



Synthesis of Metallic Nanoparticles Using Plant's Natural Extracts: Synthesis Mechanisms and Applications

Síntesis de Nanopartículas Metálicas Usando Extractos Naturales de Plantas: Mecanismos de Síntesis y Aplicaciones

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ABSTRACT

Metallic nanoparticles have a wide range of applications in health, electronics, optics, magnetism, bioremediation, chemistry, and materials science. Several methods used to produce nanoparticles are not friendly to the environment, so this review highlights the benefits of using plant extracts to prepare metallic nanoparticles to investigate an eco-friendly method. Plant extracts contain secondary metabolites, including flavonoids, alkaloids, terpenoids, phenolic compounds, polysaccharides, amino acids, and proteins. The compounds present in the extracts can reduce metal ions from salts and allow the formation of nanoparticles. The fundamentals of the *in-situ* nanoparticle synthesis were reviewed, a list of various plants used was made, the mechanisms proposed for nanoparticle synthesis, and finally, applications in several areas were addressed.

Keywords: Plant Extract; Metallic Nanoparticles; Formation Mechanism; Green Synthesis.

RESUMEN

Las nanopartículas metálicas tienen una amplia gama de aplicaciones en los sectores de la salud, la electrónica, la óptica, el magnetismo, la biorremediación, la química y la ciencia de los materiales. Varios métodos utilizados para producir nanopartículas no son amigables con el medio ambiente, por lo que esta revisión destaca los beneficios del uso de extractos de plantas para preparar nanopartículas metálicas para investigar un método ecológico. Los extractos de plantas contienen metabolitos secundarios, incluyendo flavonoides, alcaloides, terpenoides, compuestos fenólicos, polisacáridos, aminoácidos y proteínas. Los compuestos presentes en los extractos pueden reducir los iones metálicos de sales y permitir la formación de nanopartículas. Se revisaron los fundamentos de la síntesis de nanopartículas in situ, se realizó una lista de varias plantas utilizadas, los mecanismos propuestos para la síntesis de nanopartículas y, finalmente, se abordaron las aplicaciones en varias áreas.

Palabras clave: Extracto De Plantas; Nanopartículas Metálicas; Mecanismo De Formación; Síntesis Verde.

INTRODUCTION

In recent years, different researchers have improved their understanding of nanotechnology and focused their projects directly or indirectly on its associated topics. These studies include planning, synthesis, characterization, and evaluation of the properties obtained by modification of their size and shape. The term "nano", the keywords in these researches, comes from the Latin nanus, meaning "dwarf". This kind of technology is supported in physics, chemistry, materials science, biotechnology, and biosciences, among others, to achieve a multidisciplinary understanding of the phenomena that occur in the materials. A phenomenon called "nanorevolution" has been created, which aims to the manipulation and study of nanomaterials in a wide range of compositions, sizes, shapes, and morphologies (Kolahalam *et al.*, 2019; Hamers, 2017).

Nanoparticles are an important class of nanomaterials studied by nanotechnology, as they have applications in various fields, including those described by Hernández-Morales et al. (2019) who synthesized silver nanoparticles with antimicrobial capacity using Salvia hispanica L. seed extracts. Opris et al. (2017), synthesized gold nanoparticles using extracts of Sambucus nigra L. with the ability to lower the level of glucose in blood. It also reduces levels of inflammation and oxidative stress induced by hyperglycemia. Matinise et al. (2018) created iron-zinc oxide nanoparticles aided by Moringa Oleifera extract, with excellent electrochemical performance, suggesting great potential in this area. Lebaschi et al. (2017), employed extracts of Camellia sinensis to form palladium nanoparticles showing potent catalytic application for the synthesis of biaryls, by Suzuki cross coupling reaction and also reduction of 4-nitrophenol (4-NP) by NaBH₄. Samari et al. (2018), used extracts of Mangifera indica L. to synthesize silver nanoparticles capable of chemically sensing Hg²⁺ ions in water. Goutam et al. (2018) made use of Jatropha curcas L. for the green synthesis of titanium oxide, for the remediation of wastewater from tanneries, and Idrees et al. (2019) worked with Sida acuta extracts to develop silver nanoparticles that acted as suitable inhibitors for the corrosion of mild steel in 0.1 H₂SO₄ solutions. The European Union (EU) defines nano-

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materials as "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range of 1 nm – 100 nm" (Gehr, 2018). However, in the biotechnological area the size of the particle used varies between 10 to 500 nm and rarely exceeds 700 nm (Mody *et al.*, 2010).

The main reasons nanomaterials showed different properties than bulk materials are due to surface effects, since atoms on the surface have fewer neighbors than bulk atoms. This is associated with less coordination and dissatisfied bonds in nanomaterials. Therefore, they are less stable. In addition, the smaller a particle, the larger fraction of atoms on the surface, and the higher the bonding energy per atom causing a high surface area and volume ratio rate, allowing them to react much faster. Also, are due to density of states, where groups of atoms tend to form bands, and the greater the number, the higher the state density; here a gap called "forbidden" is created, which is the energy that is occupied for an electron crosses a state from lower to higher energy. These vary as the density change, being able to modify the electrical, magnetic, biological properties of the materials, among others (Roduner, 2006).

