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Green Synthesis of Nanomaterials: A Sustainable Approach in Material Science: Review

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Abstract: Nanomaterials are commonly known as materials engineered with at least one dimension less than 100 nm in size. Due to these nanoscale dimensions, nanomaterials exhibit significantly different physicochemical properties compared to their bulk counterparts. These exceptional physicochemical properties enable their diverse applications across biomedicine, environmental remediation, and the development of energy materials. While their utility remains undeniable, most of the conventional synthesis methods are based on hazardous chemicals, high energy consumption, and generate toxic waste. This mini review critically examines "green synthesis" as a sustainable and eco-friendly approach for nanomaterial fabrication. This mini review clarifies how various biological sources utilize their natural systems for bioreduction, converting metal compounds into nanoparticles. Further, we elaborate on the advantages of green synthesis, discuss advanced characterization techniques that are crucial for the validation of green-synthesized materials, and highlight current challenges and future perspectives. This review offers a holistic view of green synthesis.

Index Terms: Bioreduction, Green Synthesis, Nanomaterials, Nanotechnology, Sustainability.

1. INTRODUCTION

Nanomaterials are commonly known as materials engineered with at least one dimension less than 100nm in size. Due to these nanoscale dimensions, nanomaterials exhibit significantly different physicochemical properties compared to their bulk counterparts. These enhanced properties include enhanced surface area, improved optical properties, greater mechanical strength, and intensified reactivity. Interestingly, nanomaterials produce these unique characteristics by altering their shape and size at the nanoscale [1]. Owing to these remarkable properties, nanomaterials have become integral to various applications across multiple disciplines. As shown in *Fig.1*, they are widely utilized in biomedicine, especially for targeted drug delivery; in environmental remediation for air filtration and wastewater treatment; and the energy sector for high-performance solar cells and hydrogen fuel cells [2],[3].

