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TOPICAL REVIEW

Eucalyptus extracts-mediated synthesis of metallic and metal oxide nanoparticles: current status and perspectives

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Abstract

In recent decades, nanotechnology has received great attention due to its broad fields of application. The conventional processes applied to the synthesis processes of nanomaterials can be classified in chemical and physical methods. These technologies involve several environmental and cost problems. In order to avoid the problems caused by conventional methods, the use of biological systems such as bacteria, fungi, yeasts, and algae in the synthesis of nanomaterials has recently received extensive attention. To the same purpose, the routes of synthesis of metallic and metal oxides nanoparticles using plant extracts show promising perspectives. The methods involving plant extracts, unlike other biological methods, stand out for their ease and low implementation costs. In addition, the use of plant extracts avoids the risks associated with the use of highly toxic compounds, which are harmful to human health and the environment. This review summarizes the relevance of using plant extracts in the synthesis of metal and metal oxides nanoparticles compared to other synthesis methods and emphasizes the use of extracts of different species of *Eucalyptus*. The main topics covered by this review include (i) the effect of the synthesis parameters on the features of the nanomaterials; (ii) the effect of the composition of the extracts on the synthesis; (iii) the main mechanisms proposed to explain the formation of the nanoparticles; and (iv) future challenges related to the green synthesis of nanoparticles.

Introduction

Nanotechnology constitutes an important pillar in current scientific development, due to its multiple applications in various fields. The performance of the nanomaterials in the different applications is very much affected by their geometry, shape, and morphology [1]. The conventional methods applied to the synthesis of nanomaterials involve the use of hazardous chemical compounds and/or physical procedures with high energy requirements. In order to avoid these drawbacks, the principles of green chemistry have been applied to the synthesis of nanomaterials. Unlike the current methods of synthesis, the 'green synthesis of nanoparticles' involves processes, which are clean, safe and friendly to the environment [1]. One of the green routes of synthesis of nanoparticles (NP) involves the use of vegetal extracts. The publication by Gardea-Torresdey *et al* [2] is one of the first research papers dealing with the preparation of gold nanoparticles employing vegetal biomass from alfalfa.

To date, the use of vegetal extracts in the synthesis of nanoparticles has increased substantially. For example, several papers report on the synthesis of NP mediated by the following extracts: Azadirachta indica (Ag-NP) [3], *Ocimum sanctum* (Au-NP) [4], *Filicium decipiens* (Pd-NP) [5], *Euphorbia esula* (Cu-NP) [6], *Opuntia ficus-indica* (Li-NP), *Cacumen platycladi* (Pt-NP) [7], *Solanum nigrum* (ZnO-NP) [8], *Morinda citrifolia* (TiO_2-NP) [9], *Centella asiatica* (Ce-NP) [10], *Callistemon viminalis* (Sm_2O_3-NP) [11], *Euphorbia tirucalli* (Dy_2O_3-NP) [12], *Hibiscus Sabdariffa* (CdO-NP) [13], *Agathosma betulina* (NiO-NP) [14], *Aloe vera* (In_2O_3-NP) [15], *Camellia sinensis* (α-Fe_2O_3-NP) [16] y *Eucalyptus globulus* (MgO-NP) [17], among many others.

Extracts of different species of *Eucalyptus* are among the mostly studied extracts in the synthesis of nanoparticles, possibly due to the high presence of *Eucalyptus* worldwide. According to the 2013 FAO report, there are more than 20 million hectares of plantations of various species of *Eucalyptus* worldwide, being more than 110 species present in more than 90 countries [18]. For instance in Chile, according to the Forest Report (INFOR) published in 2018 [19], until the end of 2016, there were 2.414 million hectares for forest plantations, of which 35.6% were destined for the plantation of *Eucalyptus* (24.5% of *Eucalyptus globulus*, 11.1% of *Eucalyptus nitens*). Thus, the aim of the present review is to analyze in depth the green synthesis of nanomaterials using plant extracts, highlighting the use of extracts from different species of *Eucalyptus*.

Methods for the synthesis of nanoparticles

The choice of the synthesis methods depends on the application that will be given to the nanomaterial. In general, it is possible to classify the synthesis methods in physical and chemical methods. The physical methods include high energy ball milling, inert gas condensation, physical vapor deposition (sputtering, electron beam evaporation, pulsed laser deposition and vacuum arc), laser pyrolysis, flame spray pyrolysis, electrospraying, etc; whereas the chemical methods comprise sol-gel methods, microemulsion, hydrothermal synthesis, polyol synthesis, chemical vapor deposition, chemical vapor synthesis, and plasma enhanced chemical vapor deposition, among others [20].

The physical and chemical methods of synthesis are mainly used for their high capacity in achieving the desired features and properties of the nanoparticles to be synthesized. These methods have some drawbacks, e.g., physical methods have high costs; whereas chemical methods involve and produce highly toxic, dangerous and polluting compounds. Thus, the application of these synthesis methods on an industrial scale is difficult, due to high costs, energy consumption, and the generation of toxic compounds that are difficult to treat. In this context, obtaining nanoparticles by means of aqueous systems instead of employing organic solvents has become a great alternative. Although these aqueous methods are more environmentally friendly, it is necessary to add some agents to the system that prevent agglomeration and aggregation of the nanoparticles. Therefore, the implementation of these methods on a large scale comprises the prediction of the potential risks and problems involved in the synthesis. Moreover, if it is required to synthesize nanomaterials for use in the biomedical field, it is essential to eliminate the use of toxic chemical compounds. These topics have led to an increase in research in order to establish sustainable and eco-friendly alternatives for the synthesis of nanoparticles.

Need for green synthesis methods

Although the chemical methods of synthesis allow the control of the size, morphology, and composition of the nanoparticles, most of the agents used are highly toxic, do not degrade easily and damage the environment. Table 1 lists the most commonly used capping and reducing agents for the synthesis of nanoparticles [21, 22]. Due to the hydrophobic character of these agents, it is necessary to use high amounts of organic solvents. Many of these solvents are carcinogenic, dangerous to health, corrosive and harmful to the environment.

The adverse effect that the chemicals listed in Table 1 can produce when used at the laboratory level are of little relevance, contrary to the effects caused when used for the production of nanoparticles on a larger scale. It is possible to minimize these risks by implementing processes that are less dangerous for the environment. This challenge has led to the development and study of green methods for the synthesis of nanoparticles, which are based on the use of plant extracts as capping and reducing agents [1].