The future of nanoparticles lies in synthesizing them using greenways, living beings such as plants, microorganisms, or fungi, and seeking their effectiveness in the market (Hoseinpour and Ghaemi, 2018). There are already products with nanoscale materials in their formulations, among them are Doxorubicin (Doxil), also known as Caelyx, a cancer treatment drug. The agent mixture is inside unilaminar liposomes coated with PEG (polyethylene glycol) and is called "PEGylated liposomes". Their size varies between 80 and 90 nm (Abdellatif and Alsowinea, 2021). Additionally, Remington Nano Silver Dryer, Infinity 230 Nano Silver Tourmaline Ceramic Folding Styler by Conair, and Zazen Professional Nano-Silver Ionic Hair-dryer are hair dryers with silver nanoparticles (Taylor et al., 2017). Furthermore, Ostim is a calcium hydroxyapatite paste [Ca10 (PO4)6 (OH)2] that has osteoconduction skills, with crystals of 20 nm in diameter (Farjadian et al., 2019). Sea Hawk Cukote Biocide Plus Red-3541 is a paint with biocidal capacity with copper oxide nanoparticles whose average size is 220 nm (Adeleye et al., 2016). Nemozin is a burn ointment with zinc oxide nanoparticles of 200 nm (Swathi et al., 2013). There are more than 1814 products whose ingredients include nanoparticles, the most predominant being silver (Vance et al., 2015).

There are two methods for synthesizing nanoparticles: Top-Down and Bottom Up. Top-Down processes convert the bulk material into nano-sized particles by mechanical milling, laser ablation, or sputtering. For Botton Up methods, nanoparticles are formed from smaller molecules created by the union of atoms or molecules. It can be made through solid state methods (physical vapor deposition, chemical vapor deposition), liquid state methods (Sol-gel, chemical reduction, hydrothermal), gas phase methods (pyrolysis

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spray, laser ablation), biological methods (bacteria, fungi, plants), among others (microwaves, supercritical fluids, ultrasound) (Jamkhande *et al.*, 2019). Unfortunately, many of these methods need a lot of energy to operate or pollute substances, making them unattractive for industrial use. Social responsibility emphasizes the search for alternatives that are economical and take care of the environment. The biological synthesis of nanomaterials has been put into practice since it uses temperature, pH, and pressures considered mild conditions. In addition, it has advantages over other synthesis methods, including higher productivity and lower costs (Kalimuthu *et al.*, 2019; Sign *et al.*, 2018).

Biological synthesis uses microorganisms and plants (or their extracts). There is a particular interest in using plants because they have many phytochemicals including ketones, aldehydes, flavonoids, amides, terpenoids, carboxylic acids, phenols, and ascorbic acids. These components are known to reduce metal salts and create metal nanoparticles. However, although there are several studies on nanoparticles, the exact mechanism involved in this process remains uncertain (Singh *et al.*, 2018). Therefore, this review aims to present a current overview of the fundamentals of the synthesis of nanoparticles using the components found in plant extracts, the effect of reaction conditions, and the biological applications of these nanoparticles.

Fundamentals of Green Synthesis of Nanoparticles using Plant Extracts

Although the nanoparticle synthesis mechanisms are still under investigation, the formation of metal complexes is present in all reactions, so it is possible to consider the theory of the effective atomic number proposed by Lewis. This rule establishes that for coordination compounds, the summary of the electrons from the metal plus those donated by the ligands must be equal to the number of electrons present in the next noble gas, according to the period of the metal involved (Tolman, 1972).

During the synthesis of nanoparticles using natural extracts, the metal ions from precursors are captured and immobilized by different biological elements that function as ligands. Reduction and sintering processes are carried out to obtain the final product. The characteristics of nanoparticles depend on reaction conditions, being able to vary morphology, dispersion, performance, and size when modifying temperature, pH, and concentrations of precursors, among others (He et al., 2017; Skandalis et al., 2017; Ahmed et al., 2017). Temperature, for example, influences nanoparticle size, reaction rate, and shape of nanoparticles. In ZnO nanoparticles synthesis using Cherry fruit extracts, studied at 25 °C, 60 °C and 90 °C, researchers observed that as the temperature increased, the nanoparticle size increased. This explains that the extract is rich in ascorbic acid, which becomes unstable with increasing temperature leading to an uncontrolled reduction process and particle aggregation (Malek-Mohammadi et al., 2018). In an alternative study for silver nanoparticles synthesis using Mangifera indica leaf extract, the temperature was varied from ambient conditions to 80 °C, the intensity of SPR from ambient conditions to 40 °C was increased. This was due to the increase in reaction speed; between 60 °C and 80 °C, an increase in the amplitude of the peak was found accompanied by a decrease in the intensity of SPR, demonstrating that the ability to act as a reducing agent of the extract decreased and caused agglomerates of nanoparticles (Samari *et al.*, 2018). The temperature was also shown to affect the synthesis of silver nanoparticles using extracts of *Piper retrofractum* fruit, where the temperature was increased from 25 °C to 80 °C, and is associated with larger particle sizes due to their agglomeration. In addition, high temperatures can denature compounds in the extracts, making them unavailable to react and forming longer nanoparticles (Amaliyah *et al.*, 2022).

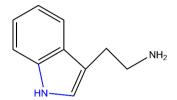
The pH of the synthesis process also effects nanoparticle size. In synthesizing silver nanoparticles using Thymus algeriensies extracts, pH from 3 to 11 was tested during the synthesis process. The resulting nanoparticles had a change in absorption length from 425 nm to 418 nm and an increase in signal intensity, indicating a decrease in size and that the alkaline environment favors the reducing and stabilizing capacity of the antioxidants present in the extract (Beldjilali et al., 2020). It has been seen that pH affects the nucleation stage in Piper chava extracts used to form silver nanoparticles. As the pH increases from 5 to 9, the absorption in SPR increases and is accompanied by a shift towards blue. This is because at low pH the aggregation of nanoparticles is induced, instead of nucleation to form new ones. At more alkaline pH, the anionic functional groups in the extract are favored to bind with silver ions and increase the nucleation sites, resulting in smaller sizes (Mahuiddin et al., 2020). The same effect is observed on silver and gold nanoparticles synthesized using Opuntia dillenii extract. When varying the pH from 1 to 13, it is observed that at low pH, there is a broadening in the bands from UV-Vis spectrum, indicating the formation of large nanoparticles. While at more alkaline pH, a narrowing of the band is observed at 400 nm indicating smaller nanoparticles (Ahmed et al., 2022).

