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Review Article

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Green Synthesized Metallic Oxide Nanomaterials for Diverse Applications

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Abstract

The increased demand for metal and metal oxide nanoparticles has led to large-scale manufacturing of these nanoparticles employing high-energy procedures with diverse toxic solvents. This pollutes the environment, necessitating the use of environmentally acceptable "green" synthesis processes. Bio-resources, such as plants and plant products, bacteria, fungi, yeast, and algae, can be used to produce metal nanoparticles as an alternative. In comparison to other methods, "green" synthesis has low toxicity and is safer for human health and the environment, making it the best method for creating metal and metal oxide nanoparticles. Considering metallic oxide nanomaterials as promising materials, we provide a comprehensive review of studies on the diverse application and green synthetic method of metallic oxide nanomaterials using biological materials as reducing agents and stabilizers. This study extensively reviews the recent research on the synthesis mechanism of zinc oxide, silver oxide, and gold oxide nanomaterials and their diverse applications.

Keywords

Green synthesis, Biogenic, Nanoparticles, Metal nanoparticles

Introduction

Currently, the scientific community is concerned with new challenges that are present in health and environmental areas. One cutting-edge area of exploration is nanotechnology, which holds great potential for diverse applications of nanoparticles, including novel fields of science and technology [1, 2]. Nanotechnology refers to the synthesis and alteration of particles smaller than 100 nm. Nanoparticles (NPs) are used in medical sciences, particularly in drug delivery, imaging, and diagnosis [3, 4]. They possess high surface-to-volume ratio due to their small size, which gives them very distinctive features [5, 6]. Researchers are planning to synthesize NPs and design nano-devices for future applications in the fields of medical sciences, environment, energy, information, communication, industry, and food technology [7, 8].

Green synthesis produces NPs for a minimal price with gentle strain, temperature, and pH that avoids the hurtful elements of their creation [9, 10]. Phytonanotechnology utilizes different parts of the plant, such as roots, stems, seeds, and leaves, in developing nanoparticles [11]. The green combination of various types of NPs comes from biomolecules (proteins, nutrients), plant extracts (flavonoids, terpenoids), and microorganisms (microbes, parasites, and yeast) [12]. There is a huge need to develop better approaches utilizing green nanotechnology to expand the capabilities of available prescriptions and antiviral/antimicrobial material. During green synthesis of NPs, products that originate in or imitate nature are used as reducing and capping agents (Figure 1). The methods involved are typically simple, environmentally friendly, and naturally compatible one-pot processes [13, 14].

Plant extracts consist of numerous phytochemicals, such as flavonoids, phenolic acids, alkaloids, saponins, carbohydrates, amino acids and proteins, and terpenoids, that play a vital role in synthesizing NPs from metallic ions and act as capping/stabilizing and reducing agents [15, 16]. Green synthesized NPs are employed in various areas of nanomedicine, chemistry, and related fields for use in drug carriers for targeted delivery, antimicrobial agents, DNA investigations, biosensors, catalysts, separation science, cancer treatment, gene treatment, and magnetic resonance imaging [17, 18].

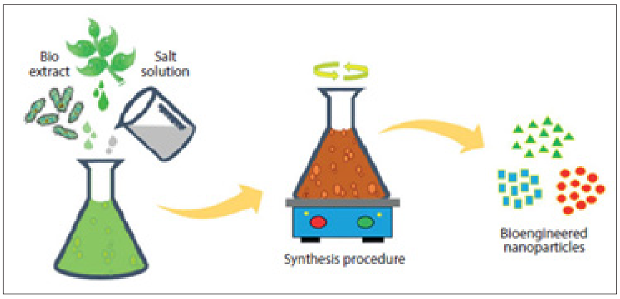

Figure 1: Green synthesis mechanism.

According to the existing literature, the two fundamental principles for the synthesis of metallic oxide nanoparticles (Mo NPs) are top-down and bottom-up techniques (Figure 2) [19, 20].

Considering metallic oxide nanomaterials as promising materials, we provide a comprehensive review of studies on the diverse application and green synthetic method of metallic oxide nanomaterials using biological materials as reducing agents and stabilizers. This study extensively reviews the recent research on the synthesis mechanism of zinc oxide, silver oxide, and gold oxide nanomaterials and their diverse applications.