The development of sustainable methods for the synthesis of nanoparticles has been the objective of many publications. In this line, it was possible to develop low-cost and eco-friendly methods using different types of biological systems. These methods are called 'biological methods of synthesis', which involve bacteria, fungi, yeasts, microalgae, macroalgae and plant extracts [1, 21–26].

Bacteria

Bacteria have attracted attention for their ability to accumulate inorganic material both intracellularly and extracellularly. As a defense mechanism, to counteract the stress produced by the presence of toxic metal ions, some bacterial strains transform toxic metal ions to nanoparticles [27]. This property of bacteria has been used to obtain nanomaterials in a relatively simple way. Some of the bacteria used in the synthesis of different types of nanoparticles are: *Rhodopseudomonas palustris* (CdS-NP) [28], *Shewanella algae* (Au-NP) [29], *Rhodobacter sphaeroides* (PbS-NP) [30], *Escherichia coli* (Ag-NP) [31], *Bacillus cereus* (Ag-NP) [32], *Pseudomonas aeruginosa*

Table 1. Capping and reducing agents, solvents employed in the synthesis of nanoparticles and their types of risk.

Type of risk	Capping agents	Reducing agents	Solvents
Flammable	Polyamidoamine	H_2, CO, $NaBH_4$	Ethanol, toluene, dimethylformamide
Corrosive	Hexadecyltrimethylammonium bromide, dodecylamine, trioctylphosphine oxide, trioctylphosphine, oleylamine	HCHO, H_2O_2, $NH_2OH{\cdot}HCl$, $NaBH_4$, oleylamine, N_2H_4	Oleylamine
Acute toxicity	Hexadecyltrimethylammonium bromide, polyethylene glycol, oleic acid, polyamidoamine, ethylenediaminetetraacetic acid, dodecylamine, linoleic acid, oleylamine	HCHO, CO, citric acid, Na_2CO_3, $NH_2OHiHCl$, ethylene glycol, ascorbic acid, $NaBH_4$, oleylamine, N_2H_4	Ethanol, toluene, oleylamine, dimethylformamide
Health hazard	Hexadecyltrimethylammonium bromide, polyamidoamine, dodecylamine, poly(acrylic acid), oleylamine	$NH_2OH{\cdot}HCl$, ethylene glycol, $NaBH_4$, oleylamine, N_2H_4	Toluene, 1-octadecene, oleylamine, dimethylformamide
May cause damage to the aquatic environment	Hexadecyltrimethylammonium bromide, dodecylamine, oleylamine	$NH_2OH{\cdot}HCl$, oleylamine, N_2H_4	Oleylamine

(Au-NP) [33], *Lactobacillus sp.* (Ti-NP) [34], *Magnetospirillum magnetotacticum* (Fe_3O_4-NP) [35], *Shewanella oneidensis* (UO_2-NP) [36], and *Bacillus sp.* (MnO_2-NP) [37].

Fungi

Fungi, like bacteria, are also capable of accumulating inorganic material intracellularly and extracellularly [38]. The extracellular synthesis of nanoparticles by fungi may produce larger nanoparticles than the intracellular route. The enormous secretory components of fungi are involved in the reduction and capping of nanoparticles [39]. Among the fungi used for the synthesis of nanoparticles it is possible to find: *Fusarium oxysporum* (Ag-NP) [38], *Coriolus versicolor* (Ag-NP) [40], *Penicillium fellutanum* (Ag-NP) [41], *Colletotrichum sp.* (Au-NP) [42], *Neurospora crassa* (Ag/Au-NP) [43], *Fusarium oxysporum* (TiO_2) [44], *Saccharomyces cerevisiae* MTCC 2918 (ZnS-NP) [45], and *Aspergillus terreus* (ZnO-NP) [46], among others.

Yeasts

The use of yeasts for the production of nanoparticles has also been addressed. Yeast possesses several advantages over bacteria for the bulk production of nanoparticles as the yeast grow more rapidly, produce higher amounts of enzymes and are easy to handle in laboratory conditions [47]. Some of the yeasts that have been studied in the synthesis of nanoparticles are: *Candida glabrata* (CdS-NP) [48], *Torulopsis sp.* (PbS-NP) [49], MKY3 (Ag-NP) [50], *Yarrowia lipolytica* NCIM 3589 (Au-NP) [51], *Yarrowia lipolytica* NCYC 789 (Ag-NP) [52], *Saccharomyces cerevisiae* (TiO_2-NP) [53], *Rhodosporidium diobovatum* (PbS-NP) [54], *Candida utilis* NCIM 3469 (Ag-NP) [55], *Saccharomyces cerevisiae* (Sb_2O_3-NP) [56], and *Schizosaccharomyces pombe* (CdS-NP) [57], among others.

Micro and macroalgae

Algae are non-vascular plants, which lack true roots, stems, and leaves. Several species were used for the production of nanoparticles, such as: *Chaetomorpha linum* (Ag-NP) [58], *Spirulina platensis* (Ag/Au-NP) [59], *Klebsormidium flaccidum* (Au-NP) [60], *Chlorella vulgaris* (Au-NP) [60], *Sargassum muticum* (ZnO-NP) [61], *Bifurcaria bifurcate* (CuO-NP) [62], *Sargassum bovinum* (Pd-NP) [63], *Chlorococcum sp.* MM11 (Fe-NP) [64], and *Laminaria japonica* (Ag-NP) [65], among others.

Synthesis of nanoparticles mediated by vegetal extracts

An additional focus on the green synthesis of nanomaterials is the use of plant extracts. The use of plant extracts for the production of nanomaterials shows several advantages [66]: (i) Easy availability of plant material. (ii) Safety of operation. (iii) Low operating costs. (iv) The ability of the biomolecules that can be found in the extracts to act as reducing, capping and stabilizing agents. (v) Elimination of elaborate maintenance of bacteria, fungi, and yeasts. (vi) Fast synthesis procedures. (vii) Involvement of environmentally friendly processes. (viii) Production of more stable nanoparticles. (ix) The possibility of better controlling the size and shape of the nanoparticles. (x) Suitability for large scale.

