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Review

Green Synthesis of Metal Nanoparticles from Plant Extracts, and Their Possible Application as Antimicrobial Agents in the Agricultural Area

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Abstract: Currently, metal nanoparticles have varied uses for different medical, pharmaceutical, and agricultural applications. Nano-biotechnology combined with green chemistry has great potential for the development of novel and necessary products that benefit human activities, while encourages the reduction of hazardous reagents for nanoparticle production. Green chemistry has an important role due to its contribution to unconventional synthesis methods of gold and silver nanoparticles from plant extracts, which have exhibited antimicrobial potential among other outstanding properties. Biodiversity-rich countries need to collect and convert knowledge from biological resources into processes, compounds, methods, and tools, which need to be achieved along with sustainable use and exploitation of biological diversity. Therefore, this review focuses on the importance of metal nanoparticles, the use of plant extract for their synthesis as well as other available methods, and the relevant antimicrobial activity that can be exploited in a sustainable model of agricultural management through a modern nanotechnological approach.

Keywords: agricultural industry; antibacterial; antimicrobial; green synthesis; gold; nano-biotechnology; nanoparticles; silver; sustainable development

1. Introduction

Currently, Green chemistry has been developed as an alternative to the use of environmentally harmful processes and products, due to the serious consequences that the world is facing, and the limited available time to find effective solutions [1-3]. According to Menges, it is suggested that green chemistry could have saved USD 65.5 billion by the end of 2020 [4].

Chen *et al.* state that circular economies should always aim to balance economic growth, resource sustainability, and environmental protection [5]. The challenge for biodiversity-rich countries and scientists is to collect and convert knowledge from biological resources into processes, compounds, methods, and tools, which need to be achieved along with sustainable use and exploitation of biological diversity [6-8]. In addition to that, biodiversity exploration has been presented to the international scientific community as a promoter of the responsible use of nature, and as a means of obtaining non-harmful components as well. For this reason, different strategies have been sought to contribute to this field through the use of green processes, such as the creation of nanoparticles (NPs) from plant extracts [9-11].

NPs are a wide range of materials with dimensions below 100 nm, which can be used in various areas such as medical, pharmaceutical, manufacturing and materials, environmental, electronics, energy collection, and mechanical industries due to their multiple properties [12-15]. In general, NPs can be classified into different groups which include fullerenes, metallic NPs, ceramic NPs, and polymer NPs [15-16]. Regarding the metallic NPs, their outstanding properties have caused the development of different methodologies for their synthesis, where gold (AuNPs) and silver (AgNPs) nanoparticles prepared from plant extracts are of great interest for the researchers in their attempt to develop suitable antibacterial and antimicrobial agents for agriculture [17-20]. Also, these initiatives are considered as low-cost processes that allow avoiding toxic-generating products and benefit the agricultural activity. It is estimated that the preparation of one kg of AgNPs would cost about USD 4 million, while one kg of raw silver costs around USD 14,000 [21,22].

In 2009, Raveendran *et al.* published one of the first green synthesis methods of metal NPs. In this approach, they employed an aqueous starch solution subjected to heating, silver nitrate, and glucose as the green reducing agent [23]. After that, researchers like Iravani, and Kumar *et al.* have presented high-quality review papers regarding the synthesis of metallic nanoparticles using plant extracts as a green chemistry approach [24,25]. Since then, synthesis of metal NPs has been performed by different research groups based on a variety of plants and their structures. Logeswari *et al.* developed an eco-friendly synthesis of AgNPs from plant powders of *Solanum tricobatum, Syzygium cumini, Centella asiatica* and *Citrus sinensis*, while Yang *et al.* performed a biosynthesis of AuNPs using an agricultural waste mango peel extract [26,27]. Verma *et al.* and Bagherzade *et al.* have shown the antibacterial, and antimicrobial activity of metal NP obtained through green synthesis using *Azadirachta indica* leaves, and *Crocus sativus L.* extracts, respectively [28,29].

Due to the nanotechnological boom, unusual physical, chemical, and biological methods have been developed for the synthesis and production of metal NPs [30-35]. Therefore, this paper seeks to describe some of these methods, the NPs' characterization techniques and also, pay particular attention to AuNPs and AgNPs' capacity as antibacterial and antimicrobial agents within the agricultural field.

2. Importance of nanoparticles

2.1. Gold Nanoparticles

AuNPs can be produced in different sizes and shapes (*e.g.* nanospheres, nanocylinders, nanowires, and nanocages). AuNPs exhibit in principle, low toxicity, and multiple interesting chemical, biological, and physical properties such as photo-thermal, optical, electrochemical, biocompatibility, and they can even act as catalysts [36-38]. Also, these nanoparticles can be synthesized with ease and can fulfill relevant roles in other fields than the agricultural, like for diagnostic probes, drug development, and functionalization with a wide range of ligands such as antibodies or genetic material manipulation. Due to the previous, the demand of AuNPs is rapidly growing as a result of their outstanding properties and multiple applications [39]. The aforementioned multi-functionality represents AuNPs high scientific value and the reason why many groups are currently carrying research about them.