Synthesis Using Natural Plant Extracts

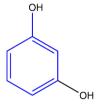
Plants are autotrophic organisms, biochemically additional to the primary metabolites necessary for the organisms' life. They synthesize secondary metabolites, also known as natural products, which are not essential for plant growth, but are compounds that help with adaptive processes, defense against predators or pathogens, ecological interactions, symbiosis, metal transport, and competition, among others. Secondary metabolites are classified into four categories according to the "British Nutrition Foundation": Terpenoids, Phenols, Nitrogen Compounds, and Sulfide Compounds (Mera *et al.*, 2019; E. Ahmed *et al.*, 2017). A representative structure of each category is shown in Figure 1. Secondary or phytochemical metabolites can act as reducing and stabilizing agents responsible for the synthesis of nanoparticles (Ovais *et al.*, 2018).



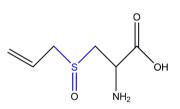
Terpene: Linalool



Nitrogen Containing Compounds: Triptamine



Phenol: Resorcinol



Sulphure Containing Compounds: Aliin

Figure 1. Representative structure of each group of secondary metabolites (The key structure is shown in blue).

Figura 1. Estructura representativa de cada grupo de metabolito secundarios (La estructura representativa se muestra en azul).

In general, nanoparticle synthesis involves mixing plant extracts with metal precursor salts. They can interact under different reaction conditions (pH, temperature, concentrations, etc.). Here, the formation of nanoparticles takes place in stages. It begins with the set of species equilibrium; once dissolved, the extracts and the precursor salt coordination complexes are formed between the metal ion and the phytochemicals of the extract. The sites where the nanoparticles will grow are created at the second nucleation stage. At the third stage of growth and adsorption, small adjacent nanoparticles come together to form particles of a larger size. Finally, during termination, the final shape of the nanoparticles occurs. The general synthesis mechanism is shown in Figure 2. The following operations consist of purification by centrifugation and washing until the impurities present are removed (Naikoo et al., 2021; Behzad et al., 2021; Bouttier-



Figueroa *et al.*, 2019a). As expected, results in the synthesis of nanoparticles show that the extract and its concentration affect the size and morphology of the nanoparticles, while temperature and pH affect the agglomeration process (Erjaee *et al.*, 2017; Koshy, 2017).

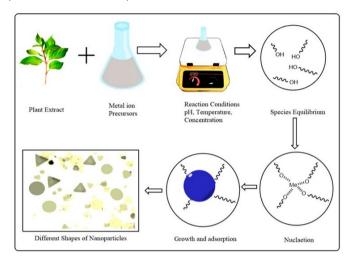


Figure 2. General mechanism for nanoparticles synthesis utilizing plant extracts (Me = metallic ion).

Figura 2. Mecanismo general para la síntesis de nanopartículas utilizando extractos de plantas (Me = ion metálico).

A list of plants used for the synthesis of nanoparticles between 2017 and 2022 is presented in Table 1. It is observable that the main phytochemicals involved in the synthesis of nanoparticles are phenolic compounds, flavonoids, carboxylic acids, carbohydrates, terpenoids, alkaloids, and proteins. They contain functional groups capable of coordinating with, and reduce, metal ions. Extracts of Azadirachta indica, Hibiscus rosa-sinensis, Murraya koenigii, Moringa oleifera, Tamarindus indica, and Spinacea oleracea contain phenolic compounds and flavonoids that act as covering agents, preventing agglomeration and stabilizing the formation of copper oxide nanoparticles (Rehana et al., 2017; Al-Jawjari et al., 2022). Extracts of Aloe vera, Hibiscus sabdariffa, Atalantia monophylla, Punica granatum, Ocimum americanum, Beta vulgaris, Cinnamomum tamala, Cinnamomum verum, Brassica oleracea var. Itálica, Acalypha fruticosa L., Alchornea laxiflora, and Syzygium Cumini contain phenolic compounds, flavonoids, tannins, organic acids, and terpenoids that can trigger the reduction of zinc salts and control the size of zinc oxide nanoparticles (Mahendiran et al., 2017; Vijayakumar et al., 2017; Mohamad et al., 2019; Narendra et al., 2019; Mohanan et al., 2020; Vijayakumar et al., 2019; Ekennia et al., 2020; Rafique et al., 2022). Origanum vulgare L. contains phenolic and carbohydrate compounds that play a vital role in the reduction of Pd²⁺ ions and act as stabilizing agents for palladium nanoparticles (Rafi et al., 2017). Moringa oleifera leaves contain amino acids, alkaloids, flavonoids, and phenolic compounds that facilitate the synthesis of iron nanoparticles (Katata-Seru et al., 2018). The extracts of Annona muricata, Coleus aromaticus, Tasmannia lanceolata, Backhousia citriodora and Tecoma capensis