Some biomolecules present in plant extracts are capable of producing nanoparticles. Polyphenols, terpenoids, amino acids, vitamins, alkaloids, flavonoids, carbohydrates, among others (Figure 1) play a major

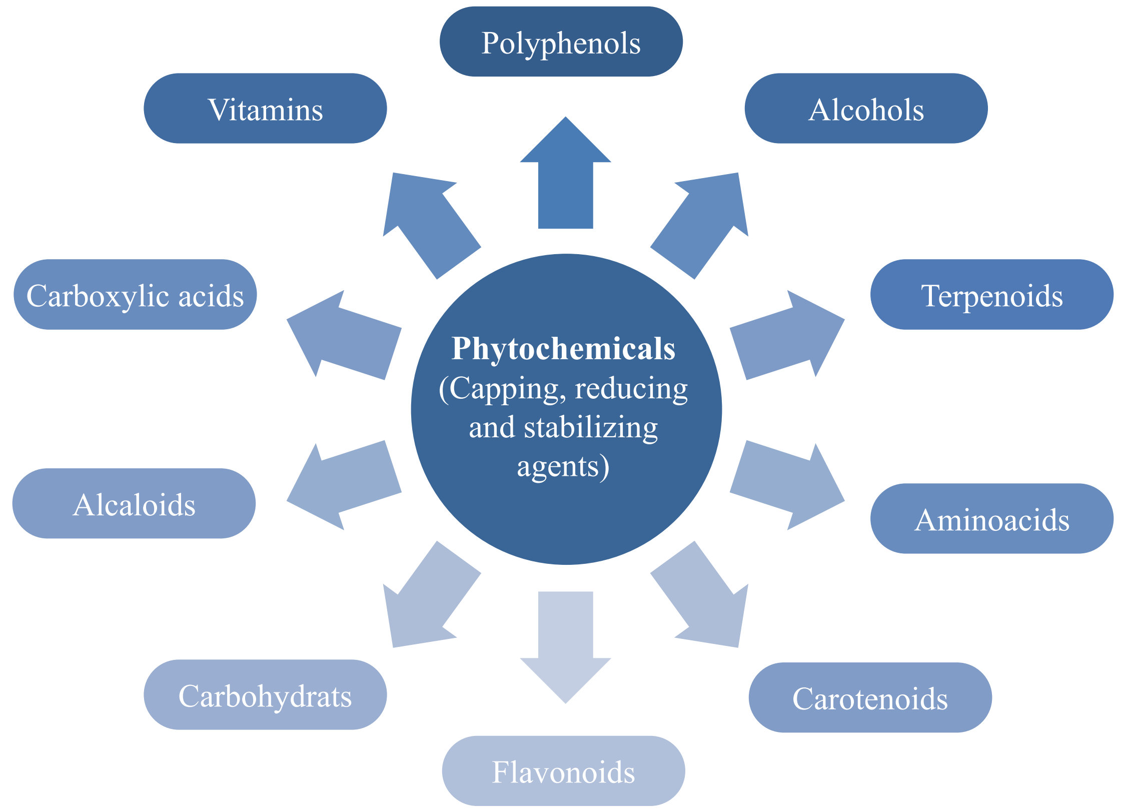

Figure 1. Main phytochemicals involved in the synthesis of nanoparticles.

role in the reduction of metal ions. A lot of work was devoted to the use of vegetal extracts from different plants in the synthesis of nanoparticles. The extracts can be obtained from different parts of the plants, such as leaves, stems, bark, seeds, pods, and fruits [67–69].

Basically, the synthesis process consists of obtaining the aqueous extracts from the plant biomass, mixing them with a solution of the metal ion at a desired temperature and pH with or without shaking [70]. Depending on the reaction conditions, the synthesis of the nanoparticles with the desired physical features can be completed quickly [71]. The basic experimental protocol for the synthesis of metal nanoparticles based on plant extracts is represented in Figure 2.

Factors affecting the synthesis of metal and metal oxides nanoparticles

The factors involved in the green synthesis of metal and metal oxide nanoparticles are not completely understood. This prevents the optimization and scaling up of the processes. For instance, the diversity of compounds present in the extracts poses a major challenge when optimizing the synthesis of nanoparticles from plant extracts. It was reported that factors such as reaction time, pH, temperature, among others, directly affect some of the physical and chemical characteristics of the nanoparticles obtained by green synthesis. Table 2 shows the main parameters that influence the green synthesis of nanoparticles and their effect.

Effect of pH

The pH of the medium in which the synthesis of nanoparticles is carried out is a key factor to be considered. The pH affects the size, shape, reduction rate and stability of metal nanoparticles. It was argued that the pH effect on these features is mainly due to an increase in the reducing activity of the functional groups in the extracts, increasing the reduction of metal ions by increasing the pH of the medium. For instance, Muthu y Priya [77], Aboelfetoh *et al* [72], Veerasamy *et al* [79] and Krishnaraj *et al* [76] studied the synthesis of Ag-NP mediated by flower extracts of *Cassia auriculata*, *Caulerpa serrulata, Garcinia mangostana,* and *Acalypha indica*, respectively. They all found a pH effect on the size, stability, and formation rate of Ag-NP. At acid pH it was proposed that the pH has a direct effect on the size and shape of the Au-NP synthesized by extracts of four different fruits (*Actini diadeliciosa*, *Malus domestica*, *Prunus persica* y *Musa acuminate*). These authors observed that at extreme basic pH the Au-NP were smaller and more spherical. Formation of an Au$(OH)_3$ precipitate would provoke a decrease