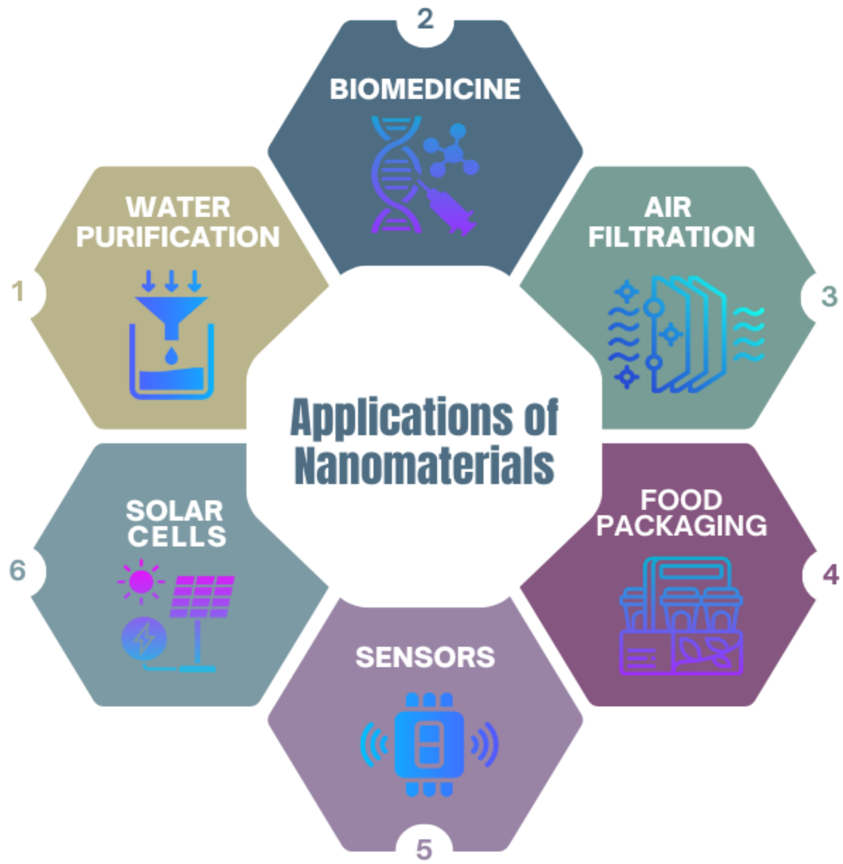

Fig. 1. Applications of Nanomaterials

Due to the broad applications of nanomaterials in major industries, the synthesis methods used to produce them play a critical role. However, the conventional synthesis methods used to fabricate the nanomaterials are primarily based on physical and chemical routes, which can often cause serious health problems and environmental issues. Widely used methods such as hydrothermal synthesis, sol-gel process, and physical vapor deposition are frequently used with hazardous chemicals like borohydrides, hydrazines, and chloroform. These chemicals are detrimental to human health and the ecosystems [4]. Further, these synthesis methods are based on the high energy consumption due to the required elevated temperature conditions, high pressure, or vacuum conditions [5]. Unreacted precursors, strong solvents, and toxic byproducts of these processes trigger the need for advanced and costly waste management methods [6],[7]. Also, the residual toxic chemicals of these processes limited the applications of the nanomaterials in sensitive areas like medicine and agriculture [8].

Considering these limitations, scientists focused on developing sustainable alternatives for the synthesis methods that align with the principles of green chemistry. This concept was introduced by Paul Anastas and John Warner to reduce or eliminate the use or generation of toxic substances [9].

2. FUNDAMENTALS OF GREEN SYNTHESIS: A BIOMIMETIC APPROACH

The concept of green synthesis of nanomaterials differs from the conventional methods because it harnesses the inherent capabilities of biological systems to synthesize the nanomaterials. Thus, these processes are known as biomimetic approaches. Within the green synthesis, naturally occurring biomolecules are used as both reducing and capping (stabilizing) agents, eliminating the need for hazardous chemicals in the process. The process typically occurs under mild conditions (ambient temperature, atmospheric pressure, neutral pH), further contributing to its sustainability.

The general approach involves the interaction of a biological extract or a living organism with a metal salt precursor, such as silver nitrate, gold chloride, or copper sulfate. The biocomponents within these living biomolecules help reduce metal ions to nanoscale particles. Often, these biomolecules are known to adsorb onto the surfaces of the newly formed nanoparticles during the reaction, serving dual functions as stabilizers of agglomeration and capping agents [10].

2.1 Biological Entities as Nanofactories.

A wide range of biological sources is used to develop different types of nanomaterials under the concept of green synthesis. Each biological source offers unique advantages in nanomaterials synthesis. Plant extract is widely used in green synthesis due to its simplicity, affordability, and rich availability of plants. Plant extracts are rich in a complex array of phytochemicals. Polyphenols such as flavonoids, tannins, and phenolic acids are known as potent reducing agents due to their ability to donate electrons [11]. Terpenoids, including monoterpenes, sesquiterpenes, and diterpenes are also act as both stabilizing and reducing agents [12]. Logeswari et al. (2012), have mentioned that the plant-extracted alkaloids contribute to the formation of silver nanoparticles (Ag NPs) and are nitrogen-containing compounds with diverse structures and biological activities. Certain plant extracts contain enzymes such as reductase that can be used to reduce the metal ions [13]. Ankamwar et al. (2005), have introduced a method to biosynthesize gold and silver nanoparticles using the fruit extracts such as amla and Indian Gooseberry [14]. *Fig.2* represents the basic steps of synthesis process. In another research, Ag NPs were synthesized by using *Azadirachta indica*

(Neem) leaves. This extract works as both a reducing and capping agent, and they have mentioned that only 15 minutes were required to convert the silver ions into Ag NPs at room temperature [15]. Extracts from *Camellia sinensis* (Green Tea) were also used to synthesize the Ag NPs. This study mentioned that the synthesized Ag NPs can be used in various fields like cosmetics, food, and medicine [16]. Further extracts from *Aloe vera*, *Cinnamon zeylanicum* plant bark, and *Moringa oleifera* leaf were also used in different studies to synthesize nanoparticles [17],[18],[19]. Silver nanoparticles are widely studied due to their exceptional antifungal and antibacterial properties. Thus green synthesis approach provides a better alternative.