have flavonoids, terpenoids and proteins responsible for the reduction of gold ions. In addition, they help in the formation and stabilization of synthesized nanoparticles (Folorunso et al., 2019; Boomi et al., 2018; Khandanlou et al., 2020; Hosny et al., 2022). Tecoma stans L. contains hydroxyl groups, alkenes, alkynes, flavonoids, carbohydrates, amines, and phosphates that act in the synthesis and formation of magnesium oxide nanoparticles (Nguyen et al., 2021). Atriplex halimus contains glycosides, terpenoids, flavonoids, and alkaloids involved in reducing and stabilizing palladium nanoparticles (Eltaweil et al., 2022). The synthesis of silver nanoparticles has been the favorite of several research groups. Several plant extracts have been used among them: Buddleja globosa hope, Lantana camara L., Viscous cleome L., Sida cordifolia, Psidium quajava L., Amaranthus cruentus, Achillea millefolium L., Phyllanthus urinaria, Pouzolzia zeylanica, Scoparia dulcis, Piper colubrinum, Phoenix dactylifera L., and Camellia sinensis. These have in common the presence of carboxylic, hydroxyl, carbonyl, and phenolic groups that are responsible for the reduction of Ag⁺ ions to Ag⁰ and act as a coating on the synthesized nanoparticles (Carmona et al., 2017; Shriniwas et al., 2017; Lakhmanan et al., 2018; Naga et al., 2017; Wang et al., 2018; Baghani et al., 2020; Yousaf et al., 2020; Nguyen et al., 2020; Santhoshkumar et al., 2021; Laouini et al., 2021).

Secondary metabolites for nanoparticle synthesis

The extracts used for nanoparticle synthesis have a wide variety of secondary metabolites involved in nanoparticle reduction, formation, and stabilization. Phytochemicals in the extracts include phenols, flavonoids, alkaloids, terpenoids, proteins, carbohydrates, and amino acids.

Phenols

Phenols are chemical compounds that contain a hydroxyl group (-OH) attached to an aromatic hydrocarbon. In plants, the term polyphenol is usually used for secondary metabolites from the biochemical pathways of shikimic acid. They may have more than one phenolic ring and do not contain functional groups based on nitrogen in their structure (Cirkovic et al., 2018). Below are reaction mechanisms for the synthesis of nanoparticles involving phenols. Gallic acid has been shown to interact with Au⁺³ ions by releasing electrons and reduce them to gold atoms. It has been proposed to form an intermediate complex during reduction that oxidizes to form guinones and gold nanoparticles. Quinones are inferred to remain on the surface of the nanoparticles, preventing their aggregation for prolonged periods (Ahmad et al., 2019). The proposed mechanism is shown in Figure 3a. In the case of silver nanoparticles, gallic acid causes the reduction of Ag ions. After reduction, it is oxidized to its quinone form and the carboxylic group (-C = O) present in the oxidized form coordinates with the surface of the nanoparticles to stabilize them (Bhutto et al., 2018). The schematic representation is shown in Figure 3b. Combining these molecules with metallic copper salts gives a polyphenolic complex with the Cu²⁺ ion, whose reduction generates nanoparticles of Cu⁰. The



Table 1. Characteristics of nanoparticles synthesized with natural extracts from different plants species. Tabla 1. Características de las nanopartículas sintetizadas con extractos naturales de diferentes especies de plantas.

Plant Species	Origin of the Extract	Nanoparticle	Nanoparticle Size (nm)	Functional Group In- volved on Synthesis	Effect	Reference
Azadirachta indica, Hibiscus rosa-sinensis, Murraya koenigii, Moringa oleifera and Tamarindus indica	Leaves	CuO	Average size of 12	Phenolic compounds and flavanoids	Anticancer	(Rehana <i>et al.,</i> 2017)
Aloe vera and Hibiscus sabdariffa	Leaves	ZnO	9 to 18	Phenolic compounds and flavonoids	Antibacterial, antioxidant, and anticancer	(Mahendiran <i>et al.,</i> 2017)
<i>Buddleja globosa</i> hope	Leaves	Ag	1 to 53	Phenols and carboxylic groups	-	(Carmona <i>et al</i> ., 2017)
Lantana camara L.	Leaves	Ag	410 to 450	Carboxylic, hydroxyl, car- bonyl, and phenyl groups	Antioxidant, antibac- terial, and cytotoxic on Brine shrimp	(Shriniwas <i>et al.,</i> 2017a)
Origanum vulgare L.	Leaves	Pd	2 to 20	Phenolic compounds and glycoside	Catalytic activity	(Rafi <i>et al.</i> , 2017)
Atalantia monophylla	Leaves	ZnO	30	Tannin, organic acids, terpenoids, aromatic dicar- boxylic acid, and amides	Antibacterial	(Vijayakumar <i>et al.,</i> 2018)
Moringa oleifera	Seeds	Fe	2.6 to 7.4	Amino acids, alkaloids, flavonoids, and phenolic compounds	Antibacterial and coagulant	(Katata <i>et al.,</i> 2018)
Cleome viscosa L.	Fruit	Ag	5 to 30	Alkaloids, phenolic compounds, amino acids, carbohydrates, and tannins	Antibacterial and anticancer	(Lakshmanan <i>et al.,</i> 2018)
Sida cordifolia	Whole plant	Ag	3 to 8	Alkaloids, carbohydrates, proteins, glycosides, flavo- noids, and tannins	Antibacterial	(Naga <i>et al.</i> , 2018)
Psidium guajava L.	Leaves	Ag	Average size of 25	Flavonoids and polypheno- lic groups	Antibacterial	(Wang <i>et al</i> ., 2018)
Annona muricata	Leaves	Au	27 to 32	Flavonoids, terpenoids, and proteins	Antibacterial and antifungal	(Folorunso <i>et al.</i> , 2019)
Punica granatum	Peel	ZnO	32.98 to 81.84	Pinucalagin, ellagic acid, caffeic acid, chlorogenic acid, and gallic acid	Antibacterial and anticancer	(Mohamad <i>et al.</i> , 2019)
Coleus aromaticus	Leaves	Au	Average size of 80	Phenolic hydroxyl, aromatic amines, and polyphenol groups	Antibacterial and anticancer	(Boomi <i>et al.,</i> 2019)
Ocimum americanum	Whole plant	ZnO	Average size of 21	Phenol, hydroxyl, and carboxyl groups	Antibacterial and anticancer	(Narendra <i>et al</i> ., 2019)
Amaranthus cruentus	Flowering shoot parts	Ag	Average size of 15	Aromatic compound, pro- teins, hydroxyl groups, and carboxylic acids	Antibacterial and anticancer	(Baghani <i>et al</i> ., 2020)
Tasmannia lanceolata and Backhousia citriodora	Leaves	Au	Average size of 7.10	Terpenoids, flavonoids, and phenolic compounds	Anticancer	(Khandanlou <i>et al.,</i> 2020)
Achillea millefolium L.	Whole plant	Ag	14.27 to 20.77	Proteins, flavonoids, and phenols such as tannic acid	Antibacterial and antioxidant	(Yousaf <i>et al.</i> , 2020)
Beta vulgaris, Cinnamomum tamala, Cinnamomum verum, and Brassica oleracea var. italica	Whole plant	ZnO	20 to 47	Hydroxil groups, proteins, aldehydes, alkanes, alkenes, ketones, and alcohol	Antibacterial and antifungal	(Mohanan <i>et al.,</i> 2020)
Phyllanthus urinaria, Pouzolzia zeylanica, and Scoparia dulcis	Leaves	Ag	4 to 52	Tannins, flavonoids, phenolics, and terpenoids compounds	Antifungal	(Nguyen <i>et al.,</i> 2020)
Acalypha fruticosa L.	Leaves	ZnO	Average size of 50	Flavonoids	Antibacterial	(Vijayakumar <i>et al.,</i> 2019)
Piper colubrinum	Leaves	Ag	10 to 50	Compunds with with OH and CO groups	Antibacterial	(Santhoshkumar et al., 2021)
Tecoma stans L.	flower, bark, and leaves	MgO	20 to 50	Hydroxyl/amino groups, alkene or alkyne, flavonoids or carboxylic compounds, saturated primary alcohol, carbohydrates, amines, and phosphates	Treatment of hazard- ous dyes from the wastewater	(Nguyen <i>et al.,</i> 2021)