Application of biologically synthesized metallic oxide nanoparticles

Plant-mediated synthesis of metallic oxide nanoparticles is stable and cost effective, and it has the potential to represent a revolution in the food, agricultural, and biomedical industries [21]. Synthesis of Mo NPs with biological products such as plants, algae, viruses, and bacteria as reducing agents is an economical and environmentally friendly way to produce novel nanomaterials with diverse applications [22, 23]. Biological products containing various bioactive compounds such as alkaloids, polyphenols, reducing sugars and proteins, etc., function as chelating agents, which are mixed with novel metal salt precursors and lead to the formation of novel Mo NPs [24]. The metallic surface of the synthesized Mo NPs allows them to bond to functional bioactive molecules, which alternatively lead to the magnetic behavior of particles and to the target [25]. Synthesis of MoNPs via green synthesis and other biological processes is cheap and environmentally friendly, involving the selection of a solvent medium, environmentally benign chelating agent, and nontoxic materials [26].

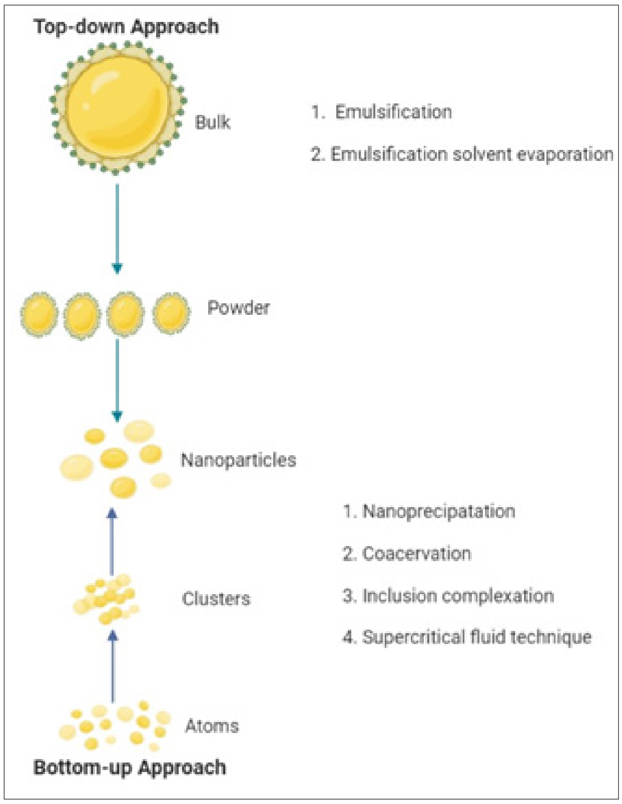

Figure 2: Bottom-up and top-down approaches to Mo NP synthesis.

Following the synthesis of the NPs, several techniques are available for the confirmation and characterization of stable MoNPs. These include Fourier transform infrared spectroscopy (FTIR), UV-Vis spectroscopy, X-ray diffraction technique (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), electron energy loss spectroscopy (EELS), atomic force microscopy (AFM), and transmission electron microscopy (TEM) [27]. The formation of the synthesized MoNPs is confirmed by the color of the colloidal solution, which is a result of reduction of the metal salt precursors [28]. Various synthesized inorganic nanoparticles such as Zn and ZnO, Ag and Ag_2O, Au and Au_2O_3, Cu and CuO, Fe and Fe_2O_3, Pd and PdO, and Pt and PtO_2 have proved their potential applications in biomedical and industrial fields [8]. Here, we summarize the application of the recently synthesized ZnO, Ag_2O, and Au_2O_3 Mo NPs.

Zinc oxide nanoparticles (ZnO NPs)

Metallic nanoparticles are very promising materials, considering their unique properties and their widespread use in pharmaceutical, biomedical, and industrial applications [29]. ZnO is an important inorganic material that is nontoxic, biocompatible Wang, chemically stable, and able to be used as a drug carrier [30]. The wide band gap of ZnO leads to unique chemical, optical, semiconducting, and piezoelectric properties [31]. In addition to its light covalent character, it also has strong ionic bonds, which increase its selectivity, durability, and heat resistance compared to other inorganic and organic materials [32]. Properties possessed by ZnO NPs allow for the synthesis of unique ZnO NPs with novel properties and applications. ZnO NPs are absorbed in the UVB (280-315nm) and UBA (315-400nm) regions, which is favorable in cosmetics production and anti-cancer, antibacterial, and antioxidant response [33]. In addition to these unique properties, ZnO NPs also possess strong photochemical and catalytic activities [33].

