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Towards Sustainable Nanotechnology: A Review on Biosynthesis Methods of Metal and Metal Oxide Nanoparticles

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Abstract: The synthesis of nanomaterials (NMs) has gained a lot of interest in the search for sustainable technological improvements since it has the potential to revolutionize a number of industries. Particularly, metal and metal oxide nanoparticles have demonstrated a variety of uses in fields like electronics and medicine. However, conventional synthesis techniques usually require toxic chemicals and energy-intensive processes, raising issues with safety and the environment. Exploring environmentally sustainable alternatives has become crucial, In the light of this, the present review aims to outline the field of biosynthesis with particular focus on the ability to produce metal nanoparticles (MNPs) and metal oxide nanoparticles (MONPs) by utilizing biological elements like bacteria, plants, enzymes and other biomaterial and reported applications of these NPs.

Keywords: Nanotechnology, Biosynthesis, Metal Nanoparticles (MNPs), Metal oxide Nanoparticles (MO NPs), Nanocomposites

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Introduction

The study and implementation of materials with a scale typically between 1 and 100 nm, where size intrinsically influences the resulting properties, comes under the field of Nanotechnology. It should come as no surprise that considerable effort has gone into utilizing and meticulously manipulating these special size-dependent electrical, magnetic, opto-electronic, catalytic, and mechanical properties to give these nanomaterials favorable and defined attributes for a variety of applications, including but not limited to medicine, national defense, energy, information technology, and environmental remediation (Hyeon *et al.*, 2015). When researchers discovered that a substance's

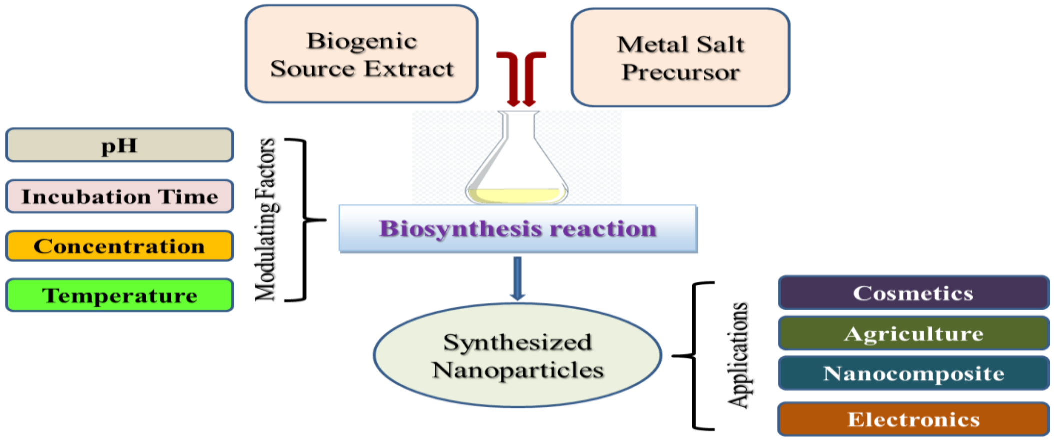

Fig. 1: Biosynthesis in a nutshell.

size affects its physicochemical qualities, including its chemical, electrical, mechanical, and optical properties, they realized the significance of NMs. Due to their special qualities, nano-particulate materials have so garnered a lot of interest (Gleiter, 2000). NPs are produced and naturally formed through a variety of processes, including photochemical reactions, forest fires, straight-forward erosions and volcanic eruptions (Saleh, 2020).