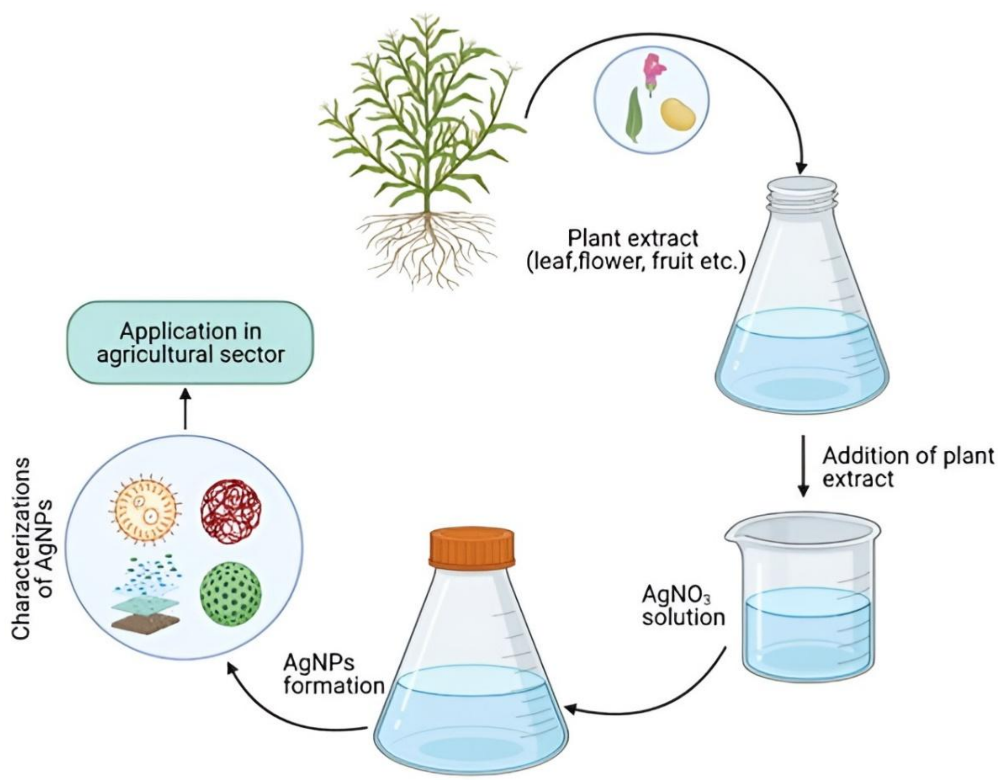

Fig. 2. Schematic diagram for synthesis of Ag NPs by using plant extracts. Created with Biorender [72].

Gold nanoparticles (Au NPs) are widely used as a therapeutic agent, a catalyst, and a drug delivery agent. Green synthesis plays a crucial role in Au NPs synthesis by reducing the use of toxic chemicals such as sodium borohydride [20]. Most of the researches were conducted by using plant extracts as reducing agents to synthesize the Au NPs by eliminating the need for toxic reducing agents like sodium borohydride. For example, *Cinnamomum camphora* leaf extract [21], *Olea europaea* (Olive) leaf extract [22], and *Cymbopogon citratus* (Lemongrass) [23] were used to synthesize the gold nanoparticles under the green synthesis. Zinc oxide nanoparticles (ZnO NPs) exhibit antimicrobial and photocatalytic activities. The extracts from *Ocimum tenuiflorum* (Holy Basil) [24] and *Solanum nigrum* [25] were used to synthesize ZnO NPs. Copper oxide nanoparticles have been used in batteries, catalysts, gas sensors, and high-temperature superconductors. Also, ZnO NPs have an antimicrobial effect and are thus used for the antimicrobial coating in the textile industry [26]. The conventional synthesis process of ZnO NPs was also replaced by the *Magnolia kobus* [27] and *Calotropis gigantea* leaf extract [28] to reduce the use of toxic chemicals and their byproducts.