Several studies have demonstrated the synthesis of ZnO NPs using different plant extracts. Many applications of ZnO NPs have recently been explored in a biomedical context and is a result of their solubility in various medium and strong biocompatibility when compared with other metals oxide [33, 34]. Basic structural properties of ZnO NPs make them a suitable candidate for various industrial and biomedical applications [35].

The synthesis of the ZnO NPs can be achieved through various techniques, including hydrothermal, sublimation, combustion, polymerization, solution synthesis, and sol-gel methods [34, 36]. Huzaifa et al. [36] synthesized metallic ZnO NPs using Albizia lebbeck extract as a stabilizing agent at a very low temperature (60 °C) for a period of 5 hours (Figure 3). The synthesized ZnO NPs showed sub-acute toxicity on experimental animals and strong antioxidant, antimicrobial, and cytotoxic potential against MDA-MB 231 and MCF-7 human breast cancer cell models [34, 36]. In addition, with increasing concentration, the synthesized ZnO NPs revealed significant changes in tissue morphology and biomedical parameters in experimental rats [37] (Figure 4). Flower-shaped crystalline ZnO NPs with unique optical properties were successfully synthesized at a temperature of 90 °C using zinc acetate dihydrate [38]. Ecofriendly ZnO NPs synthesized using Cassia fistula and Melia azedarach at a temperature of 70 °C revealed strong antibacterial activities against *Staphylococcus aureus* and *Escherichia coli* [39]. In addition, [40] synthesized ZnO NPs using Camelia sinensis extract as a chelating agent at 70 °C and found that these had strong antimicrobial potential against *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

Silver oxide nanoparticles (Ag_2O NPs)

Silver oxide nanoparticles (Ag_2O NPs) are the most popular nanomaterials, used in medicine, modern pharmacology, and cosmetology, due to their high conductivity, biocompatibility, and powerful signal capacity. Studies have revealed Ag_2O NPs to have great potential for industrial and biomedical applications [41]. Based on the abovementioned properties, they can also have an important role in electrochemical sensor platforms. More than 20 years ago, scientists concentrated on the design of novel nanomaterials using Ag_2O NPs and composites [41]. Among all the nanomaterials, Ag_2O NPs are the most popular in electronic, textile, food industry, pharmaceutical, anti-microbial, and cosmetics contexts [42]. They can be synthesized using biological, chemical, and physical methods. Ag_2O nanomaterials also have antibacterial, anti-cancer, and anti-fungal potential [43].

Iqbal et al. [40] synthesized Ag_2O NPs with unique bio-interaction and physicochemical properties and anti-cancer potential using a co-precipitation technique with silver nitrate. Eco-friendly Ag_2O NPs synthesized using *Zephyranthes Rosea* flower extract as a chelating agent revealed antibacterial potential against *Escherichia coli*, *Staphylococcus aureus*, and as well as antioxidant and anti-diabetic activity [44]. Significant