Depending on the end-user property demand, nanomaterials are synthesized using various processes. There are two main methods to synthesize nanomaterials: bottom-up and top-down. Bottom-up methods combine small molecules or atoms to create nanomaterials, whereas top-down methods reduce the size of bigger molecules to the nano-scale. These methods use a variety of synthesis techniques and fall into four main categories: chemical, physical, mechanical, and biological. The top-down strategy typically uses techniques including high-energy ball milling, extreme plastic deformation, etching, mechanical alloying, lithography, reactive milling, and micromachining techniques. Molecular self-assembly, sol-gel, electron (or ion) beams, metal-organic chemical vapor deposition, vacuum arc deposition, inert gas condensation, molecular beam epitaxy, electrode position, physical/chemical vapor deposition, and ultrasonic dispersion are examples of bottom-up methods (Tulinski and Jurczyk, 2017; Mazari *et al.*, 2021). Due to impurity residues and poor finishing, it has been noted that the synthesis processes have an impact on the toxicities of the nanomaterials. Nanomaterials can be harmful to people and have negative effects on their heart, nervous system, and other organs, and can also cause neurotoxicity or immunotoxicity (Mazari *et al.*, 2021). Despite being efficient, wet chemical methods for manufacturing MNPs can produce toxic by-products, or the chemical agents used in chemistry-based processes, such as sodium hydrazine hydrate, borohydride, dimethyl-formamide (DMF), etc., may remain adsorbed at the surface of the MNPs, which ultimately limits their applications, particularly in medicine (Mohamed *et al.*, 2020). The aforementioned chemicals, such as hydrazine, are recognized for their carcinogenicity, genotoxicity, and cyto-toxicity (Nath and Banerjee, 2013). While the physical methods have higher energy and capital costs in addition to not having higher yields, the chemical methods have the potential to be harmful. By using biological processes (Fig. 1), which offer a secure, affordable, and environ-mentally friendly method for the synthesis of MNPs without requiring any high or expensive needs, this conundrum of energy balance, cost effectiveness, toxicity, and eco-friendliness is resolved (El-Seedi *et al*., 2019; Khalil *et al*., 2022).

Plant-Mediated Synthesis

In this approach, we use plant extracts or plant biomass to reduce metal ions from their salts to nanoparticles. Alkaloids, flavonoids, saponins, steroids, tannins, and phenolic acids are a few of the secondary metabolites that are commonly present in plants. Numerous investigations have demonstrated that many of these metabolites function as lowering and stabilizing agents and prevent the non-hazardous aggregation and agglomeration of the new metallic NPs *et al*., 2019). There are three main phases utilized in the biosynthesis of metal nanoparticles using plant extracts. The first step is the activation phase, during which metal ions' reduction and nucleation occur. In the second phase, namely the growth phase, the small nearby NPs combine to create larger particles, along with a rise in the thermo-dynamic stability of the nanoparticles. The termination phase is the last step in giving the NPs their final shape (Makarov *et al*., 2014). The morphology of the NPs created is influenced by the type of plant extract and its concentration, whilst the growth and size of the NPs are governed by the temperature and pH of the extract media (El-Seedi *et al*., 2019). An aqueous extract of the plant is often combined with an aqueous solution of the relevant metal salt to mediate bio-reduction.

The reaction takes place at room temperature usually and typically takes a few minutes to finish (Mittal *et al*., 2013). Table 1 summarizes some of the reports on plant extract's role in the creation of nanoparticles between the year 2016 and 2023. In a reported study on green synthesis of zinc nanoparticles in which zinc acetate and *Ixora coccinea* leaf extract were utilized to produce very stable and spherical zinc oxide nanoparticles (Yedurkar *et al*., 2016). In another study, iron oxide nanoparticles were synthesized using *Lagenaria siceraria*. The research showed that the NPs' typical size fell between 30 and 100 nm. When compared to the reference medication, the antimicrobial property of the synthesized Fe_3O_4 NPs revealed that the nanoparticles have moderate antimicrobial activity, with better antibacterial activity against *Escherichia coli*, while moderate activity against *Staphylococcus aureus* was observed (Kanagasubbulakshmi and Kadirvelu, 2017). Nagar and Devra (2018) synthesized copper nanoparticles using the leaf broth of *Azadirachta indica*, and examined the impact of several reaction parameters, including precursor salt concentration, leaf broth percent-tage, temperature, and pH of the medium (Nagar and Devra, 2018). By utilizing rose (*Rosa santana*) petal extract and microwave irradiation, Jahan *et al*. (2019) photosynthesized silver nanoparticles. They also investigated the antibacterial effects of the synthesized silver nanoparticles against selected gram-positive and gram-negative microorganisms using the agar-well diffusion method. The zone of inhibition against *S. aureus* was found to be larger (11.73 ± 0.25 mm) than against *E. coli* (10.20 ± 0.36 mm)(Jahan *et al*., 2019).