Microbial synthesis is another aspect of green synthesis. Advantages of microbial synthesis include its scalability, precise control over the morphology of nanoparticles, and the potential of genetic manipulations to enhance the efficiency and selectivity of the synthesis process [29]. Intracellular and extracellular synthesis of nanoparticles was performed using both gram-positive and gram-negative bacteria. The process often involves enzymes like nitrate reductase or NADH-dependent reductases that facilitate the reduction of metal ions. Examples include *Bacillus licheniformis* and *Pseudomonas stutzeri* isolated from textile soil was used in past studies to synthesize Ag NPs [30],[31]. Fungi can secrete a wide range of enzymes, including reductase as well. Vigneshwaram et al. (2006), highlighted the ability of *Aspergillus flavus* to accumulate the Ag NPs on the surface of its cell wall [32]. *Fusarium oxysporum* fungus biosynthesized the extracellular platinum nanoparticles, eliminating the need for toxic chemicals like sodium borohydride ($NaBH_4$) [33]. Further, *Penicillium chrysogenum* for ZnO NPs is are notable example [34]. Algae contain various compounds, such as proteins and pigments, which can act as reducing and stabilizing agents. For example, *Chlorella vulgaris* for Ag NPs and *Sargassum wightii* for Au NPs [35],[36]. *Fig.3* represents the role of microorganisms in green synthesis.

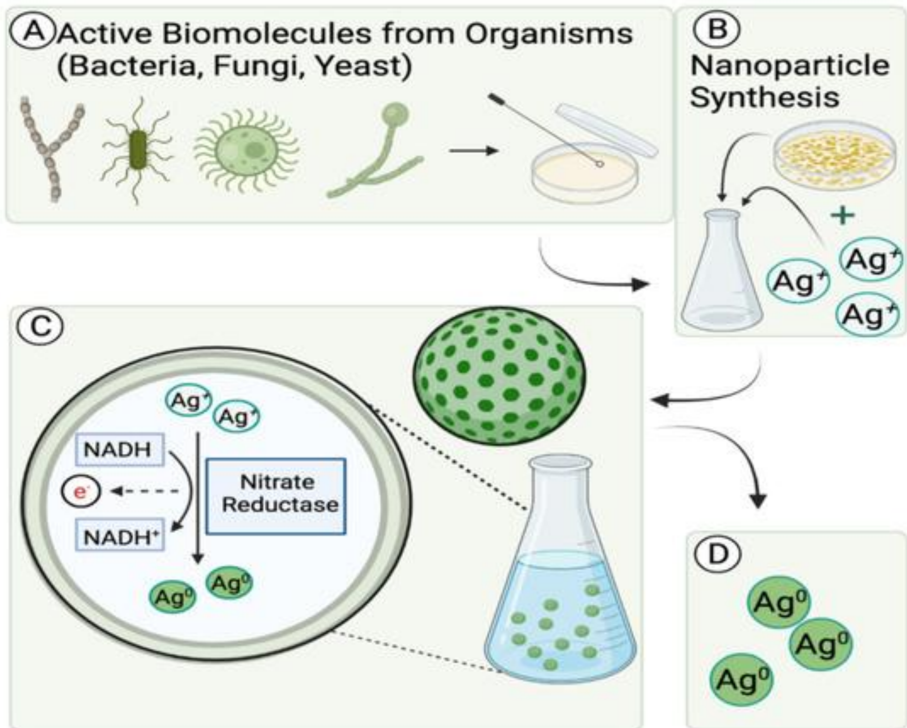

Fig. 3. Representation of the role of active molecules in green metallic nanoparticle synthesis [73].

Biomasses like agricultural residues and food waste are also used in the green synthesis under the principles of waste management and circular economy. These materials are composed of organic compounds such as proteins, carbohydrates, and cellulose that can serve as reducing and capping agents. Yee et al. (2017), have extracted the bioactive compounds from the rice husk that exhibit reducing abilities. Acid and alkali pretreatment extraction(AAPE) was used to biosynthesize the Ag NPs. Synthesized Ag NPs were stable and spherically shaped with a size of <15 nm [37]. Another study highlighted the green synthesis of silver chloride nanoparticles (AgCl NPs) and Ag NPs from aqueous corn husk extracts. Further, they mentioned that the synthesized nanoparticles had an antimicrobial effect against *Escherichia coli* and *Staphylococcus aureus* [38]. Yasser et al. (2021), green-synthesized Ag NPs using pomegranate and orange peel extracts. Synthesized Ag NPs were used as an antifungal agent [39]. Food waste from banana peels was used in another research to synthesize the Ag NPs, and they were used for banana preservation. In this process, extracts from banana peels were used as both reducing and capping agents [40]. Ahmed et al. (2015), was also introduced a method to green synthesize the Ag NPs using spent tea leaves extract [41]. Due to the high consumption of coffee, a large amount of coffee grounds is produced. Antonio et al. (2022), introduced a method to green-synthesize the Ag NPs using coffee grounds, which contain a high level of phenolics and other bioactive compounds that work as stabilizing and reducing agents for synthesizing metal nanoparticles [42].