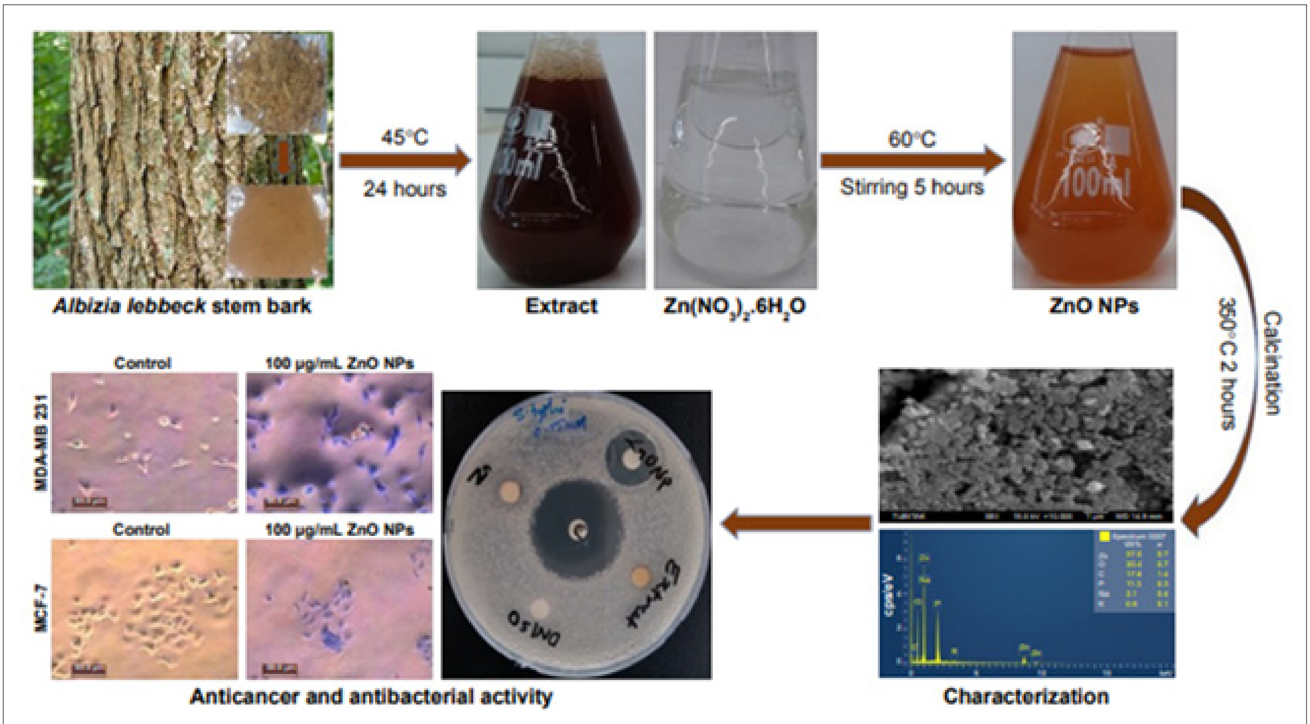

Figure 3: Summary of the synthesis and biomedical activity of biosynthesized ZnO NPs (Umar et al., 2019).