In a study carried out by Sati *et al*. (2020) the leaf extract of Bedu (*Ficus palmata*) was used as a reducing agent and supported by natural fibers in the environmentally friendly synthesis of metal nanoparticles (Ag NPs and ZnO NPs). They concluded that synthesized nanoparticles are in the nano range (1–100 nm). Ag NPs with polydispersity and a spherical shape are typically 30 nm in size, whereas synthesized ZnONPs are typically 34 nm in size and appear to have a distorted spherical shape (Sati *et al*., 2020). Plants are highly preferred to synthesize NPs because they are renewable, biocompatible, and toxicity-free, and they readily supply natural stabilizing agents to the NPs (Ghorbanpour *et al*., 2020).

Microbial-Synthesis

The fabrication of nanomaterials (MNPs) based on microbial agents (varieties of bacteria and fungi, yeasts, viruses, marine algae and their products) have been the focus of a great deal of research in recent years. These microbes act as a scaffold for the generation and organization of well-defined

Table 1: Some reported plant species used for biosynthesis of metallic nanoparticles

Plant species	Part utilized	NPs	Size(nm)	Effect	References
Pinus brutia (PB)	Leaf	ZnO	37.47-73.70	-------------	Ismail *et al.* (2023)
Lupinus albus and Lupinus pilosus	Whole Plant	ZnO	19.70 - 28.13	Antibacterial, Photocatalysis	Mirza *et al.* (2023)
Scoparia dulcis	Leaf	ZnO	20.2	Antibacterial, Antifungal, Antioxidant	Sivasankarapillai *et al.* (2022)
Caricaceae (Papaya)	Shell	TiO2	15	Antifungal	Saka *et al.* (2022)
Lemon	Peel	TiO2	80–140	Optical Photocatalytic	Nabi *et al.* (2022)
Ocimum basilicum	Leaf	ZnO	30- 40	Antimicrobial	Nabi *et al.* (2022)
Acalypha fruticosa	Leaf	ZnO	50–60	Antimicrobial	Vijayakumar *et al.* (2020)
Lawsonia inermis	Leaf	ZnO	75-100	Antibacterial	Upadhyaya *et al.* (2018)
Tecoma castanifolia	Leaf	ZnO	70–75	Antioxidant, Antimicrobial	Sharmila *et al.* (2019)
Punica granatum	Fruit peel	ZnO	32.98 - 32.98	Cytotoxicity, Antibacterial	Sharmila *et al.* (2019)
Cucurbita pepo	Leaf	Au	10-15	Role of plant ageing	Gonnelli *et al.* (2018)
Monsonia burkeana	Waterplant extract	ZnO	5-15	Anticancer, Antibacterial, photocatalytic activity	Ngoepe *et al.* (2018)
Trigonella foenum-graecum	Leaf	TiO_2	20–90	Antimicrobial	Subhapriya and Gomathipriya, (2018)
Jatropha curcas L.	Leaf	TiO_2	13	Photocatalytic	Goutam *et al.* (2018)
Cynodon dactylon	Leaf	TiO_2	13 – 34	Antibacterial, Anticancer	Hariharan *et al.* (2017)
Morinda citrifolia	Leaf	TiO_2	10	Antimicrobial	Sundrarajan *et al.* (2017)
Echinacea purpurea	Whole plant	TiO_2	120	---------------	Dobrucka (2017b)
Tectona grandis (L.)	Leaf	ZnO	59	Antibacterial, Antioxidant, anti-arthritic cytotoxicity	Senthilkumar *et al.* (2017)
Arnica montana L.	Water extract	TiO_2	30 nm	Photocatalytic	Dobrucka (2017a)

nanostructures (nanoparticles)(Shah *et al*., 2015). Many studies have shown that both extracellular and intercellular synthesis of micron and nano-sized materials can be achieved from unicellular and multicellular organisms, cultivating micro-organisms in particular environments can also assist in promoting coupled oxidation and reduction phenomena (Mann, 1996; Shah *et al*., 2015). Microorganisms act as nano factories for the eco-friendly and cost-effective synthesis of various metallic nanoparticles such as silver nanoparticles, copper nanoparticles, zinc oxide nanoparticles, titanium oxide nanoparticles, gold nanoparticles, palladium nanoparticles etc. These nano-sized structures could come in all sorts of different shapes and sizes, like nano-tubes, nano-conjugates, nano-rods, and nano-wires (Shah *et al*., 2015). Scientists have discovered magnetite particles produced by magnetotactic bacteria while researching the natural processes for the synthesis of nanoparticles by microorganisms, which are regarded as effective and environmentally friendly green nano factories (Sathiyanarayanan *et al*., 2017).