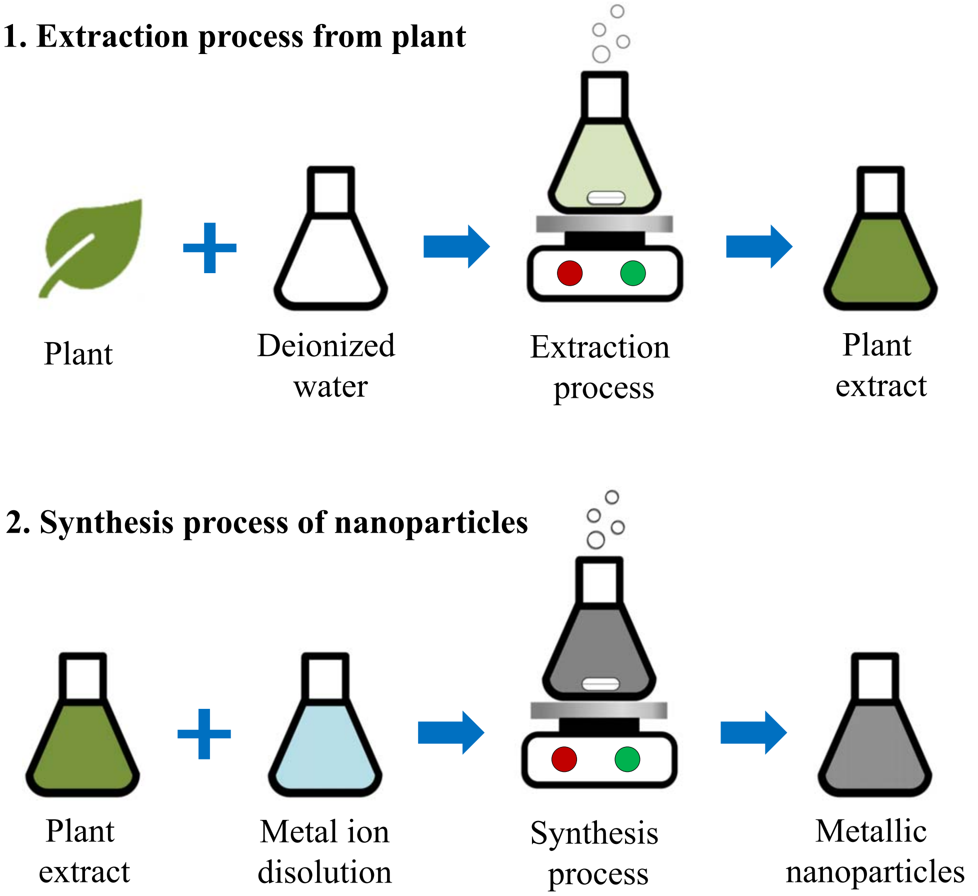

Figure 2. Experimental protocol for the green synthesis of metal nanoparticles.

Table 2. Experimental factors and their main effects on the green synthesis of nanoparticles.

Parameter	Effect	References
pH	Size, shape, reduction rate, stability	[72–80]
Temperature	Size, shape, reduction rate, stability	[75, 77, 79, 81]
Reaction time	Size, shape	[72, 75–77, 79, 81]
Plant species	Reduction rate, size, shape	[82–86]
Extract concentration	Size, shape, reduction rate, stability	[72–74, 77, 81]
Precursor concentration	Nanoparticles concentration, size, shape, stability	[17, 70, 73, 81, 87]

of the availability of Au^{3+} to react with the reducing compounds present in the extracts, affecting the generation of Au-NP. Polyakova *et al* [78] also performed a detailed analysis of the pH effect on some features of Au-NP synthesized from an extract of the *Citrus limon* juice. The authors found that the size and shape of the nanoparticles depend on the type of Au^{3+} species predominant in the reaction system. They reported that at acid pH a rapid reduction of Au^{3+} ions takes place, leading to Au-NP with various shapes and mainly aggregated. At neutral and basic pH the authors obtained Au-NP with more spherical forms, but their formation is slower compared to that observed in syntheses performed at acidic pH. Zeta potential measurements of the nanoparticles as a function of pH showed that, at acid pH, Au-NP have a greater tendency to precipitate. Zhan *et al* [80] reported that the size of Au-NP obtained from extracts of *Cacumen platycladi* decreases with increasing pH, being higher the reduction rate of Au^{3+}. Jebakumar y Sethuraman [74] studied the pH effect in the synthesis of Ag-NP mediated by extracts of *Acacia nilotica*. They reported that the medium pH has no effect on the shape of the nanoparticles, but they found that at neutral and basic pH smaller and more monodispersed nanoparticles are obtained. These authors also found that the most stable nanoparticles were obtained at neutral pH. Khalil *et al* [75] evaluated the effect of the medium pH in the range from 2 to 11 on the formation of Ag-NP mediated by extracts of olive leaves. They found that the average size of the silver nanoparticles was tunable by simply changing the extract concentrations used and pH of the reactions. The reduction of the silver precursor was promoted at elevated pH due to increased activity of olive leaf extract constituents. In contrast, Aromal *et al* [73] reported that smaller Au-NP are obtained from extracts of *Trigonella foenum-graecum* under neutral or basic conditions compared to acid medium.

The pH effect on the synthesis of metal nanoparticles using extracts of *Eucalyptus* was also studied in the literature. For example, Ali *et al* [88] analyzed the pH effect on the synthesis of Ag-NP using extracts of *Eucalyptus globulus* and microwaves. These authors found that increasing the pH of the medium favors the reduction of Ag^+ ions to yield Ag-NP. In addition, Pinto *et al* [89] studied the effect of system pH on the synthesis of Au-NP from extracts of *Eucalyptus globulus* bark. These authors reported that larger and more stable of Au-NP are obtained at neutral and basic pH than at acid pH. They attribute this behavior to the main Au^{3+} species present at neutral and basic medium: $[AuCl_2(OH)_2]^-$ and $[AuCl(OH)_3]^-$, which are less reactive than $[AuCl_3(OH)]^-$, the species present at acid pH. The authors assign the high stability at higher pH values to the increase in the content of anionic biomolecular species that not only are able to reduce Au(III) ions but also act as stabilizing/capping agents. The negative surface charge of the Au NPs surfaces results in an increase in the electrostatic repulsion between them, providing an increased stability. The morphology of the nanoparticles is also slightly affected by the medium pH.

The pH effect on the formation of metal oxide nanoparticles by extracts of *Eucalyptus* was also investigated. For example Saleem *et al* [87] studied the effect of pH on the formation of NiO-NP from extracts of *Eucalyptus globulus*. These authors suggest that the first step in the formation of NiO-NP, which takes place at higher pH, Ni^{2+} ions are reduced to Ni^0. The deprotonation of the biomolecules at higher pH could increase the ability of these molecules to reduce Ni^{2+} ions. In the second step there is an oxidation in the presence of air to yield the NiO-NP. Moreover, Ali *et al* [90] reported that increasing the pH of the medium increasing the size of CuO-NP using extracts of *Eucalyptus globulus*.

Effect of temperature

Temperature is a factor that also plays an important role in the main characteristics of nanoparticles. There are some reports on the effect of temperature on the synthesis of metal nanoparticles by plant extracts. For example, Muthu and Priya [77] investigated the effect of temperature on the synthesis of Ag-NP by flower extracts of *Cassia auriculata*. The authors report an increase of the formation rate of the nanoparticles and a decrease their size with increasing temperature. Veerasamy *et al* [79] studied the effect of temperature on the formation of Ag-NP by extracts of *Garcinia mangostana*. The authors reported that a temperature increase results in a faster formation of bigger nanoparticles. Khalil *et al* [75] reported that an increase in temperature causes a direct effect increasing the rate of formation and the total amount of Ag-NP.