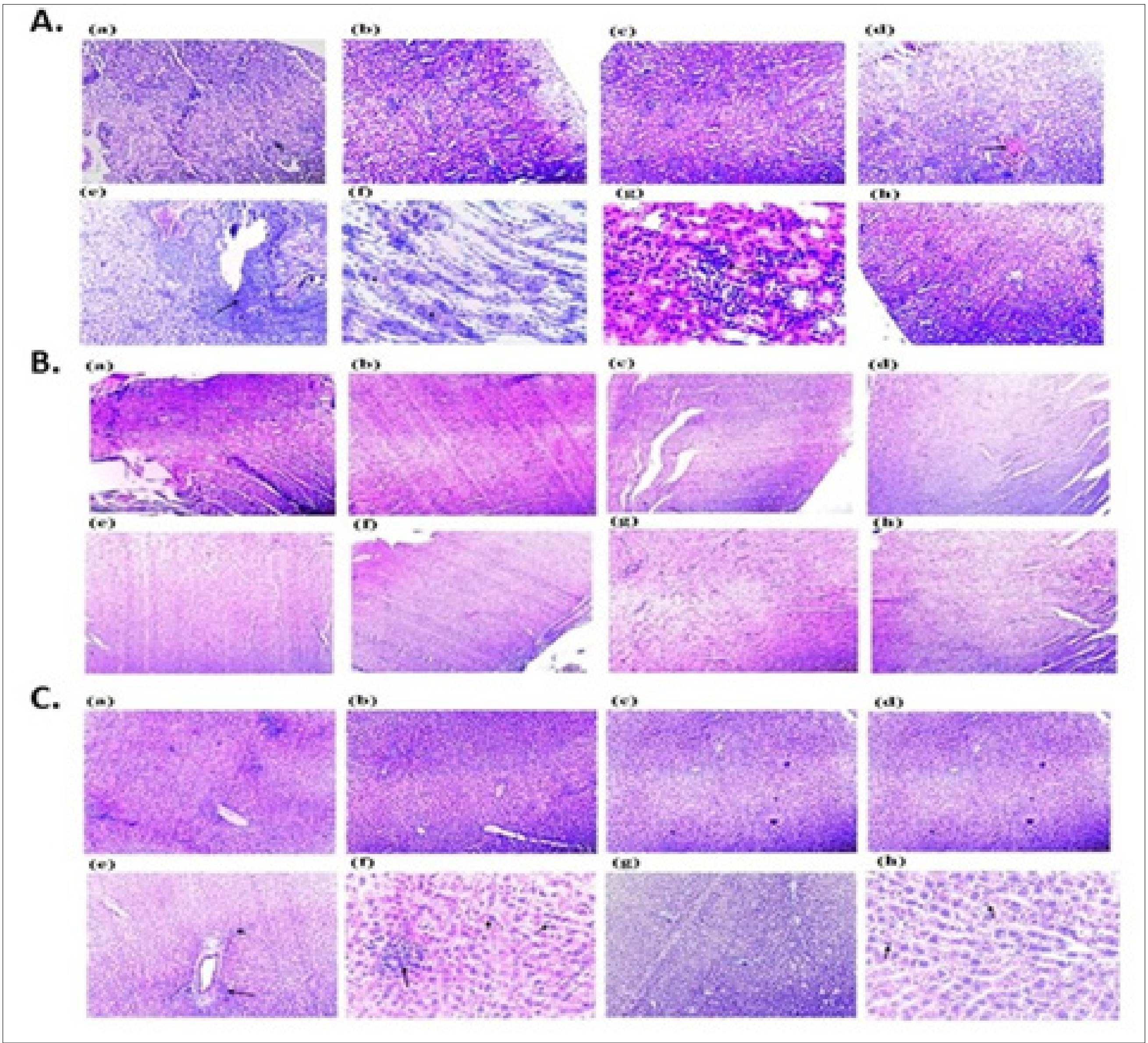

Figure 4: Photomicrographs of: A. Kidney B. Heart C. Liver, section of rats from different groups following 28 days repeated oral exposure to biosynthesized ZnO NPsAL. (a) Control group (b) 0.01M ZnO NPsAL (80 mg kg−1) (c) 0.01 M ZnO NPsAL (40 mg kg−1) (d) 0.05 M ZnO NPsAL (80 mg kg−1) (e) 0.05 M ZnO NPsAL (40 mg kg−1) (f) 0.1 M ZnO NPsAL (80 mg kg−1) (g) 0.1 M ZnO NPsAL (40 mg kg−1) (h) Zinc nitrate solution with different concentrations at 0.01 M, 0.05 M, and 0.1 M (He-matoxylin and eosin stain × 100). Abbreviations: ZnO NPsAL; Zinc oxide nanoparticles [36].

antibacterial and anti-metastatic potential of metallic Ag NPs synthesized using *Ficus ingens* leaf aqueous extract against highly metastatic human breast cancer cell line MDA-MB 231 [45] (Figure 5). Rashmi et al. [46] revealed photocatalytic, antibacterial, and anti-fungal activities from synthesized Ag_2O NPs using Centella Asiatica and Tridax plant powder as a chelating agent. *Zephyranthes Rosea* flower extract substitute Ag_2O NPs created using a green synthesis technique revealed small, spherical NPs with antibacterial, antioxidant, anti-inflammatory, and anti-diabetic activity [46]. In addition, nanostructured silver particles successfully synthesized using *Cleome gynandra* leaf extract revealed strong cytotoxic potential against *Staphylococcus aureus* and *Escherichia coli* [47]. Ag and Ag_2O NPs were successfully synthesized using Artemisia Herba-Alba aqueous leaf extract as a capping agent at room temperature, and both NPs revealed insecticidal and antibacterial activity against some specific species [48].

Overview of synthesis, characterization, and antibacterial activity of silver nanoparticles using Ficus ingens leaf extract.