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Plant Species	Origin of the Extract	Nanoparticle	Nanoparticle Size (nm)	Functional Group In- volved on Synthesis	Effect	Reference
Alchornea laxiflora	Leaves	ZnO	Average size of 200	Polyphenols, flavonoids, tanins, alkaloids, and saponins	Photocatalyst	(Ekennia <i>et al.</i> , 2021)
Citrus limon	Fruit	Cu	5 to 28	Alcohols, phenols, car- boxylic acids, and amino groups	Antibacterial	(Amer <i>et al</i> ., 2021)
Phoenix dactylifera L.	Leaves	Ag/Ag ₂ O	37.71 to 28.66	Carboxyl, carbonyls, ami- des, and phenols	Photocatalytic activity for azo dye degradation	(Laouini <i>et al.,</i> 2021)
Syzygium Cumini	Leaves	ZnO	64 to 78	Hydroxyl and amide groups	Fertilizer in agricul- ture and catalyst for dye removal from polluted water	(Rafique <i>et al.,</i> 2022)
Tecoma capensis	Leaves	Au	20 to 25	Alkaloids, flavonoids, glyco- sides, terpenoids, tannins, and phenolic compounds	Photocatalytic, anticancer and antioxidant	(Hosny <i>et al</i> ., 2022)
Spinacea oleracea	Leaves	CuO	13 to 17	Phenols and flavonoids	Antioxidant and anticancer	(Al-Jawhari <i>et al.</i> , 2022)
Atriplex halimus	Leaves	Pt	1 to 3	Glycosides, terpenoids, flavonoids, and alkaloids	Antibacterial, antio- xidant, and catalytic	(Eltaweil <i>et al.</i> , 2022)
Camellia sinensis	Leaves	Ag	15 to 33	Polyphenols, proteins, flavonoids, saponins, and glycosides	Antibacterial	(Widatalla <i>et al.</i> 2022)

ions can subsequently be oxidized with oxygen to form stable CuO nanoparticles (Veisi *et al.*, 2021). The mechanism of biogenesis is shown in Figure 3c. The general mechanism for the synthesis of nanoparticles using phenols is described by Malapermal *et al.* (2017), who speculate that the conversion of biomolecules with C-OH groups to C=O groups is responsible for the reduction of ions, in the case of their study Ag ⁺ to Ag⁰, leaving as a result a keto compound. The proposed mechanism is illustrated in Figure 3d.

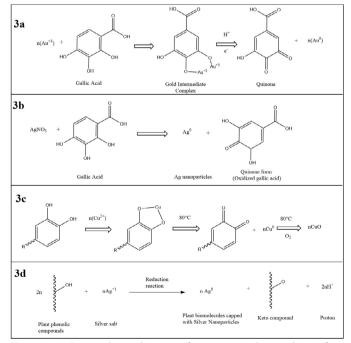


Figure 3. Proposed mechanisms for nanoparticle synthesis from phenols compounds. Adapted from references [Cirkovic *et al.*, 2018; Ahmad *et al.*, 2019; Bhutto *et al.*, 2018; Veisi *et al.*, 2021; Malapermal *et al.*, 2017]. **Figura 3.** Mecanismos propuestos para la síntesis de nanopartículas a partir de compuestos fenólicos. Adaptado de referencias [Cirkovic *et al.*, 2018; Ahmad *et al.*, 2019; Bhutto *et al.*, 2018; Veisi *et al.*, 2021; Malapermal *et al.*, 2018; Ahmad *et al.*, 2019; Bhutto *et al.*, 2018; Veisi *et al.*, 2021; Malapermal *et al.*, 2017].