There are also some literature works dealing with the temperature effect on the formation of metal oxide nanoparticles. Jeevanandam *et al* [81] studied how temperature affects the synthesis of MgO-NP by a mixture of *Amaranthus tricolor*, *Andrographis paniculata,* and *Amaranthus blitum*. The authors found that at 60 °C the highest production of MgO-NP was obtained, decreasing its yield below and above that temperature. A very plausible explanation to these observations is that at a lower temperature the energy needed to optimize MgO-NP production is not obtained, whereas at a higher temperature it is possible that the biocompounds responsible for the formation of MgO-NP decompose.

Regarding the use of extracts of *Eucalyptus*, Pinto *et al* [89] studied the effect of temperature on the synthesis of Au-NP from extracts of *Eucalyptus globulus*. Their results show that there are no significant changes in the type of crystal structure of the Au-NP when they are synthesized at 0, 25 or 80 °C. The authors also found that the temperature does not play a significant role in the zeta potential, size, and shape of the synthesized Au-NPs. Ali *et al* [88] reported that increasing the temperature on the synthesis of Ag-NP using extracts of *Eucalyptus globulus* would cause an increase in the size of Ag-NP.

Effect of reaction time

The reaction time in which the synthesis of the nanoparticles is carried out is a factor that can directly affect the size, shape, and speed of their formation. There are several reports dealing with the effect of the reaction time in the synthesis of metallic nanoparticles. Muthu and Priya [77] studied the effect of time on the synthesis of Ag-NP by flower extracts of *Cassia auriculata*. These authors reported that the longer the reaction time, the higher the yield of production of Ag-NP. Krishnaraj *et al* [76] evaluated the effect of the reaction time in the synthesis of Ag-NP using extracts of *Acalypha indica*, and also found that the longer the reaction time, the greater the yield of Ag-NP synthesized. On the other hand, Aboelfetoh *et al* [72] studied the role of reaction time on the formation of Ag-NP mediated by *Caulerpa serrulata*. They also observed larger yields at longer reaction times, without observing any significant changes in the size of the Ag-NP. Veerasamy *et al* [79] studied the effect of reaction time on the formation of Ag-NP by extracts of *Garcinia mangostana*. They reported that an optimum yield of small particles is obtained at 60 min of reaction, after that time bigger Ag-NP are obtained due to agglomeration phenomena. Khalil *et al* [75] observed that an increase in the reaction time in the formation of Ag-NP by extracts of olive leaves increases the production yield of these nanoparticles.

The role of the reaction time on the formation of metal oxide nanoparticles by plant extracts has also been analyzed. Jeevanandam *et al* [81] studied the synthesis of MgO-NP by extracts of *Amaranthus tricolor*, *Andrographis paniculata,* and *Amaranthus blitum* at 5 min, 10 min, and 15 min. The researchers found that 10 min of reaction at 60 °C, was the optimal time for obtaining larger amounts of small size MgO-NP nanoparticles.

The effect of the reaction time was also studied in the synthesis of metallic nanoparticles by extracts of *Eucalyptus*. For instance, Pinto *et al* [89] studied the role of the reaction time in the synthesis of Au-NP by extracts of *Eucalyptus globulus*. The authors observed that the absorption band in the visible associated with the formation of Au-NP increased with time, indicating an increase of the amount of AuNP formed up to at least 24 h of reaction. The reaction time had no major influence on other parameters, such as the size and shape of the Au-NP. On the other hand, Pourmortazavi *et al* [91] reported that an increase in the reaction time in the formation of Ag-NP by extracts of *Eucalyptus oleosa* induces a decrease in particle size. Ali *et al* [88] observed that the longer the reaction time, the greater the production of Ag-NP from extracts of *Eucalyptus globulus*.

Regarding the role of reaction time on the synthesis of metal oxide nanoparticles by extracts of *Eucalyptus*. Jeevanandam *et al* [17] analyzed the size of MgO nanorods synthesized by extracts of *Eucalyptus globulus* after 10, 20, 30, 40, 50 and 60 min of reaction. These authors found that the smallest particles were obtained after 20 min of reaction. They assign this behavior to the fact that a longer reaction times favors the agglomeration of the nanoparticles, causing an increase in the size of the MgO nanorods. Another plausible explanation is based on the decomposition of the biomolecules present in the extracts after longer reaction time, preventing them from acting as stabilizing agents. Saleem *et al* [87] studied the effect of the reaction time on the formation of NiO-NP from extracts of *Eucalyptus globulus*. They reported an increase in the yield of formation of NiO-NP with increasing reaction time.

Effect of plant extract

The diversity of the composition of plant extracts is a factor that is very important in the yield and features of the synthesized nanoparticles. Yang *et al* [86] studied the effect of extracts of *Actini diadeliciosa*, *Malus domestica*, *Prunus persica* and *Musa acuminate* on the size of Au-NP synthesized at a controlled pH (pH = 11.0). The authors found that the average sizes found for Au-NP were 4.5 ± 2.0 nm, 6.0 ± 1.5 nm, 5.9 ± 2.0 nm and 2.6 ± 1.1 nm for *Actini diadeliciosa*, *Malus domestica*, *Prunus persica* and *Musa acuminate*, respectively. Even though the difference in the size of the Au-NP obtained is significant, it was not possible to attribute this effect to the composition of the extracts, since the authors did not analyze the concentration of biomolecules in the extracts. Xiao *et al* [85] studied the synthesis of iron nanoparticles by 15 different types of extracts. Out of the extracts analyzed, *S. jambos (L.) Alston* and *D. longan Lour* showed the highest capacity to form nanoparticles. The extract of *Oolong tea* showed moderate capacity for nanoparticle formation; whereas the extracts *N. indicum* and *A. moluccana (L.) Willd* showed the lowest capacity for nanoparticle formation. Unfortunately, the study does not compare the physical features of the iron nanoparticles obtained with the different extracts. In another work Wang *et al* [84] studied the effect of extracts of *Eucalyptus tereticornis*, *Melaleuca nesophila*, and *Rosemarinus officinalis* on the formation of nanoparticles formed from ferric complexes. The authors noticed that the UV-visible spectrum of the nanoparticles synthesized by extracts of *Rosemarinus officinalis* was different from the others. SEM images of the nanoparticles prepared from *Rosemarinus officinalis* showed aggregation and irregular shapes, whereas the extracts of *Eucalyptus tereticornis* and *Melaleuca nesophila* yielded very well distributed nanoparticles of spherical shape. The authors assign these differences to the chemical composition of the extracts. Ramezani *et al* [83] evaluated 12 different extracts for the synthesis of Au-NP and found that *Eucalyptus camaldulensis*, has the highest capacity for the formation of nanoparticles. The authors also compared the size of Au-NP obtained from extracts of *Eucalyptus camaldulensis* and *Pelargonium roseum* They found that extracts of *Eucalyptus camaldulensis* and *Pelargonium roseum* produced gold nanoparticles in the size ranges of 1.25–17.5 and 2.5–27.5 nm with an average size of 5.5 and 7.5 nm, respectively.