Bacteria are capable of reducing metallic ions to form nanoparticles, making them an ideal candidate for the synthesis of nanoparticles due to their easy handling and high growth rate. One other positive aspect of using this microorganism is that they are easy to mould and manipulate genetically (Iravani, 2014). Bacteria are constantly exposed to severe and toxic environmental conditions due to high levels of heavy metal ion present in their environment. To overcome these stress conditions, bacteria have developed a variety of natural defenses, including intracellular storage, efflux pump (for instance, ATP-dependent pumps, proton gradients, and chemiosmotic pumps) activity, alteration of metal ion concentration, and extracellular precipitation (Faramarzi and Sadighi, 2013). Hamk *et al.* (2023) reported an extracellular synthesis of ZnO nanoparticles achieved by bacteria *Bacillus subtilis* ZBP4. These ZnO nanoparticles (ZnO NPs) were crystalline, spherical or pseudo-spherical in shape, with diameters ranging from 22 to 59 nm. The study also suggested that ZnO nanoparticles may be effective antibacterial agents against a wide range of Gram-positive pathogens and Gram-negative pathogens (Hamk *et al*., 2023). Alfryyan *et al*. (2022) reported biosynthesis of AgNPs using *Bacillus cereus.* A face-centered cubic structure, with an average crystallite size of 45.4 nm and 90.8 nm was demonstrated for intracellular and extracellular biosynthesized Ag NPs, respectively. Catalytic reduction of methylene blue (MB) dye was shown after 80 min, extracellular Ag NPs had a 100% MB reduction efficacy, while intracellular Ag NPs 50.6% and 24.1%, respectively in the presence and absence of it (Alfryyan *et al*., 2022).

Majeed *et al*. (2021) revealed that *Proteus vulgaris* can potentially reduce ferric chloride into Iron oxide nanoparticles (IO NPs). In this study the average size of synthesized NPs found to be in the range of 19.23 - 30.51 nm and also has shown outstanding antibacterial properties and were effective against the MRSA pathogen (Majeed *et al*., 2021).

Another simple and basic method that has been actively explored for nanoparticle manufacturing is fungus-based biosynthesis. Fungi have more productivity yield in the generation of nanoparticles than bacteria, and have a higher tolerance to metals, particularly when it comes to the high binding of metal ions to biomass. In a study Ag NPs were biosynthesized by *Aspergillus niger* (Farrag *et al*., 2020). In this study Silver nanoparticles were mostly spherical, cylindrical, and single-crystalline, with an average diameter of about 10.31 nanometers (Farrag *et al*., 2020). Win *et al*. (2020) reported synthesis of silver nanoparticles of average size between 3-10 nm using fungus *Alternaria sp*.

Factors Affecting the Synthesis of Nanoparticles

There are a number of factors that influence the synthesis process of nanoparticles. Primary factor is adequate environmental variables such as pH, medium composition, metallic salt concentration, and temperature and another factor is organic functional molecules found on cell walls that promote bio-mineralization if microbial synthesis is concerned (Klaus-Joerger *et al*., 2001). In a recent study, effect of different pH on the synthesis of ZnO NPs has been reported (Ismail *et al*., 2023). They concluded that the pH value has a significant impact on all of the ZnO NPs' obtained characteristics. The pH value has also a considerable effect on the quality and average crystal size of the hexagonal-wurtzite ZnO NPs produced (Ismail *et al.*, 2023). There are several ways that time can affect NPs. For example, because of the extended storage period, NPs mixed with plant extracts may aggregate, and particles may shrink or grow. As a result, particle characteristics may have a lifespan (de Jesus *et al.*, 2021). It is therefore important to comprehend how the properties change over time for a variety of reasons, including manufacturing, product stability, environmental and health effects, and storage/shelf life (Baer, 2011). In a comparative study done by Mankad *et al.* (2020), aqueous 1 mM $AgNO_3$ was mixed with varying volumes of neem leaf extract (5 ml, 10 ml, 15 ml, and 20 ml, respectively) and exposed to sunlight for 5, 10, 15, and 20 min to create green synthesis of silver nanoparticles. The hue transitioned from yellow to reddish brown as the length of exposure to sunshine increased. They concluded that higher concentrations of the plant extract may not effectively reduce the particle size and antibacterial activity of synthesized Ag NPs peaked at 5 ml of plant extract and 10 min of sun exposure (Mankad *et al.*, 2020). Research findings indicate that increased biomass dosage concentrations of plant extract lead to enhanced production and modifications in the shape of nanomaterials. Different environmental factors are crucial for the synthesis of nanoparticles and must be used and regulated accordingly for the optimal yield synthesis.