Grimaldi *et al.* present a comparison regarding two production technologies; the conventional batch production, and an innovative milli-continuos flow. The latter provides attractive features, such as high controllability of product quality, simple operation, and high efficiency in the recovery of energy, as well as in the reduction of wastes. The research reported environmental impact and costs advantages from the adoption of a continuous-flow production, instead of the conventional method. In first place, human toxicity, ecotoxicity of water, and depletion of gold resources are reduced. Additionally, the strategy implies lower costs due to milder cleaning procedures, less complex operations, reduced use of hazardous substances, and waste generation. Therefore, the proposed approach recalls the importance of recycling natural products for the production of AuNPs to avoid the depletion of natural gold resources [40].

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2.2. Silver Nanoparticles

The synthesis AgNPs is a well-established field of work. In ancient times, silver nanoparticles were used as decorative pigments in crafts, staining glass, or ceramics. These materials have great potential and versatility as they are applicable in textiles, optoelectronics, catalysis, and environmental remediation processes as well. The latter, in particular, is due to inorganic silver's antimicrobial character, recognized as a bactericidal agent since it is an antagonist of microorganism due to its propensity for dissolution of toxic silver ion [41,42]. AgNPs show great variability in their characteristics depending on their shape and size (Figure 1). Pal *et al.* have reported that the bactericidal power of these NPs increases as they decrease in size since they have a larger surface area [43].

Silver has been used as a potent antimicrobial agent in different applications, having an important role in water treatment, chemical industries, food preservation, aquaculture ponds, and biomedical applications. Due to the current influence of nanotechnology, AgNPs are seen as an option towards improving agricultural productivity, through a production process that goes in harmony with the environment [44,45].

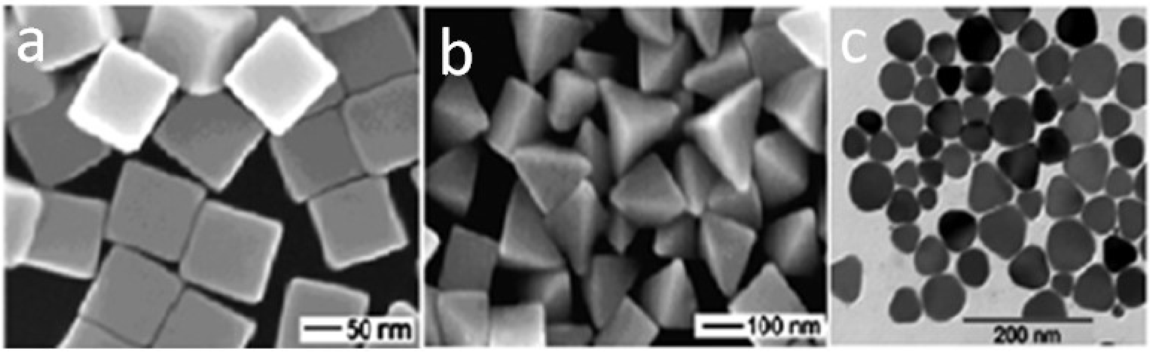

Figure 1. Silver nanoparticles: a) cubes, b) pyramids, and c)prisms. Adapted with permission from Marin, S. *et al*. Synthesis and characterization of silver nanoparticles and their application as an antibacterial agent. *Int J Biosen Bioelectron* 5:166-173. Copyright (2019) MedCrave [9].

3. Conventional methods for the synthesis of gold and silver nanoparticles

There is an incredible demand for NPs because of their fascinating properties. Due to the previous, various chemical or physical methods, and more recently biological or green chemistry-based methods have been used to streamline the process. However, among the mentioned, chemical methods are the most commonly employed, and usually have two stages: nucleation and growth. In this type of method, synthesis generally requires certain components such as a metal precursor, a reducing agent, and a stabilizing agent [46,47].

Physical parameters like size, size distribution, and shape can be achieved by controlling the nucleation stage, while nanoparticles growth can be controlled by adjusting experimental parameters such as the precursor used for reaction, concentration, pH, temperature, and reducing agents involved [48,49]. Cieśla *et al.* evaluated the effect of different synthesis conditions such as silver nitrate ($AgNO_3$) concentration, temperature, and mechanical agitation on the properties of AgNPs. Different optical properties were observed according to NPs size and shape, as a result of the method variations tested. In this case, the mixing of reagents influenced size and shape, regardless of the process temperature. However, unmixed samples exhibited solely as spherical nanoparticles [50].