3. CORE PROCESS OF GREEN NANOPARTICLE FORMATION

The concept of green synthesis differs from the conventional synthesis processes because it uses natural living systems to create nanoparticles. As shown in *Fig.4,* green synthesis of nanoparticles undergoes a natural three-step process [43],[44].

3.1. Converting metal ions into metal atoms (Reduction)

The first step in this process is to convert the metal ions into their neutral form, which is commonly known as the reduction. These neural atoms are the building blocks of nanoparticles. Under the plant extracts, like phenols, they donate electrons to the metal ions and transform them into a neutral form. Inside the microorganisms, they use biological catalysts called enzymes to complete this process.

3.2. Nanoparticle formation (Nucleation and Growth)

Once enough neutral atoms are formed, they begin to clump together to form tiny formations called "nuclei". These nuclei grow larger as more atoms are attached. The final morphology and the size of the nanoparticles are influenced by the speed of this process and the amount of available metals.

3.3. Stabilization of nanoparticles (Capping)

To keep the formed nanoparticles in the nano range and restrict them from sticking together and forming large particles, a capping agent should be added. Capping agents act as a protective shield around the nanoparticles, ensuring they remain tiny, separate, and stable.

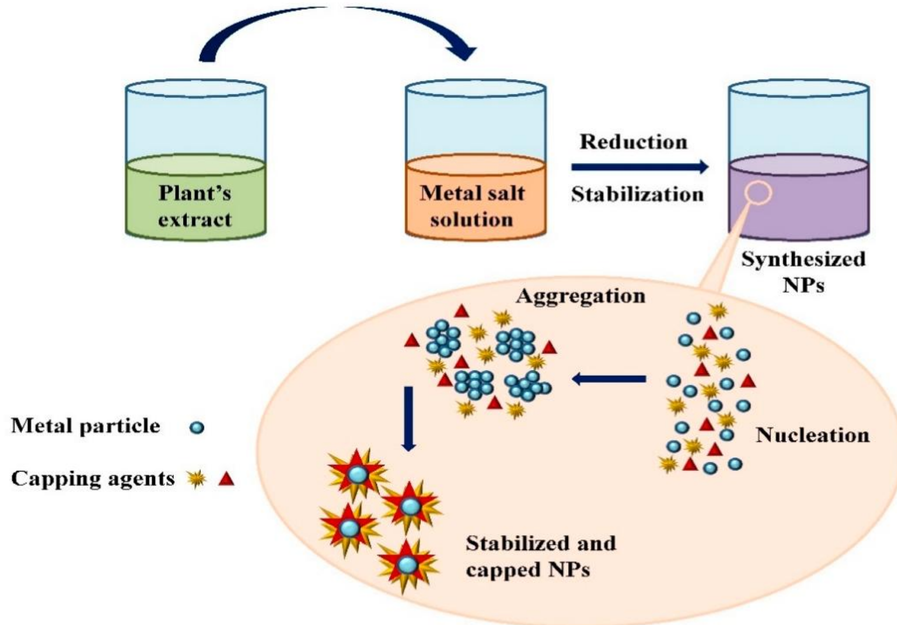

Fig. 4. Mechanism of nanoparticle synthesis using phytoextracts [43].