Applications of Biosynthesized Nanoparticles

Green nanoparticles are important with applications in translational research spanning agriculture, the environment, and biomedical science. Biologically synthesized nanoparticles offer remarkable insecticidal characteristics, opening up new options for their use in the effective control of pharmaceutical and veterinary insect pests (Srivastava and Bhargava, 2022). Nano-particles have been effectively employed in agriculture to improve germination, elemental uptake, nutrient utilization, agricultural production increase, and stress tolerance in a variety of plant species (Singh *et al.*, 2020). Biosynthesized metal-based NPs have a wide range of applications, including antimicrobial coatings, medical imaging, and medication delivery, as well as catalytic water treatment and environmental sensors (Schröfel *et al.*, 2014). As biological nanoparticles offer a higher efficiency for biomedical applications than physiochemical nanoparticles, they have been used in a variety of biomedical contexts, including anticancer and antibacterial uses (Singh *et al.*, 2016). In a study, researchers explored the biosynthesis of copper oxide nanoparticles (CuO NPs) by mediation of *Abies spectabilis* plant extract (Liu *et al.*, 2020). In this study it was concluded that treatment with CuONPs reduces peritoneal leukocyte infiltration and carrageenan-induced paw edema, confirming the inhibitory action of As-CuO NPs against carrageenan-induced inflammation. These findings demonstrated that As-CuO NPs can be a promising option for nociception and inflammatory disorders (Liu *et al.*, 2020). In a study reported by Song *et al.* (2021) DSS-induced UC (ulcerative colitis) in C57BL/6 mice was successfully attenuated by dietary supplementation with 0.6 mg kg^1 Se in the form of SeNPs, synthesized using *Kluyveromyces lactis* GG799. This study also provided evidence that biogenic SeNPs isolated from *Kluyveromyces lactis* GG799 eased UC in mice by reducing intestinal inflammation, oxidative stress, and intestinal barrier dysfunction (Song *et al.*, 2021). Naiel *et al.* (2022) synthesized ZnO NPs by using Sea Lavender (*Limonium latifolium*), which have shown significant anticancer efficacy against A-431 cell lines. Both the plant extract and its green synthesized ZnO NPs had no cytotoxic or adverse effect on normal cells (WI-38) at concentrations up to 250 g/ml, indicating their biocompatibility. In addition, ZnO NPs and plant extract showed superior antibacterial action when compared to Gentamycin. Moreover, they had comparable antioxidant activity (Naiel *et al.*, 2022). Ahmed *et al.* (2021) demonstrated potential antibacterial efficacy of biogenic ZnONPs against rice panicle blight pathogens *burkholderia glumae* and *Burkholderia gladioli*. In this study *B. cereus* RNT6 strain was used to synthesize these Biogenic ZnO NPs (Ahmed *et al.*, 2021). Biosynthesized nanoparticles have been utilized in the removal of antibiotics, agriculture, heavy-metal sensing and remediation of dyes and pesticides and for environmental applications (Srivastava and Bhargava, 2022).These studies show the potential of biosynthesized NPs in various domains of science and technology.

Conclusion

This review provided information on the environmentally friendly biosynthesis of nano-particles (NPs), involving mediation of different biogenic sources e.g. plants, fungi, bacteria etc. In a one-step process, biomolecules from plant extracts are involved in the reduction of metal ions to nanoparticles because they contain a wide range of metabolites (e.g., carbohydrates, alkaloids, terpenoids, phenolic compounds, and enzymes. The current review also discussed the elements that influence NP biosynthesis, as well as some of their applications in commerce and industry.

Ethical Statement

This is a review article hence no Ethical Approval needed.

Author Contributions

Each author has contributed equally to the study's planning, writing, and editing. They collaborated in designing the research, drafting the manuscript, and refining its content. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest

The authors declare no conflicts of interest.

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