Chemical reduction synthesis mechanisms of AuNPs and AgNPs have been extensively used through different methods such as the Turkevich, synthesis with sodium borohydride ($NaBH_4$) with

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or without citrate, seeding-growth, synthesis by ascorbic acid, and Brust-Schiffrin [51]. Nevertheless, a major concern arises due to the use of reagents such as $NaBH_4$, sodium citrate, ascorbate, elemental hydrogen, Tollen reagent, N, N-dimethylformamide (DMF) and block copolymers of poly (ethylene glycol) for reduction of compounds. The mentioned substances can lead to toxic by-products and damage the environment. For this reason, the use of a green pathway for the design and synthesis of NPs is currently being explored, since in this approach reducing agents are provided by plants' biomass [51,52].

Although chemical methods are the most widely used and well-reported for high-quality synthesis, these may lead to NPs with a narrow size distribution, and involve the use of hazardous chemical agents (*e.g.* toxic organic solvents), which limit NPs applications [53]. On the other hand, physical methods include simple one-step procedures and provide large-scale production in a short time, but it is common that the resulting NPs exhibit size, shape, and size distribution defects [54].

4. Unconventional methods for the synthesis of gold and silver nanoparticles

"Green methods" were created and introduced to achieve not only high social benefit but also, reducing the impact on the ecosystem. Thus, through their development and use, scientists are providing possible solutions to the issues encountered when using traditional synthesis methods, like the employment of environment-friendly solvents and reagents, as well as reducing energy consumption [55-57]. These methods consist in the use of non-toxic biomolecules such as DNA, proteins, enzymes, carbohydrates, and plant extracts for the synthesis of biocompatible metallic NPs by reducing metal ions in aqueous solutions [58,59].

In addition to the previous, these unconventional synthesis methods of AuNPs and AgNPs have the advantage of producing large quantities of NPs that are free from contamination and possess better-defined size and morphology than some of the obtained through conventional or physicochemical methods [60,61]. On the other hand, a disadvantage of these types of bioassays is the difficulty to establish adequate work conditions because biological raw material nature limits the set of conditions under which they can be used, and this can impact NPs formation. Therefore, it is necessary to provide well-defined specifications regarding temperature, pH, metallic solution composition, and the reaction time as well [60].

AgNPs synthesis through an eco-friendly and sustainable process is an important aim for nanomaterial development [62,63]. Arreche *et al.* studied two commercial brands of yerba mate (*Ilex paraguariensis*) for the preparation of aqueous extracts to synthesize AgNPs at room temperature (Figure 2). The obtained NPs were spherical, hexagonal, and triangular, with an average particle size of 50 nm and surface plasmon peak at 460 nm. The antimicrobial activity was evaluated against *E. coli* and *S. aureus*. The minimum inhibitory concentrations required for *E. coli* were 7.66 and 17.66 $\mu g*ml^{-1}$ using the treatment brand 1 and brand 2, respectively. On the other hand, the values for *S. aureus* were 23.25 and 50.60 $\mu g*ml^{-1}$ for the treatment brand 1 and brand 2, respectively. The study suggested that polyphenols present in yerba mate leaf extract take action as a reducing agent and stabilizer of the nanoparticles [64].

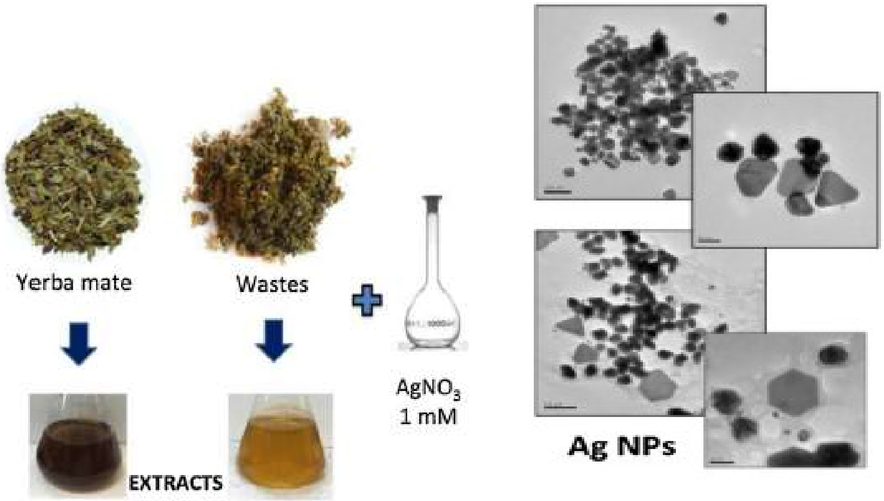

Figure 2. Synthesis of AgNPs using extracts from yerba mate (*Ilex paraguariensis*) wastes. Reprinted with permission from Arreche, R. *et al*. Synthesis of Silver Nanoparticles Using Extracts from Yerba Mate (*Ilex paraguariensis*) Wastes. *Waste and Biomass Valorization* 73(6):1712-1720. Copyright (2018) Springer [64].