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Flavonoids

They are hydroxylated phenolic substances synthesized by plants in response to microbial infections. The chemical structure is a propane diphenyl skeleton with fifteen carbon atoms in its primary nucleus: two six-membered rings linked with a three-carbon unit, which may or may not be a part of a third ring. In addition, two benzene rings (rings A and B) are linked through a third heterocyclic oxygen-containing pyrene ring (Karak, 2019). Flavonoids have hydroxyl and carbonyl groups that can bind metal ions through a chelating effect. This chelating ability is associated with a nucleophilic character of the aromatic ring. The antioxidant property of flavonoids is related to their ability to donate electrons and hydrogen atoms. Trivalent gold ions can form complexes in aqueous solutions with flavonoids when they oxidize to ketone groups and form the nucleus of nanoparticles (Irfan et al., 2017). The proposed mechanism is shown in Figure 4a.

The flavonoid orientin contains an aromatic hydroxyl group capable of adhering to nickel ions by forming complexes with each other. Subsequently, an annealing process is applied to break down the complex and form NiO nanoparticles (Mayedwa et al., 2018). The proposed mechanism of orientin with nickel ions is shown in Figure 4b. Quercetin contains hydroxyl groups with high reductive activity. It has been used to reduce Aq⁺ ions by forming complex intermediates, followed by oxidation by hydrogen abstraction forming a hydrate (Kobylinska et al., 2020). The schematic is shown in Figure 4c. A general proposal for the formation of nanoparticles with flavonoids, taking silver as an example, is given by Sherin et al. (2020). They indicated that hydroxyl groups are strong ligands that can reduce ions from Ag⁺ to Aq⁰. They suggested that if sodium hydroxide is added to the reaction medium, the reducing power of these phytomolecules is improved, and the formation can be accelerated at room temperature. The possible proposed mechanism is illustrated in Figure 4d.

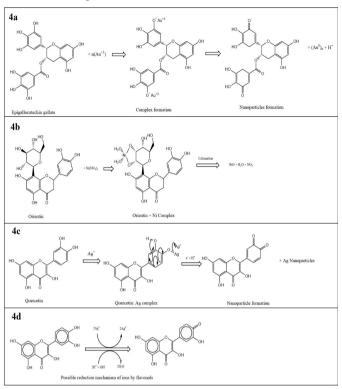


Figure 4. Proposed mechanisms for nanoparticle synthesis from flavonoids compounds. Adapted from references [Irfan et al., 2017; Mayedwa et al., 2018; Kobylinska et al., 2020; Sherin et al., 2020].

Figura 4. Mecanismos propuestos para la síntesis de nanopartículas a partir de compuestos flavonoides. Adaptado de referencias [Irfan et al., 2017; Mayedwa et al., 2018; Kobylinska et al., 2020; Sherin et al., 2020].

Alkaloids

These are molecules present in plants with a nitrogen at any position of the molecule but must not belong to an amide or a peptide bond (Rios *et al.*, 1989). They have demonstrated participation in the formation of platinum and palladium nanoparticles; alkaloids of *Peganum harmala* seeds showed rearrangement and deprotonation in their O-H and C-O groups, indicating the participation in the bioreduction of nanoparticles (Fahmy *et al.*, 2021). In another study, this same plant was used to reduce silver nanoparticles. In this case, five

main alkaloids, Harmine, Harmaline, Harmalol, Vasicine, and Vasicinone were identified, indicating the participation of the same groups in the reduction of nanoparticles (Almadiy *et al.*, 2018). *Conocarpus lancifolius* presents two alkaloids, Scopolamin and Hyoscine, that can act as metal chelators and participate in silver nanoparticle formation (Raheema *et al.*, 2020). *Terminalia catappa* has alkaloids involved in Nd_2O_3 nanoparticles formation, acting as essential sources for obtaining $Nd(OH)_3$ complexes in hydrolysis processes necessary for the formation of nanoparticles (Lembang *et al.*, 2018). Although it is known that alkaloids participate in the formation of nanoparticles, there are still few publications on the subject, and there is a lack of deepening in the reaction mechanism of the formation process. Hence, further research in this area is necessary.

Terpenoids

They are metabolites of plants with different atomic carbon units, where $C = 5, 10, 15, 20, \dots, n > 40$, and are thus classified as hemiterpenes (C5), monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20), triterpenes (C30), tetraterpenes or carotenoids (C40), and polyterpenes (Cn, n > 40) (Proshkina et al., 2020). Extracts of only terpenes from Lantana chamber plant have been used to synthesize silver nanoparticles; these participate in reducing Ag⁺ ions to Ag⁰ ions (Shriniwas et al., 2017b). Withania coagulans has poly-oxygenated biomolecules called withanolides (C28 - steroidal lactone triterpenoids), which are involved in synthesizing silver nanoparticles (Tripathi et al., 2019). The Terpenoids present in Annona squamosa help in the synthesis of gold nanoparticles; their hydroxyl and carbonyl groups are complexed with Au³ ions and reduced to Au^o by the oxidation of carbonyl and carboxyl groups (Gangapuram et al., 2018). Pentacyclic terpenoids (lupeol and β-sitosterol) of Euclea natalensis participate in forming zirconium oxide nanoparticles, and the –OH groups are responsible for the reduction. The tautomeric transformation of enol compounds to keto is thought to release hydrogen atoms, accountable for removing the zirconium molecule (Da Silva et al., 2019). The proposed mechanism is shown in Figure 5a. In this aspect, research has begun to offer reaction mechanisms, but it is still necessary to understand the process in detail.