As far as we know, there is only one work dealing with the effect of different types of *Eucalyptus* species on the synthesis of nanoparticles [82]. The authors of that work evaluated the synthesis of Ag-NP by extracts of *Eucalyptus urophylla*, *Eucalyptus citriodora,* and *Eucalyptus robusta*. Their results showed that Ag-NP synthesized by *Eucalyptus urophylla* and *Eucalyptus citriodora* are smaller than those synthesized by *Eucalyptus robusta*. The authors also reported that the Ag-NP formed by *Eucalyptus urophylla* present higher crystallinity than those formed by *Eucalyptus citriodora* and *Eucalyptus robusta*.

Effect of the extract concentration

The concentration of the extracts is in general associated with the efficiency in the production of metal nanoparticles. Aboelfetoh *et al* [72] studied the effect of varying the concentration of extracts of *Caulerpa serrulata*on the synthesis of Ag-NP. They reported that an increase in the concentration of the extract induces the formation of a greater amount of smaller Ag-NP. Muthu and Priya [77] investigated the effect of the concentration of flower extracts of *Cassia auriculata* on the synthesis of Ag-NP. Their results indicate that an increase in the concentration of the extracts causes an increase in the yield of Ag-NP, but does not affect the nanoparticles size.

Jebakumar and Sethuraman [74] reported that increasing the concentration of extracts of *Acacia nilotica* results in an increase of the size and yield of the Ag-NP synthesized. However, Khalil *et al* [75] observed that an increase in the concentration of extracts of olive leaf, in addition to causing an increase in the production of Ag-NP, induces them to reduce their size. The authors did not observe any changes in the shape of the Ag-NP. Aromal *et al* [73] reported a considerable decrease in the size of the Au-NP in syntheses performed with increasing concentration of the extracts of *Trigonella foenum-graecum*.

Research has also focused on studying the effect of the concentration of plant extracts on the formation of metal oxide nanoparticles. Jeevanandam *et al* [81] studied the effect of the concentration of extracts of *Amaranthus tricolor*, *Andrographis paniculata* and *Amaranthus blitum* in the synthesis of MgO-NP: these authors reported that, in general, at a higher concentration of extracts larger MgO-NP are formed.

Pinto *et al* [89] studied the effect of the concentration of extracts of *Eucalyptus globulus* in the synthesis of Au-NP. These researchers observed that by adding 1 mg l^{-1} of the extract, formation of Au-NP occurred rapidly. But, when the concentration of the extract decreased, the rate of formation of the Au-NP also decreased. These authors also observed that increasing the concentration of the extracts resulted in the production of smaller Au-NP with lower stability. The authors also failed to observe changes in the shape of the Au-NPs by changing the concentration of *Eucalyptus globulus* extracts. Ali *et al* [88] studied the effect of the concentration of extracts of *Eucalyptus globulus* on the synthesis of Ag-NP. These authors reported an increase in the production of the nanoparticles by increasing the concentration of the extracts.

As far as we know, there is only one work dealing with the effect of different types of the concentration of *Eucalyptus* extracts on the synthesis of nanoparticles [17]. These authors reported a decrease in the size of MgO nanorods when solutions of a higher concentration of *Eucalyptus globulus* are employed in the synthesis procedure.

Effect of the concentration of the precursor

It has been proposed that the concentration of the precursor salts will have an influence mainly on the efficiency of the synthesis of metallic nanoparticles by plant extracts. Muthu and Priya [70] studied the effect of the concentration of Ag^+ ions in the synthesis of Ag-NP by flower extracts of *Cassia auriculata*. Krishnaraj *et al* [73] studied the effect of Ag^+ concentration in the synthesis of Ag-NP by extracts of *Acalypha indica*, finding that the higher Ag^+ concentration the more efficient the production of Ag-NP.

Other works report the effect of the concentration of precursor salts on the synthesis of metal oxide nanoparticles by plant extracts. Jeevanandam *et al* [81] reported that at higher concentrations of Mg^{2+} in the synthesis of MgO-NP by extracts of *Amaranthus tricolor*, *Andrographis paniculata,* and *Amaranthus blitum* MgO microparticles were obtained, whereas at lower concentrations of Mg^{2+} MgO-NP were mainly formed.

The effect of the concentration of precursors has also been studied using extracts of some *Eucalyptus* species in the synthesis of metal oxide nanoparticles. Saleem *et al* [87] found that increasing the concentration of Ni^{2+} ions the yield of NiO-NP by extracts of *Eucalyptus globulus* also increased. Jeevanandam *et al* [17] found that the size of the MgO nanorods formed by *Eucalyptus globulus* increases with increasing the concentration of Mg^{2+} ions.

Regarding the effect on the variation in the concentration of metal ions in the synthesis of metallic nanoparticles by extracts of *Eucalyptus*, Ali *et al* [88] found that increasing the concentration of Ag^+ ions increases the amount of Ag-NP formed in the presence of extracts of *Eucalyptus globulus*.

When analyzing the effect of each of the factors mentioned here, it is quite clear that it is necessary to advance in establishing the optimal nanoparticle synthesis conditions. It is also essential that studies continue to be conducted to look for the best species of plants that yield a greater and better production of nanoparticles, and to investigate how these extracts are related to the type of nanoparticle that is required to synthesize (type and concentration of precursor), besides considering the importance of the pH, temperature and reaction time.

Table 3. The total phenolic composition of extracts of *Eucalyptus*.