Sasidharan *et al.* used the pericarp of *Myristica fragans* fruit extract for the eco-friendly synthesis of AgNPs. In this approach, the aqueous fruit extract of the plant fulfilled reducing and stabilizing functions for the preparation, and the obtained AgNPs exhibited good catalytic and antibacterial activities [65]. In another approach, Alkhalaf *et al*. conducted a study to identify the effect of the green synthesis of AgNPs from a *Nigella sativa* plant extract, resulting in NPs that exhibit antioxidant activity [66]. Also, Sk *et al.* synthesized AuNPs and AgNPs using aqueous extract of leaves from *Malva Verticillata.* AuNPs were found to have outstanding catalytic activity toward the hydride transfer reduction of the aromatic nitro Schiff bases, while AgNPs displayed interesting antibacterial activity [67].

5. Methods for obtaining plant extracts

Extraction methods are used for the separation of plant metabolites. In the case of AuNPs and AgNPs synthesis, the main extraction methods employed are (a) solvent-based extraction, (b) microwave-assisted extraction, and (c) maceration extraction [68]. The ideal extraction method should be cost-effective, simple, less time-consuming, and carried out with ease in any laboratory [69].

5.1. Solvent-based extraction

This technique allows soluble components in the solid material to be integrated with a solvent-based extraction for mass transfer, which ratio decreases with the increase in concentration of the soluble compound in the solvent [70]. Recently, the application of green solvents has caught attention in different disciplines. These solvents are seen as a non-toxic, biocompatible, and biodegradable alternatives to the conventional ones. In addition to that, they are easier to prepare and are cost-effective. Some advances regarding green solvent technologies are deep eutectic solvents (DESs), natural deep eutectic solvents (NDESs), ionic liquids (ILs), surfactants, and bio-derived solvents [71,72].

5.2. Microwave-assisted extraction

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This method employs microwave energy for the partition of analytes from the sample into the solvent by rapid heating, which allows materials to reach the necessary level of energy associated with the dielectric susceptibility of both, solvent and plant raw material [68,73]. Through its implementation; extraction time and solvent volume are reduced compared to other methods [74]. The aforementioned explains why it is recognized as a green technology [75]. Aside from that, studies have shown improved recovery of analytes and reproducibility when executing the extraction by this method. However, it is necessary to take into consideration two important aspects. In first place, special concerns have to be foresee for preventing the thermal degradation of the samples, and second, research groups need to be aware that this method is limited to small-molecule phenolic compounds [76].

5.3. Maceration extraction

This process may be achieved by following three basic steps: (a) grinding the plant in small pieces, (b) adding the appropriate solvent in a closed vessel, which will determine the type of compound that is going to be extracted from the sample, and (c) filtration to separate the liquid phase [77,78]. Although this may be considered the easiest and simplest method, organic wastes can become an issue due to large amounts of solvents used, making it necessary to have a proper chemical waste management process [79].

6. Synthesis methods of gold and silver nanoparticles from plant extracts

The use of plant extracts is strongly arising and is conceived as a feasible alternative for the synthesis of AuNPs and AgNPs because physicochemical approaches are being considered obsolete due to costly, and hazardous materials. Plant extracts can be presented in multiple forms, and are a rich source of polyphenols, flavonoids, sugars, enzymes, and/or proteins, which can also be used as reducing and stabilizing agents for the biosynthesis of metallic NPs. A great variety of plant extracts used for generating metallic NPs have been processed and applied in various fields [80-81]. In general, this method can represent a cost-effective, environmentally-friendly, simple, and suitable option for large-scale production processes [82].

This method is quite diverse from others since extracts can be obtained from multiple parts of the plant or its derivate products that have demonstrated their aptitude to be considered a metal NP natural source, such as leaves, bark, stem, shoots, seeds, latex, secondary metabolites, roots, twigs, peels, fruits, seedlings, essential oils, and tissues. The extracts usually contain a large number of organic compounds in the non-volatile fraction of the active ingredients, which allows their obtention by several techniques such as extraction with polar and non-polar solvents (Figure 3) [83].

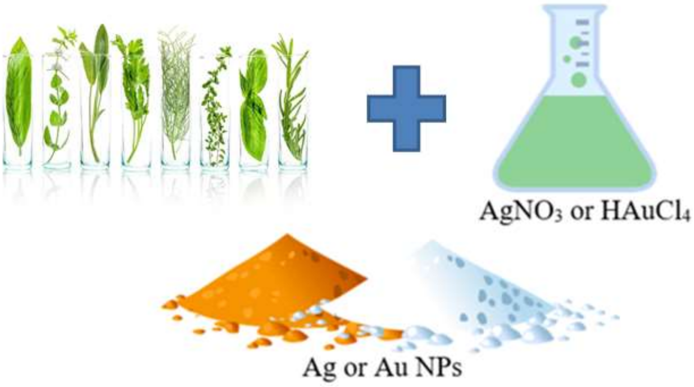

Figure 3. Synthesis of silver and gold nanoparticles using plant extracts.