4. ADVANTAGES OF GREEN SYNTHESIS

The basic concern of green synthesis is the eco-friendliness. But the advantages of green synthesis extend beyond more environmental compliance. The main benefit of the green synthesis is the elimination or reduction of hazardous chemical usage. Consumption of reducing agents like sodium borohydride, hydrazine, toxic organic solvents, and strong acids/bases can be drastically minimized through this sustainable approach [45]. Also, it reduces the generation of toxic byproducts and waste as the process often yields biodegradable byproducts. Green synthesis typically occurs at room temperature and atmospheric pressure. Thus, energy consumption is lower than conventional synthesis methods [46].

Green synthesis pairs with biological sources like plant extracts, microorganisms, and agricultural residues. These sources are cost-effective, abundant, and renewable [47]. In many green synthesis methods, both reduction and stabilization occur simultaneously. This one-pot nature simplifies the synthesis process and reduces the required labor and equipment [48]. The absence of remaining hazardous chemicals makes synthesized nanomaterials more biocompatible and less cytotoxic [49]. This is critical when the nanomaterials are used in medical applications such as drug delivery and medical imaging. The capping agents used in green synthesis add therapeutic properties like antimicrobial, anti-inflammatory, and antioxidizing to the nanomaterials that creating a synergetic effect [50]. Even though some challenges exist, most of the green synthesis methods involve large-scale production. Researchers are actively developing advanced bioreactors to improve scalability.

By carefully controlling the synthesis parameters such as pH level, temperature, extract volume, and precursor concentration, the desired morphology of nanoparticles can be achieved through green synthesis [51]. This approach can synthesize diverse nanomaterials. It's not limited to metal nanoparticles but can also synthesize metal oxides, sulfides, and even some bimetallic nanoparticles.

5. CHARACTERIZATION METHODS USED IN GREEN-SYNTHESIZED NANOMATERIALS

5.1. Spectroscopic techniques

UV-Visible Spectroscopy is used to detect the Surface Plasmon Resonance (SPR) peaks generated by the silver and gold nanoparticles. The position and intensity of SPR peaks can determine the size and the concentration of formed nanoparticles. Fourier Transform Infrared (FTIR) Spectroscopy is another technique crucial for identifying various functional groups of biomolecules. By considering the FTIR spectra before and after synthesis, the involvement of a certain functional group as a stabilization agent can be determined [52],[53].

5.2. Microscopic techniques

The morphology, size distribution, and crystallinity of formed nanoparticles can be characterized by using Transmission Electron Microscopy (TEM). Further, Scanning Electron Microscopy (SEM) provides topographical information and morphology of the formed nanoparticles [54]. The Atomic Force Microscopy (AFM) allows for a 3D image of nanoparticles with sub-nanometer resolution [55].

5.3. Diffraction and Thermogravimetric Analysis (TGA)

X-ray Diffraction (XRD) characterization provides information about the crystalline structure and phase composition of the formed nanoparticles by using Bragg's law. Details of capping agents can be determined by TGA. It quantifies the amount of organic material around the nanoparticles by measuring the weight loss caused by the heating process [56].

6. APPLICATIONS OF GREEN-SYNTHESIZED NANOMATERIALS.

6.1. Biomedicine and health sector.

Green synthesized nanoparticles are comparatively less cytotoxic, thus ideal candidates for medical purposes. They are mainly used for targeted drug delivery. For example, Ag NPs, Au NPs, and polymer-based NPs are loaded with the therapeutic agents and sent to the diseased cell or tissue [52]. Nanoparticles have an antimicrobial effect on bacteria, fungi, and even some viruses. This mechanism involves membrane damage, oxidative stress, and DNA/protein disruption [57]. Due to the antimicrobial properties of Ag NPs and ZnO NPs, they are used for wound healing [58]. Also, green-synthesized nanoparticles are used to deliver the drug to cancer cells by minimizing the harm to healthy tissues. Further, Au NPs and quantum dots are used for diagnostics and bioimaging [59].

6.2. Environmental Remediation

They are good adsorbents for heavy metals (e.g., lead, cadmium, arsenic) and organic pollutants (e.g., dyes, pharmaceuticals) from contaminated water [60]. High surface area and reactivity facilitate high removal efficiencies. TiO_2 NPs and ZnO NPs, often green-synthesized, act as photocatalysts, degrading organic pollutants to less toxic compounds under UV or visible light irradiation [61]. Green-synthesized Fe-based NPs are effective for the reductive degradation of chlorinated organic contaminants [62]. Nanofiber membranes incorporated with green-synthesized nanoparticles can effectively capture particulate matter and gaseous pollutants in the air, offering high-efficiency air purification systems [63].