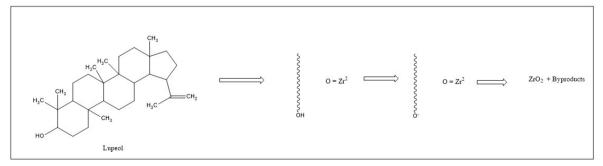


Figure 5. Proposed mechanism for nanoparticle synthesis from terpenoid compounds. Adapted from Gangapuram *et al.* (2018). **Figura 5.** Mecanismo propuesto para la síntesis de nanopartículas a partir de compuestos terpenoides. Adaptado de Gangapuram *et al.* (2018).



Amino acids and proteins

Proteins are biomolecules constructed from the covalent polymerization of amino acids (Mora et al., 2020). Camellia sinensis extracts have been used for the synthesis of zinc oxide nanoparticles. These contain amino acids that are not directly involved in the formation of nanoparticles but stabilize the nanoparticles in suspension (Dhanemozhi et al., 2017). Ajwa and Barni were used for the synthesis of platinum nanoparticles. As a result, it was found that amino acids and proteins participate in coating the nanoparticles (Al-Radadi, 2019). Carissa carandas proteins coat and stabilize nanoparticles, as demonstrated by being employed to synthesize silver nanoparticles. Hydroxyl, carbonyl, and other functional groups in amino acids and peptides (C=O, -OCH, C-O) can bind metals, forming a coating around the metal nanoparticle. Also, the presence of the -OH group in benzenes contained in the extract participate in the formation of nanoparticles since they can release a proton, change to its anionic form, stabilize itself by its resonance structure, provide electrons that function as reducing agents, and oxidize the metallic salt (Joshi et al., 2018). Moringa oleifera extract proteins also function as coating agents of nanoparticles, in this case confirmed by Transmission Electron Microscopy (TEM) (Mateus et al., 2018). The participation of these biomolecules is not directly related to the process of nanoparticle formation but to their stabilization.

Carbohydrates

These molecules composed of carbon and hydrogen atoms, have different monomeric units and degrees of polymerization; glycosidic bonds join them and in nature, they are found together with proteins, lipids, amino acids, etc. The binding of various carbohydrates is called a polysaccharide (Mena-García *et al.*, 2019). Carbohydrates present in *Astragalus membranaceus* possess weak reducing activity, and have been used for the synthesis of silver nanoparticles due to the electron-accepting nature of Ag⁺ ions and the electron-donating nature of hydroxyl groups in polysaccharides (Ma *et al.*, 2017). *Acacia* gum and pectin have been used for the synthesis of palladium nanoparticles. They have reduced

sugars in their structure, which coordinates metal ions in their carbonyl groups, allowing the synthesis of metal nanoparticles (Emam *et al.*, 2020). A representative schematic is shown in Figure 6. *Castanea mollissima* has glucans with a large number of OH groups that have been used to synthesize selenium nanoparticles (Li *et al.*, 2019). Galactomannans in *Prosopis spp* can function as nanoreactors to synthesize zinc oxide nanoparticles by coordinating the OH groups present in these polysaccharides (Bouttier-Figueroa *et al.*, 2019b).

Nanoparticles applications

Recently, nanotechnology has emerged as a science with a wide range of applications. Nanoparticles formed using nanotechnology have qualities that have allowed them to be used in different fields, such as food, agriculture, medicine, catalysis, and water treatment.

Food

Silver nanoparticles synthesized from *Madhuca latifolia* L. extracts can inhibit bacterial growth and be used in food packaging. Nanoparticles act as molecules that can penetrate the bacterial cell wall and affect their metabolic pathways. They can destabilize ribosomal function and DNA, causing cell death (Biswal and Misra, 2020).

Agriculture

Aqueous extract of *Ulva lactuca* allows the synthesizing of silver nanoparticles capable of inhibiting the proliferation of bacteria and fungi of agricultural importance by functioning as pesticides. Nanoparticles come into contact with bacteria entering their cell wall and interrupt cell permeability by interacting with enzymatic cofactors, sulfur, and phosphorous groups of DNA. In the case of fungi, the nanoparticles form pits on the cell surface, which causes changes in morphology and prevents proliferation (Amin, 2020). The extract of *Cornus mas* fruits has been used to synthesize Fe_2O_3 nanoparticles to improve the growth of barley seedlings serving as fertilizers. Nanoparticles work as an iron source; when absorbed by plants they change the concentrations of reactive oxygen species, causing a stimulus in the plant's growth (Rostamizadeh *et al.*, 2020).

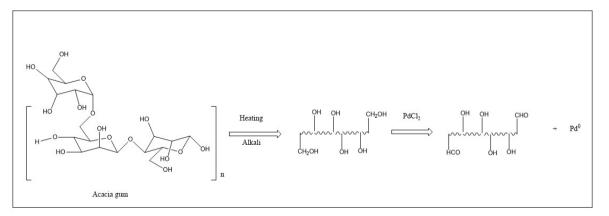


Figure 6. Proposed mechanism for nanoparticle synthesis from a polysaccharide compound. Adapted from Emam et al. (2020). **Figura 6.** Mecanismo propuesto para la síntesis de nanopartículas a partir de polisacáridos. Adaptado de Emam et al. (2020).

Water treatment

Ficus benjamina leaves have been used to obtain extracts to form silver nanoparticles that can remove Cd(II) from contaminated water, functioning as ionic or elemental removers. Their results indicated that nanoparticles behave according to a Freundlich model, where Cd(II) adsorption occurs due to multiple layers of heterogeneity of the adsorbent surface (Al-Qahtani, 2017). *Fumariae herba* has been used to synthesize platinum nanoparticles, which can perform catalysis activities to remove organic dyes. This ability is attributed to their relatively large surface-to-volume ratios. Platinum nanoparticles showed enhanced catalytic activity for the degradation of organic dyes (Dobrucka, 2019).