Many studies have produced AgNPs from different plant extracts, such as the ones from *Citrus limetta, Luffa acutangula, Parkia speciosa, Melia azedarach, Artocarpus heterophylus, Azadirachta indica, Gomphrena globosa*, and others [84-89]. On the other hand, different attempts have successfully synthesized AuNPs as well, through the application of a green process such as the ones reporting the use of *Hygrophila spinosa, Caulerpa racemosa, Eclipta alba, Dunaliella salina*, and *Jasminum auriculatum* plant extracts [90-94].

According to Jamklande *et al.*, there are two kinds of synthesis methods depending on the starting material for NPs preparation. In first place, the top-bottom synthesis path is employed when raw material is at larger scales than the nano, allowing to break down its particles by grinding, lithographic techniques, sputtering, or thermal ablation. On the other hand, the bottom-up synthesis path includes the creation of nanoparticles from atoms that join in nucleation centers (Figure 4). In this case, the chemical reduction processes of the compounds are fundamental [95].

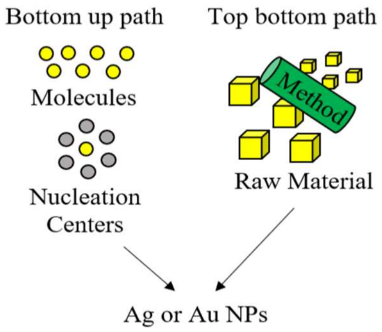

Figure 4. Synthesis of metal NPs from Top-bottom and Bottom-up paths. Reprinted with permission from Zhang, T. *et al.* Synthesis of Silver Nanostructures by Multistep Methods. *Sensors* 14(4):5860-5889. Copyright (2014) MDPI [52].

7. Nanoparticles characterization

The term characterization refers to the study of composition, structure, and other NPs properties such as physical, chemical, electrical, and magnetic. Characterization is relevant in any study in order to guarantee reproducible synthesis of the NPs of interest. Many techniques are currently available for developing analytical methods for NPs characterization purposes since these possess unique physical, chemical, and mechanical properties from bulk solids and molecules [96-98].

Nanomaterials have a large surface area to volume ratio, which differs greatly from the macroscopic materials [99,100]. The physicochemical properties such as size distribution, morphology, surface properties, chemical composition, kinetic behavior, stability, and interactions with other compounds exhibited by AuNPs, AgNPs, and NPs in general, depend on factors like surfactant additives, reactant concentrations, temperature, and solvent, as previously discussed. Therefore, the nanotechnology expansion requires to use analytical techniques based on spectroscopy, diffraction, thermal analysis, imaging, and others, for the study and characterization of nanoparticles, for which new combinations of techniques are being developed [100-102].

7.1. Instrumental techniques for the characterization

Research groups have extensively used spectroscopy to detect gold and silver NPs through the use of UV-vis methods, as these elements generate a specific signal while being reduced [103]. However, using one technique is not enough for a high-quality characterization of a sample, and usually, a degree of uncertainty is seen in each of them [102]. Therefore, the analysis and results from spectroscopy or any other must be supported by the combined use with other instrumental techniques (Figure 5) [104].

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Usually, the verification of the intended synthesis product can be done by measuring the vibrational frequencies exerted by the chemical bonds between the functional groups in the sample, which is possible thanks to Fourier transform Infrared Spectroscopy (FT-IR) when that vibrational energy is in the range of 1013-1014 Hz (*i.e.* infrared radiation). In addition to that, nanoparticles size is studied using IR, near-infrared spectroscopy (NIR), and Fourier transform near-infrared spectroscopy in the diffuse reflectance mode (DR-FTNIR) [105-107].

Another useful technique, X-Ray Diffraction (XRD), allows assessing the physical properties of the NPs since the diffraction pattern can give a valuable information of their average size and structure distortions of the lattice, as well as orientation. Regarding the previous, the analysis provides signals to determine whether the sample presents crystalline structures or identify the periodicity of non-crystalline amorphous phases. The two-dimensional images obtained can be converted to three-dimensional when using Fourier transform (FT) [108,109].

In addition to that, the thermal analysis performed through Differential Scanning Calorimetry (DSC), and Thermogravimetry (TG) support XRD findings. In first place, DSC thermograms enable determining if NPs possess a crystalline structure based on the form of their melting peak. Also, according to the changes from that thermal event, it is possible to determine if they interact chemically or physically with other substances. Thus, this analysis provides relevant references for chemical incompatibilities, and physical transitions such as anomerizations, crystallizations, and amorphizations [110,111]. On the other hand, TG goes into detail about mass loss of NPs due to the volatilization of one or more components such as solvents under programmed conditions of temperature to understand events like absorption, desorption, adsorption, decomposition, oxidation, and reduction [112-114].