The flowchart shows a summary of the collection of the Figus ingens and the preparation of the extract solutions. The extract solutions were then mixed with the silver nitrate at a certain temperature and time to produce the nanoparticles. Characterization was done using the AFM, SEM, FTIR, UV-Vis spectrophotometer, and XRD [46].

Gold oxide nanoparticles (Au_2O_3 NPs

Gold oxide nanoparticles (Au_2O_3 NPs) are among the most preferred nanomaterials and have gained momentum due to their special optical and electrical properties, which differ from those of bulk materials, as well as their application in the treatment and diagnosis of cancer, angiogenesis, and other related diseases [49]. Various secondary metabolites that were utilized as reducing agents during the synthesis of stable Au_2O_3 NPs exhibited an advantage over their chemical counterparts [50, 51]. Au_2O_3 NPs revealed unique colloid colors that made them attractive, caused as a result of surface plasmon resonance (SPR) [52]. Reaction conditions such as pH, incubation period, temperature, metal salt concentration, and plant extract concentration play an important role in determining the morphology and size of the synthesized Au_2O_3 NPs (i.e., pH_2 = larger size and rod-shaped; pH 3–4 = smaller size and rod-shaped; pH 8 = small size and spherical, oval, or polyhedral shape; pH 9-10 = small size and spherical or rod-shaped) [53]. Au_2O_3 NPs are also non corrosive-resistant metal as Au and biologically unreactive because of their high surface area, which gives it more affinity to conjugate and functionalize with proteins and therapeutic drugs [54]; Kumar Dikshit et al., 2021) [24]. Gold chloride in hydrate form is commonly used in the synthesis of Au_2O_3 NPs due to its solubility in both polar and non-polar solvents [55, 56].