Medicine

The leaves of Coptis chinensis allow the synthesis of silver nanoparticles with anticancer activity against lung cancer cells. Nanoparticles interact with cells, affecting the metabolic pathways of mitochondria causing apoptosis and destruction of the mitochondrial membrane. Nanoparticles alter the production of Bcl2 family proteins, altering cell susceptibility to promote the production of caspase 3 and Bax proteins that cause apoptosis (Pei et al., 2019). Andrographis paniculata, Phyllanthus niruri, and Tinospora cordifolia have in their extracts agents capable of synthesizing silver nanoparticles with antiviral activity against the chikungunya virus. Nanoparticles interfere with the virus binding to the host cell, preventing it from entering, but the exact mechanism of action still needs to be studied (Sharma et al., 2019). Zinc oxide synthesized with Urtica dioica extract has been employed in rats to lower insulin levels, functioning as an antidiabetic agent. Zinc present in nanoparticles acts by mimicking the activity of insulin, the fundament being that the pancreas of a healthy person contains a greater amount of zinc than a person with diabetes (Bayrami et al., 2020).

Paeonia emodi has been used to synthesize gold nanoparticles essential for cardiovascular diseases treatment. Nanoparticles are loaded with drugs since they can enter tissues and release them directly at the site of action. They decreased the levels of alanine aminotransferase, aspartate aminotransferase, lactate dehydrogenase, and creatine phosphokinase, which cause heart damage (Ibrar et al., 2018). Zinc oxide nanoparticles have been synthesized with Aloe socotrin leaf extracts, allowing the distribution of antimicrobial agents. The nanoparticles eliminated microorganisms that cause urinary infections by destroying their membrane due to the formation of reactive oxygen species (Fahimmunisha et al., 2020). Extracts of Rose indica L petals can synthesize zinc oxide nanoparticles, which can be used in nail paint with antifungal activity. Understanding of ZnO mechanism of action in fungi needs to be better developed. It is known that H₂O₂ is formed, and the creation of bonds between cellulose molecules in their hydroxyl groups and oxygen atoms leads to the inhibition of fungal growth (Tiwari et al., 2017).

Electronic

Titanium oxide, synthesized from lemon peels, has optical and photocatalytic properties that allow its potential use in electronic devices. It is capable of degrading rhodamine B due to its high photocatalytic activity created by the rapid detachment capacity between the photogenerated electrons and holes (Nabi *et al.*, 2022).

Nanoparticles Packaging

Recent research avoids mentioning the materials used to store the synthesized nanoparticles. It is essential to consider an appropriate type of material to store the nanoparticles, preserve their properties, and allow transport in safe conditions. The U.S. Food and Drug Administration (FDA) has a section that regulates materials used to store food, drugs, and cosmetics. It can be extrapolated to nanoparticle storage. Permitted materials include (Marsh *et al.*, 2007):

Glass: It does not have aroma, is chemically inert, impermeable to gases, allows good insulation from the outside, can be produced in different ways, and being transparent, allows observation of the stored product.

Metal: Focuses on aluminum and steel. These provide excellent barriers to moisture, air, odors, light, and microorganisms; they are ductile, easily recyclable, and highly accepted by the consumers.

Plastics: They are chemically resistant and cheap to manufacture. In industrial applications, they can be heat-sealed, printed, and stored on-site. The main disadvantage is that they are permeable to light and gases.

Paper and cardboard: This material mainly stores and transports product-filled containers.

Nanoparticles characterization

After synthesizing nanoparticles, it is important to know their morphological and physicochemical properties since, depending on their size, shape, surface morphology, structure, and homogeneity, their properties can vary. The most used characterization techniques are: Uv-vis, XRD, FTIR, DLS, EDAX, SEM and TEM (Gour *et al.*, 2019).

- UV-visible: It is used to know the wavelength at which nanoparticles absorb, which is related to their Surface plasmon reverberation, providing information about their size.
- XRD: It is used to know the crystalline structure of nanoparticles.
- FT-IR: It is used to study the functional groups present on nanoparticles surface, which are responsible for the reduction and stabilization.
- DLS: Provides information about the surface charge of nanoparticles.
- EDAX: Estimates the abundance of elements present over nanoparticles surface.
- SEM and TEM: They provide information about nanoparticle morphology, size, and homogeneity.

Other techniques less used, include condensation particle counter, photon correlation spectroscopy, and field



emission scattering electron microscopy. Authors such as Mourdikoudis *et al.* (2018) have already described more details about the characterization techniques.

CONCLUSIONS

This review presented information on nanoparticle synthesis using different plant extracts with a particular interest in the reaction mechanisms involved in the formation. The synthesis using natural plant extracts has allowed the elaboration of materials greenly (friendly to the environment, cost reduction, easy obtaining of raw material, and use of nontoxic solvents). The biomolecules present in the extracts are directly related to the reduction of metal ions, participation in the capture of ions, formation of complexes, and finally, the protection of the synthesized material. The development of nanotechnology has allowed applications in different areas such as electronics, medicine, chemistry, physics, engineering, environment, etc. These materials are synthesized invitro and participate in many secondary metabolites in their formation, including alkaloids, carbohydrates, phenols, and Terpenoids. Recent research focuses on specific metabolites for their role in nanoparticle formation. Further studies on the role of selected metabolites in the formation of nanoparticles are needed. The current overview of nanoparticle storage needs to be described in the literature, and there is a research opportunity to study the effects on packaging. This review addresses the characterization techniques, emphasizing the role of each of them in order to introduce their fundamentals. In this way, it will be possible to understand their physical and chemical properties better and subsequently standardize production processes at the industrial level.

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CONFLICTS OF INTEREST

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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