Finally, Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) have been widely used for NPs characterization, where both can show the size, aggregation degree, as well as dispersion within the sample [115]. SEM is a versatile technique able to provide information about the morphology, composition, and topography of NPs surface by generating signals due to interactions presented between the electron beam and the sample [116,117]. Nevertheless, TEM is considered to be the most popular technique for NPs characterization among the electron microscopy. When compared to SEM, TEM has greater capacity in providing good quality spatial resolution equal to the level of atomic dimensions, and also can perform better analytical measurements in terms of morphology, composition, and crystallographic information [117,118].

Studies have shown that plant extracts from different species can produce the same shaped NPs. The aforementioned is well illustrative by four studies, which reported the synthesis of spherical AgNPs through different extracts like the ones from *Tribulus Terrestris* fruit, *Alternanthera dentate* leaves, *Acorus calamus* roots, and *Boerhaavia diffusa* species whole plant [119-122]. On the other hand, differences in shape are expected to happen when using different structures from the same plant for the extraction process. However, as reported by Rajakumar *et al.* the use of *Eclipta prostrate* leaves for AuNPs synthesis produced NPs with triangle, pentagon, and hexagon shapes [110].

Green synthesis of AgNPs was performed by Katta *et al.* using *Tagetes erect* plant extract. The XRD analysis confirmed the presence of pure silver phases with a face-centered cubic structure. The UV-vis spectroscopy analysis showed an absorption peak at 420 nm, and FTIR displayed relevant vibration peaks related to silver-ion binding process and yielded polyphenols at 3401 cm^{-1}, the presence of aromatic compounds at 2940 cm^{-1}, and the stretching peak of C-N bond at 1104 cm^{-1} due to the presence of plant-based amines. In addition to that, NPs morphology was assessed using SEM, where they were found to be in the range of 24-49 nm [123].

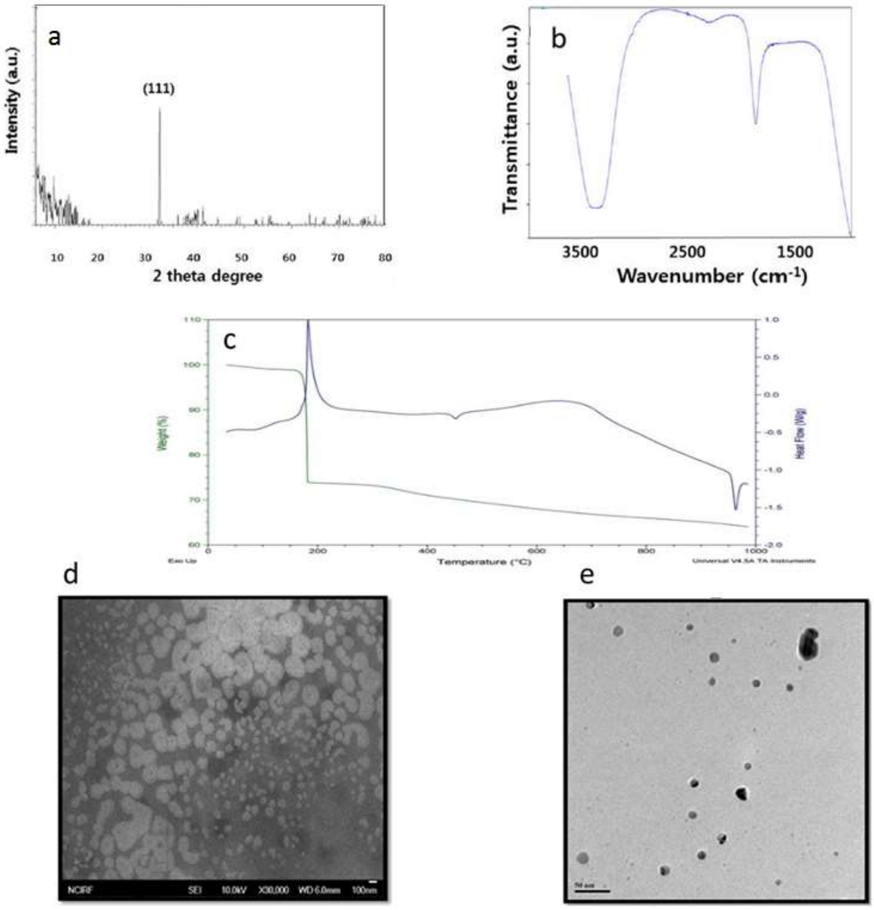

Figure 5. Characterization of silver nanoparticles a) XRD, b) FT-IR, c) DSC-TG, d) SEM, and e) TEM. Reprinted with permission from Zhang, X. *et al.* Silver Nanoparticles: Synthesis, Characterization, Properties, Applications, and Therapeutic Approaches. *Int. J. Mol. Sci* 17(9):1534-1538. Copyright (2016) MDPI [124].