Species	Part of the plant	Extraction method	Fraction analyzed	Total phenolic content (mg GAE/g)	References
Eucalyptus globulus	Bark	Solid-liquid	Methanol:H_2O	407.41 ± 16.68	[93]
			Ethanol:H_2O	159.57 ± 6.75	
		Supercritical fluid	CO_2/Ethanol	33.10 ± 0.53	
			CO_2/Ethyl acetate	16.59 ± 0.10	
			CO_2/H_2O	9.22 ± 0.27	
			CO_2	10.92 ± 0.23	
Eucalyptus urophylla x Eucalyptus grandis	Leaves	Reflux	H_2O	119.1	[94]
Eucalyptus uropellita				137.8	
Eucalyptus urograndis				115.9	
Eucalyptus grandis	Bark	Soxhlet extraction	Methanol/H_2O	385.63 ± 11.02	[95]
Eucalyptus urograndis				346.72 ± 7.76	
Eucalyptus maidenii				203.86 ± 4.37	

Synthesis of nanoparticles by *Eucalyptus* extracts

Although the synthesis of nanoparticles mediated by plant extracts is relatively easy, there are many aspects that have been difficult to understand. One of these topics is to understand which biomolecules present in the extracts are responsible for the reduction of the metal ions of the precursor and which biomolecules act as stabilizing agents of the nanoparticle [92]. For this reason, it is essential to analyze the composition of the extracts to understand the green synthesis of nanoparticles.

The composition of *Eucalyptus* extracts

In the literaturemost of the studies of the composition of the extracts of different *Eucalyptus* species were focused to the search for phenolic compounds, as shown in Table 3.

From the results summarized in Table 3 it can be inferred that when obtaining extracts of plant species, either for the green synthesis of nanoparticles or for another purpose, it is necessary to consider among other factors the type of extraction, the type of solvent used, the species and the part of the plant from which extracts are desired. Santos *et al* [93] studied the extraction of phenolic compounds from the bark of *Eucalyptus globulus* by two different extraction methods and with different solvents. The results show that a solid-liquid extraction method is from 5 to 44 times more efficient for the extraction of total phenolic compounds than the extraction with a supercritical fluid. Chapuis-Lardy *et al* [94] examined the total phenolic content of three different species of *Eucalyptus* extracted by reflux. The results show no significant differences between the species studied. In other work Santos *et al* [95] reported the total phenolic content extracted by the Soxhlet method and by a mixture of methanol/H_2O from the bark of three different species of *Eucalyptus*. The authors were able to find significant differences in the phenolic content of the species analyzed (see Table 3).

The variability in the methods used for the extraction of phenolic compounds is not only reflected in the total content of phenolic compounds, but also in the type of phenolic compounds. Table 4 shows some examples of how the type of phenolic compound extracted can vary depending on the method used, the plant species, the part of the plant from which the extracts are obtained and the type of solvent used.

Santos *et al* [93] studied the effect of CO_2 and CO_2/Ethanol as supercritical fluids in the extraction of phenolic compounds from the bark of *Eucalyptus globulus*. The results indicate that the use of a supercritical fluid with polar characteristics such as CO_2/Ethanol favors the extraction, identifying up to 11 additional compounds compared to the analysis made to the extract obtained by CO_2. Chapuis-Lardy *et al* [94] identified the same phenolic compounds in three different species of *Eucalyptus* obtained by maceration of the leaves. In a semi-quantitative analysis, the authors did not find significant differences in the concentrations of the phenolic compounds contained in the three different extracts. However, Santos *et al* [95], in another work, identified the phenolic compounds in barks from three different species of *Eucalyptus* by Soxhlet extraction and using methanol/H_2O as solvent. The results reported show variability in the type of phenolic compounds depending on the species of *Eucalyptus*. It should be noted that when comparing the analysis of phenolic compounds carried out by Santos *et al* [95] and Chapuis-Lardy *et al* [94] of *Eucalyptus urograndis* different identified compounds are appreciated. This is probably due to the different extraction methods, the solvents used in the extractions, or by the part of the analyzed plant (leaf and bark). As already mentioned, there is no doubt that the

Table 4. Identification of the main phenolic compounds in *Eucalyptus* species.

Species	Part of the plant	Extraction method	Fraction analyzed	Identification of compounds	References
Eucalyptus globulus	Bark	Supercritical fluid	CO_2/Ethanol	Gallic acid, protocatechuic acid, digalloylglucose, isorhamnetin-hexoside, ellagic acid, taxifolin, methyl-ellagic acid-pentose, methyl-ellagic acid, eriodictyol, luteolin, isorhamnetin, naringenin	[93]
			CO_2	Digalloylglucose	
Eucalyptus urophylla x *Eucalyptus* grandis	Leaves	Maceration	H_2O	Gallic acid, protocatechuic acid, chlorogenic acid, p-Hydroxybenzoic acid+gentisic acid, caffeic acid, p-hydroxybenzaldehyde, p-coumaric acid, ferulic acid	[94]
Eucalyptus uropellita				*Idem*	
Eucalyptus urograndis				*Idem*	
Eucalyptus grandis	Bark	Soxhlet extraction	Methanol/H_2O	Quinic acid, gallic acid, protocatechuic acid, methyl gallate, catechin, Galloyl-bis-hexahydroxydiphenoyl-glucose, digalloylglucose, epicatechin, ellagic acid-rhamnoside, ellagic acid, Isorhamnetin-rhamnoside.	[95]
Eucalyptus urograndis				Quinic acid, gallic acid, protocatechuic acid, methyl gallate, galloyl-bis-hexahydroxydiphenoyl-glucose, epicatechin, ellagic acid-rhamnoside, ellagic acid, isorhamnetin-rhamnoside	
Eucalyptus maidenii				Quinic acid, gallic acid, protocatechuic acid, methyl gallate, catechin, galloyl-bis-hexahydroxydiphenoyl-glucose, digalloylglucose, epicatechin, chlorogenic acid, galloyl-bis-hexahydroxydiphenoyl –glucose, dihydroxy-isopropylchromone-hexoside, isorhamnetin-hexoside, ellagic acid-rhamnoside, ellagic acid, taxifolin, quercetin-hexoside, methyl-ellagic acid-pentose, myricetin-rhamnoside, mearnsetin, mearnsetin-hexoside, eriodictyol, quercetin, isorhamnetin, naringenin	

extraction method and the experimental parameters employed in the extraction of biocompounds of vital importance.

Role of biocompounds in the green synthesis of nanoparticles

The different biocompounds that can be found in plant extracts play a very important role in the green synthesis of nanoparticles. Below we analyze some of the main biocompounds mentioned in literature and their role in the green synthesis of nanoparticles.

Phenolic compounds

The phenolic compounds are one of the biocompounds of greater presence in the extracts of *eucalyptus*, and therefore, one of the main compounds responsible for the formation of nanoparticles from plant extracts. Shahwan *et al* [96] were able to synthesize Fe-NP from green tea extracts, proposing in this work that the polyphenols present in the extracts act as both reducing and capping agents. Additionally, Devatha *et al* [97] suggested that in the synthesis of iron nanoparticles mediated by extracts of *Mangifera indica*, *Murraya koenigii*, *Azadirachta indica* and *Magnolia champaca*, the main reducing biomolecules are polyphenols. Khan *et al* [98] and Sravanthi *et al* [99] studied the synthesis of Fe-NP from extracts of *Hibiscus sabdariffa* and *Calotropis gigantea* respectively, finding that the polyphenols present in these extracts act mainly as reducing and capping agents.