One-step synthesis of Au_2O_3 nanocomposites (NCs) was achieved using pulsed laser ablation in liquid. It revealed enhanced catalytic activity and bi-functional behavior with special optical and magnetic effects (Lin et al., 2010) [57]. Another photochemical method was also employed to synthesize gold nanorods with excellent photothermal conversion efficiency via green synthesis [58]. [59] revealed green synthesis of Au_2O_3 NCs using biomass of *Brassica oleracea* var. gongylodes (*B. oleracea*) as reducing agents. The resulting NCs had antioxidant and anti-cancer potential at a low concentration against low metastatic human breast cancer cells MCF-7 [60]. Au NPs synthesized using aqueous extract of *S. filamentosa* and *S. lomentaria* through a constant and eco-friendly green route showed strong antioxidant activity with IC_{50} value of 38.84 and 32.804 µg/mL respectively and significant antimicrobial activity against *E. coli* and *S. typhi* [12] (Figure 6). Green-synthesized Au NPs using bacterium Vibrio alginolyticus as reducing agent also revealed significant antioxidant and anti-cancer potential on human colon cancer cell models (HCA-7) [60].

The flowchart shows a summary of the process, starting with the collection of the seaweed and the preparation of the

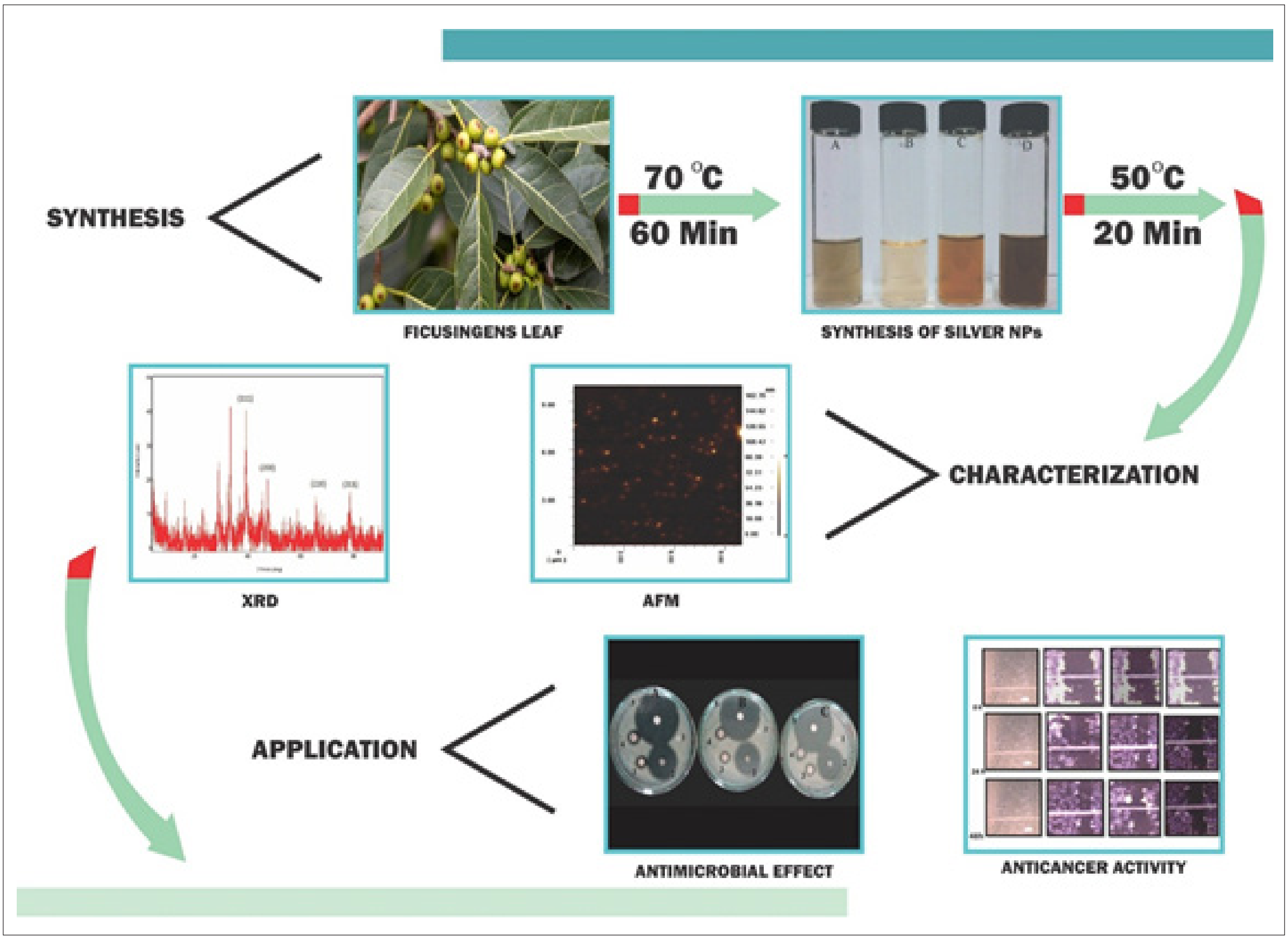

Figure 5: Overview of synthesis, characterization, and antibacterial activity of silver nanoparticles using *Ficus ingens* leaf extract.