Furthermore, it has been found that characterization techniques may be affected by the properties of samples regarding the material type, composition, dimensions, and the environment where the study is conducted. For that reason, novel and sophisticated combinations of different techniques are being developed to characterize NPs, and overcome the identified limitations [125].

8. Gold and Silver nanoparticles applications in agroindustry:

In general, the synthesis of NPs is of great interest because of their unique properties which can be incorporated into composite fibers, biosensor materials, cryogenic super-conducting materials, cosmetic products, and electronic components [126]. However, due to climate change, and the depletion of natural resources, the synthesis of AuNPs and AgNPs from plant extracts is a major topic for encouraging sustainable development. Because plants are the basis of this kind of green synthesis, the created AuNPs and AgNPs can be used in many agroindustry-related processes, from the application in the soil to the food chain [127-129].

Applications of nanotechnology in the food and agriculture sectors were proclaimed in June 2009 in a joint venture of the FAO and World Health Organization (WHO), with the inclusion of wide-ranging fields, such as nanostructured ingredients, nanosized biofortification, food packaging, nanocoating, and nanofiltration [130]. NPs may also act as “magic bullets”, containing nutrients or other substances such as beneficial genes, and organic substances, which are targeted to specific

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plant areas or structures to enhance their productivity. Thus, NPs represent smart nano-delivery systems for agricultural administration, specifically on crop nutrition [131].

Regarding direct applications of AuNPs and AgNPs, it was found that many of the researches on this field were focused on seed germination, root elongation, and plant responses towards the presence of metal NPs, like cellular oxidative stress or cytotoxicity [127,132]. In addition to that, metal NPs also have functions like nano-fertilizers, and nano-pesticides [133]. However, there are indirect applications of these NPs in the areas of food packaging, based on the antimicrobial and antibacterial activity of the AuNPs, and AgNPs [131].

8.1. Antimicrobial and antibacterial properties.

In the case of metal NPs, it is well known that they can be used as antioxidants, biosensors, and for heavy metal detection [134-136]. Moreover, their unique physicochemical properties such as the ability to bind biomolecules, large surface area to volume ratio, high surface reactivity, easy to synthesize and characterize, reduced cytotoxicity, and their visible light extension behavior allow their use as antimicrobial agents [137-140]. However, this property is primarily due to their ultra-small size and shape (250 times smaller than bacteria), which enables an electrostatic interaction between the gold or silver from the NPs, and the negative charge on the cell wall or surface of microorganisms, leading them towards cellular death [141,142]. In addition to that, the high concentrations of steroids, sapogenins, carbohydrates, and flavonoids act as reducing agents of ions, and as cover agents, which provide high stability to AuNPs and AgNPs [143].

Many research papers in which AuNPs have shown promising antimicrobial activities have highlighted a majority spherical shape character of the NPs. Nevertheless, rod-shaped, triangular, hexagonal, and cubic NPs have also been found as part of the obtained mixture [144]. Thangamani *et al.* synthesized AuNPs using *Simarouba glauca* leaf extract. Size and shape of the NPs were sensitive to leaf broth concentration; particles tended to decrease in size with an increase in leaf broth concentration, while different morphologies were obtained such as a mixture of the prism and spherical like particles. Aside from that, they assessed the antimicrobial activity of the synthesized AuNPs by testing them against gram-positive and gram-negative organisms. The antimicrobial assay showed better results for *Staphylococcus aureus*, *Streptococcus mutans*, *Bacillus subtilis*, *Escherichia coli*, *Proteus vulgaris*, and *Klebsiella pneumonia* [145].

A study by Lediga *et al.* functionalized AgNPs with extracts of *S. birrea* and *E. autumnalis*, for which were found to exhibit remarkable antimicrobial properties against two gram-negative and two gram-positive bacterias. Both, the *S. birrea* and *E. autumnalis* AgNPs exhibited negligible or low toxicity [146]. In another approach, Montes de Oca *et al.* evaluated the impact of AgNPs usual concentrations in nature soils that are grown with Arabian Coffee in customary and organic operating systems. In this study, biomass, extracellular enzyme activities, and diversity of the soil microbial community were studied in a microcosm experiment as a function of time. After 7 days of incubation, the increase in the microbial biomass was found to be independent of AgNPs concentration [147]. In contrast, after 60 days, there was a decrease in gram-positive, and actinobacterial biomass in soils in all the evaluated AgNPs concentrations. The physicochemical properties of the soil and the enzymatic activities were not affected by AgNPs. Within the composition of the microbial community, only a few differences were observed in abundance relative to the phylum level and gender in the fungal community [147]. The results indicated that the environmental factors of AgNPs affect microbial biomass but had a low impact on microbial diversity, and may have a poor effect on soil biogeochemical cycles by extracellular enzyme activities [147,148].

