiO_2 and other metal oxides demonstrate high photocatalytic activity, but their effectiveness depends on several conditions, such as pH level, light intensity, and the presence of additional catalysts. pH levels, can affect the surface charge and light intensity directly impacts the electron-hole pairs which is a critical factor for photocatalysis. At the same time the availability of a co-catalysts can improve the overall efficiency [159]. Furthermore, silver and gold nanoparticles exhibit potential antimicrobial effects against harmful viruses and bacteria [160]. Moreover, the efficiency and sustainability of the wastewater treatment process are enhanced by magnetically responsive nanoparticles due to their easy recovery and reusable properties. Table 4 demonstrates a summary of recent research works

3. Conclusions

Green synthesis of BNPs using plants, bacteria, fungi, and algae presents a promising and eco-friendly alternative to conventional methods. The diverse biochemical properties of these biological entities enable the production of nanoparticles with varied shapes and sizes, enhancing their applicability across multiple fields. BNPs have shown significant potential in therapeutics as antimicrobial, anti-inflammatory, antioxidant, and anticancer agents. Additionally, they are being integrated into fuel cells and energy generation systems, providing green energy solutions. In wastewater treatment, BNPs offer an effective and environmentally friendly approach to removing heavy metals, organic pollutants, and microbial contaminants. However, further research is essential to optimize synthesis processes, fully elucidate their mechanisms of action, and expand the scope of their applications. BNPs can address some of the pressing challenges in medicine, energy, and environmental sustainability, paving the way for innovative and sustainable technological advancements. The continued exploration and development of bio-nanoparticles for advancements in material engineering, hybridization strategies, and computational design hold great promise for the future, offering sustainable solutions that align with the growing demand for environmentally conscious technologies.

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Abbreviations

The following abbreviations are used in this manuscript:

ATR-FTIR	Attenuated total reflectance Fourier-transform infrared spectroscopy
BET	Brunauer–Emmett–Teller
DLS	Dynamic light scattering
EDAX	Energy-dispersive X-ray spectroscopy
EDS	Energy-dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
FESEM-EDX	Field emission scanning electron microscopy with energy dispersive X-ray spectroscopy
FTIR	Fourier-transform infrared spectroscopy
HRSEM	High-resolution scanning electron microscopy

HRTEM	High-resolution transmission electron microscopy
SEM	Scanning electron microscopy
SEM-EDX	Scanning electron microscopy with energy dispersive X-ray spectroscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analyzer
UV–vis	Ultraviolet–visible spectrophotometer

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