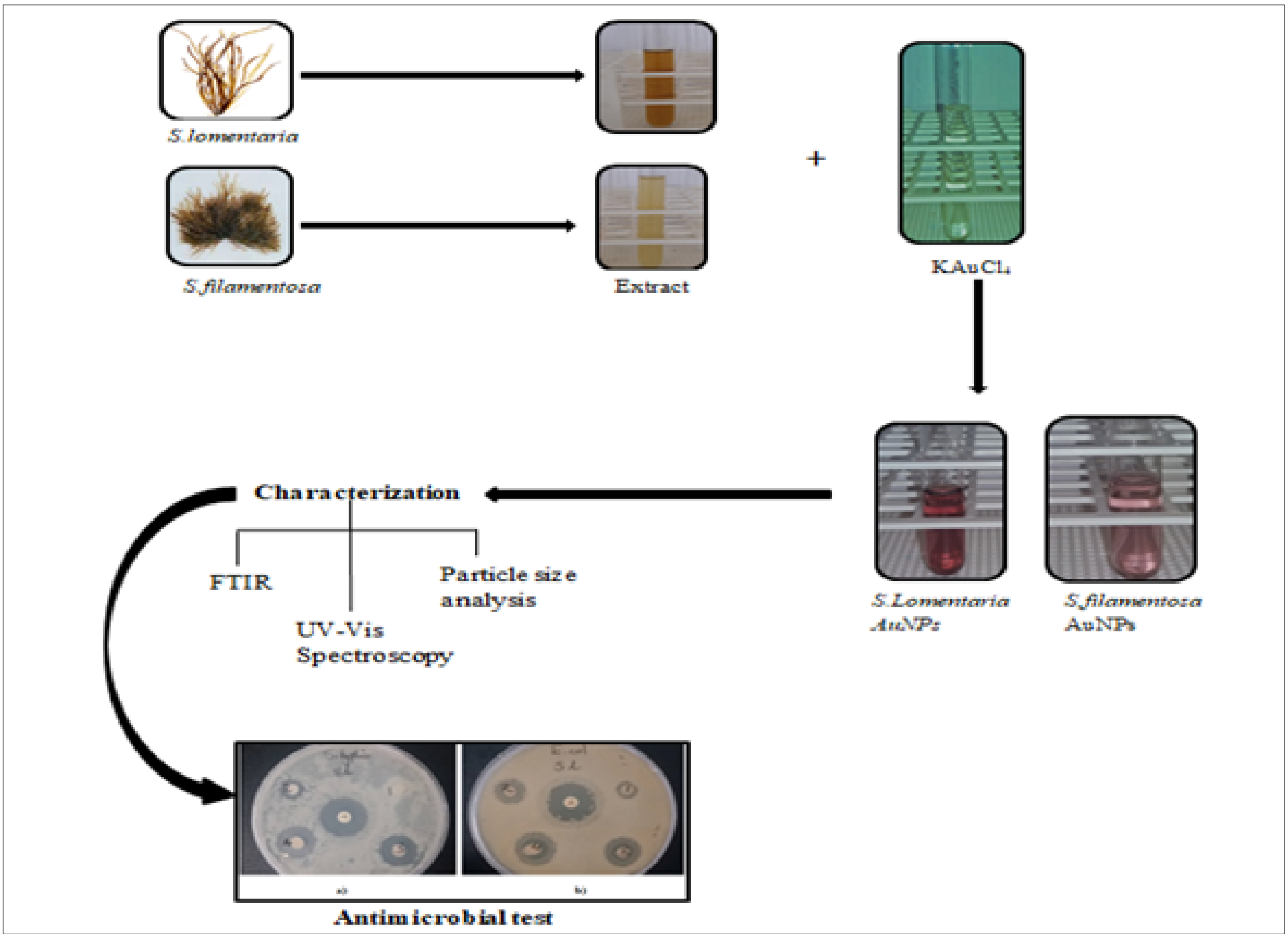

Figure 6: Overview of synthesis, characterization, and antibacterial activity of gold nanoparticles using *S. lomentaria* and *S. filamentosa* extract.

extract solutions. The extract solutions are then mixed with the potassium tetrachloroaurate at a certain ratio to produce the nanoparticles. Next, characterization is done using the FTIR, UV-Vis spectrophotometer, and Mastersizer. The antibacterial test is then performed using the disc diffusion method [11].

Mechanism of synthesis of metal oxide nanoparticles

Metal oxide nanoparticles synthesis mediated by plant extract is achieved when metal precursors mix with the extract at a certain pH or temperature. Reaction conditions (concentration, pH, and temperature), as well as phytochemical constituents of the plant, play an important role in the Mo NPs formation and stability [61, 62]. The phytochemicals present in the plant extract have the potential to reduce and stabilize metal ions to stable metallic oxide nanoparticles [63] as illustrated in figure 7. The main phytochemicals responsible for reducing and stabilizing nanoparticles are flavonoids, terpenes, saponins, carboxylic acids, aldehydes, proteins, and carbohydrates [64]. Obtaining Mo NPs using plants as stabilizing agent is less hazardous, more simple, and more stable [65]. A phytochemical called eugenol, the active organic compound of *Cinnamomum zeylanisum* (cinnamon) extracts, is responsible for the reduction of $HAuCl_4$ and $AgNO_3$ metal salts into their Mo NPs [66].

Conclusion and Future Prospects

"Green" synthesis of metal oxide nanoparticles (Mo NPs) is an interesting alternative research area, and it has wide applications in the biomedical, pharmaceutical, and renewable energy fields. The techniques used in the synthesis are simple, stable, cheap, and environmentally friendly. Various biological products (e.g., plants, yeast, bacteria, and fungi) are utilized as stabilizing agents during the synthesis/fabrication of Mo NPs, but plant materials/extracts show especially high efficiency in this process.

This review covered the synthesis mechanism and diverse applications of zinc oxide, silver oxide, and gold oxide nanomaterials. The synthesis mechanism was also reviewed based on the existing literature, which revealed simple solutions to existing problems in the synthesis of Mo NPs via green synthesis. Mo NPs (i.e., ZnO, Ag_2O and Au_2O_3 NPs) are among the most preferable nanomaterials and have gained momentum due to their high conductivity, biocompatibility, and special optical and electrical properties, which differ from those of bulk materials, as well as their applications in the pharmaceutical, biomedical, environmental, and industrial fields. However, green synthesis of Mo NPs using fungi, algae, and some marine plants still remains unexplored. Also, there are few studies on

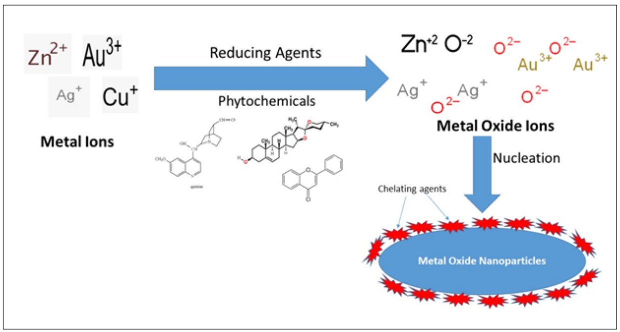

Figure 7: Mechanism of metallic oxide nanoparticle synthesis via green methods.

the synthesis and application of gold and gold oxide nanoparticles. Therefore, there is need for further exploration of these areas and other synthesis methods that are more stable, cheap, and simple.

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