9. NPs interactions with plants

9.1. Accumulation and harmfull effects of NPs in plants and crops

Special attention should be paid to the interaction between NPs and plants (*e.g.* crops) when these materials are used within the agricultural field. Hashimoto *et al.* have found that accumulated AgNPs can translocate to roots and shoots of two terrestrial agro-crops; *Vigna unguiculata* and *Triticum aestivum*. Recently, it has been demonstrated that AgNPs under aerobic soil conditions are able to maintain their intact nature (88%), while a transformation to Ag_2S also occurs in the same extension [149].

While it is not clear how metal NPs affect the environment, some studies reveal that plants overexposure to them may reveal pathways involved in the cytotoxicity. Proteomic studies on *Oryza sativa* (Asian rice) have increased protein precursors for oxidative stress tolerance, calcium regulation and signaling, apoptosis, and other kinds of damages [150]. This can be used for studying NPs limits in the environment. Also, high concentrations of silver can be overwhelming to the seed like for *A.thaliana,* which should not be exposed to AgNPs during its germination [151]. In contrast, there is no toxic effect on seed germination and root elongation of *Cucurbita pepo* (zucchini). This suggests that different mechanisms of action might occur across plant species concerning the effect on germination [152]. Furthermore, germination in *Lolium perenne*, *Hordeum vulgare*, and *Linum usitatissimum* showed to be affected at low concentrations of AgNPs but never fully inhibited [153].

Kaveh *et al.* studied the model agro crop *Arabidopsis thaliana* and reported the phytoaccumulation of AgNPs [154]. Another approach developed by Taylor *et al.* described *M. Sativa L.* (alfalfa) tendency to accumulate metal NPs of different sizes [155]. Also, gold is taken up in *A. thaliana* predominantly in an ionic form. It has been reported that AuNPs exposure results in the upregulation of plant genes causing downregulation of specific-metal transporters to reduce gold uptake [155].

Courtois *et al.* published an important study of the impact of silver species introduced into the soil via sewage sludge. As mentioned before, AgNPs are incorporated into many conventional and novel products due to their special physicochemical and antimicrobial properties. However, the discharge of these products into wastewater causes an accumulation of AgNPs and derivates such as Ag_2S in sewage sludge. The major concern is related to land application of sewage sludge for agricultural purposes since soils receive a great source of contamination for plants and crops. Soil exposure to metal NPs may lead to changes in microbial biomass, and can also affect plant growth causing physiological, biochemical, and molecular effects on them. Nonetheless, much is still unknown about the ecotoxicology of silver species, where several doubts are focused on the possibility of transfer along the trophic chain via accumulation in plants, and for that, research to evaluate the long-term impact of AgNPs on plants is ongoing [156].

9.2. NPs in soils

Needless to say, the growing use of AgNPs due to their recognized antimicrobial activity has led to their accumulation in soil ecosystems [157,158]. Although their environmental impact on the soil microbial community is a concern that is still under consideration, several authors have concluded that the toxic effects on microbial communities are highly dependent on the AgNPs concentration in the soil [159-163]. However, most studies have evaluated AgNPs at higher levels than actually occur in nature [164-167].

Meier *et al.* presented the concern that anthropogenic activities can disrupt soil ecosystems, resulting in the reduction of its microbial health. In order to evaluate the previous, they exposed freshly collected sandy loam soil to solutions ranging from 0-2000 mg/kg of AgNPs. After that, they expanded traditional soil microbial analysis with genomics-based tests through the measure of alterations in community taxonomic structure and function using 16S-rDNA profiling and metatranscriptomics. The research group found that AgNPs affected bacterial taxonomic structure, as well as genes involved in heavy metal resistance, and also, their presence induced some toxicity response pathways to become highly upregulated [168].

Another study by Li *et al.* described the impact of AgNPs on the soil. Ag_2S is more likely to be the form in which silver is retained in soils. They examined Ag_2S retention from 11 natural different soils and discovered that more than 99% of the NPs were retained irrespective of the soil properties. Since the retention of Ag_2S in soils is conceived as a critical factor for their toxicity and availability to sustain life (*e.g.* plants), the results obtained by this group can be a good approach for explaining the differences in phytoavailability exhibited by soils compared to what is established in the literature for liquid media [169].

10. Conclusions

Green chemistry is an innovative and growing resource in the search for more environmentally friendly processes. Using plant extracts for the synthesis of metal NPs is a recently growing area of interest due to its benefit in comparison to the traditional physicochemical methods. AuNPs and AgNPs generated by green synthesis have potential applications in agriculture and agroindustry, especially as antimicrobial agents of certain microorganisms for which their efficacy has been scientifically proven. Although recent studies suggest that environmental concentrations of AuNPs and AgNPs affect microbial biomass with low impact in their diversity, further research needs to be addressed in order to determine the effects they could produce to the soil, plants, and the environment in general due to long-term exposure.

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