6.3. Energy Sector

Tin Oxide (TiO_2) and ZnO NPs are prominent for the dye-sensitized solar cells. They improved the light harvesting and efficiency of the solar cells. Green-synthesized nanoparticles can act as electrocatalysts in fuel cells. They can enhance the reaction kinetics due to their high surface area [64].

6.4. Agriculture and food industry.

Green-synthesized nanoparticles are incorporated to form nanofertilizers, which can provide slow and controlled release of nutrients. This may reduce the fertilizer runoff and improve the efficiency of fertilizer usage. Antimicrobial properties of green-synthesized nanoparticles are used for food packaging. They can extend the shelf life and prevent microbial spoilage of foods [65].

7. CHALLENGES AND FUTURE ASPECTS.

While green synthesis has made significant advancements in the field of nanoscience, several challenges remain to be addressed to realize its potential fully. In the field of science, it's crucial to have consistent and repeatable results. But when plant extracts are made, there is a possibility of having natural variations in the chemical content of the extracts based on the plant type, how the plant was grown, and the extraction method [66]. Thus, it's crucial to develop standard methods for the synthesis process. This will be challenging, while the green synthesis is based on the natural variability. On a large scale, achieving high yields and purity compared to conventional methods is quite challenging, while green synthesis often produces a broad size distribution of nanoparticles. And also the separating nanoparticles from residues and unreacted precursors can be challenging.

Understanding of the biological pathways, especially the specific biomolecules involved in reduction, nucleation, and stabilization, often remains incomplete. A deep understanding of these mechanisms would enable better control over the synthesis process [67]. The transformation of laboratory-scale green synthesis into an industrial level is challenging, as it requires advanced and large-scale bioreactors to provide optimized mixing and better temperature control [68]. Long-term stability of green-synthesized nanoparticles in diverse application environments needs further investigation. The organic capping agents tend to degrade due to long-term performance. Nanoparticles like metal oxides tend to oxidize easily due to their high surface energy. Thus, they require an inert atmosphere to maintain stability [69].

Despite the various challenges associated with green synthesis, the prospects of green synthesis remain bright. Computational tools like Artificial Intelligence (AI) and machine learning (ML) predictive models are being developed to predict critical information like optimal synthesis conditions and identify the key biomolecules [70]. Ongoing research to develop advanced bioreactors that have high scalability is another positive perspective of the green synthesis [68]. Genetically modified microorganisms can be used to improve the synthesis capabilities. Through the overexpression of specific reductase enzymes, such as NADH-dependent nitrate reductases or Metalloreductases, microbes can achieve improved metal ion reduction efficiency [29]. Studies focused on exploring novel biological sources, such as Extremophiles, indicating the possibility of nanoparticle synthesis at extreme conditions [71]. Finally, the intention of the modern scientific world to develop eco-friendly and sustainable methods for synthesizing nanoparticles gives an additional good perspective for the future. Ultimately, the growing commitment of the modern scientific world to developing eco-friendly and sustainable approaches adds a better perspective to the future of green nanotechnology.

8. CONCLUSION

The green synthesis method is a paradigm shift in how nanomaterials are made, more sustainable and environmentally friendly than traditional techniques. This approach mitigates critical health and ecological issues tied to traditional synthesis routes by utilizing natural biological systems such as plant extracts, microorganisms, and even biomass. The natural biocompatibility of the green-synthesized nanomaterials makes them useful in high-impact fields like medicine, environmental cleanup, agriculture, and renewable energy. Despite the issues of reproducibility, scalability, and their detailed mechanisms, rapid progress in biotechnology, analytical chemistry, and process engineering is systematically addressing these challenges. Given increasing global demand for sustainable development, green synthesis will likely become the main method for producing nanomaterials, guiding us towards a safer and more sustainable world. Interdisciplinary efforts are essential to gain the benefits of green synthesis and provide real solutions, so we need continued fundamental research, solid engineering, and comprehensive policy guidelines.

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