The importance of the phenolic compounds present in extracts of *Eucalyptus* for the synthesis of nanoparticles has been widely studied. In an exhaustive study, Xiao *et al* [85] examined the effect of 15 extracts of different plant species and their content of reducing sugars, flavones, polyphenols and proteins on the synthesis of iron nanoparticles. The authors were able to find an excellent relationship between the polyphenolic content of the 15 extracts studied (among which those from *Eucalyptus citriodora* stands out) and the production of nanoparticles, concluding then that the polyphenols were the main Fe^{3+} reducing agents in the system. In this line, authors as Wang *et al* [100] and Pinto *et al* [89] have proposed that in the synthesis of iron and gold nanoparticles the polyphenols present in extracts of *Eucalyptus* act as both reducing and stabilizing agents. Santos *et al* [101] analyzed the phenolic content of *Eucalyptus globulus* extracts by HPLC-MS before and after carrying out the synthesis of Ag-NP and Au-NP. The authors found that the polyphenols derived from gallic acid were the main reducers of Ag^{+} and Au^{3+} ions; whereas the ellagic acid and isorhamnetine derivatives acted as stabilizers of the synthesized nanoparticles.

In contrast, it has been reported that polyphenols are not only able to reduce metal ions and form metallic and metal oxide nanoparticles, but can instead form nanoparticles composed of metal complexes. For example, Wang *et al* [102] reported that the polyphenols present in extracts of *Salvia officinalis* were able to form nanoparticles of ferric complexes. Similarly Markova *et al* [103] proposed the participation of polyphenols from green tea extracts in the formation of nanoparticles of ferrous and ferric complexes. Wang *et al* [84] studied the type of nanoparticles formed between Fe^{3+} ions and polyphenols in extracts of *Melaleuca nesophila*, *Rosemarinus officinalis,* and *Eucalyptus tereticornis*, reporting that they were composed of polyphenol-Fe^{3+} complexes. Wang *et al* also reported in two additional works the formation of nanoparticles formed by polyphenol-Fe^{3+} complexes using extracts of *Eucalyptus tereticornis* [104, 105].

Terpenoids

Terpenoids are an important group of polymeric organic compounds. Shankar *et al* [42] proposed that the terpenoids found in extracts of *Pelargonium graveolens* were the main reducing compounds implied in the formation of Au-NP. Mashwani *et al* [106] in an article on the importance of terpenoids in the synthesis of Ag nanoparticles propose that the main role of terpenoids is related to their capacity to reduce Ag^{+} ions, besides to the stabilization of the nanoparticles obtained.

The implication of terpenoids in extracts of *Eucalyptus* has also been addressed. Saleem *et al* [87] proposed that terpenoids present in extracts of *Eucalyptus* are able to reduce metal ions to form NiO nanoparticles, using both aldehyde and hydroxyl groups present in terpenoid molecules. In this line Jeevanandam *et al* [17] found that eucalyptol, a terpenoid present in extracts of *Eucalyptus globulus*, was one of those responsible compounds for the formation of MgO nanowires from Mg^{2+} ions, whereas other molecules of the terpene type act as stabilizing agents.

Carbohydrates

Among the carbohydrates that can be found in vegetable extracts, there is a type called reducing carbohydrates, capable of reducing metal ions. In this way, Castro *et al* [107] used sugar beet pulp for the synthesis of Au nanowires, considering that the carbohydrates present in the pulp are one of the main reducers. In a similar way

Shankar *et al* [108] found that the carbohydrates in the extracts of *Azadirachta indica* acted as stabilizers in the synthesis of Ag-NP and Au-NP. In the same line, Ortega-Arroyo *et al* [109] used starch in the synthesis of Ag-NP, finding that glucose acted as the main agent of Ag^+ ion reduction.

On the other hand, Santos *et al* [101] found the presence of glucose and fructose in extracts of *Eucalyptus globulus*. The authors found that both glucose and fructose at low concentrations do not act as reducing agents in the formation of Ag-NP and Au-NP, but rather as stabilizing agents.

Proteins

It is possible to find some publications that have addressed the role of proteins present in plant extracts in the synthesis of nanoparticles. For example, Patra *et al* [110] proposed that the proteins present in extracts of *Butea monosperm* play a reducing role in the formation of Ag-NP and Au-NP. Li *et al* have shown in two works that the synthesis of Ag-NP [111] and Se-NP [112] by extracts of *Capsicum annuum* is mediated by the proteins in the extract.

Regarding the participation of proteins from extracts of *Eucalyptus* species in the formation of nanoparticles, Mo *et al* [82] proposed that the proteins and polyphenols present in extracts of *Eucalyptus urophylla*, *Eucalyptus citriodora,* and *Eucalyptus robusta*, were the main reducing compounds in the formation of Ag-NP from Ag^+. In contrast, Santos *et al* [101] and Ali *et al* [88] reported that the main function of the proteins found in extracts of bark and leaves of *Eucalyptus globulus* played the role of stabilizers, but not of reducing agents.

Alkaloids

There are some works in which the ability to form nanoparticles is attributed to some alkaloids present in plant extracts. For example, Weng *et al* [113], Wu *et al* [114], Huang *et al* [115], Kuang *et al* [116] and Huang *et al* [117] proposed that the caffeine contained in tea extracts was able to form iron nanoparticles acting as a reducing and stabilizing agent. Feng *et al* [118] found that in the synthesis of Pd-NP and Pt-NP supported on graphene oxide the caffeine added to the system acted directing the structure of the nanomaterial and as a capping agent. Augustine *et al* [119] raised the possibility that the alkaloids present in the extracts of *Piper nigrum* leaves act as reducing agents in the formation of Ag-NP. Kumar *et al* [120] found that the alkaloids found in the extracts of *Zingiber officinale* used in the synthesis of Au-NP act as capping agents. On the other hand, Begum *et al* [121] observed that the caffeine-rich extract obtained from CH_2Cl_2 from black tea leaves was not able to synthesize Ag-NP and Au-NP.

To our knowledge, there are not too many studies that address the presence of alkaloids in *Eucalyptus* extracts and their influence on the formation of nanoparticles. Dubey *et al* [122] proved the existence of alkaloids in extracts of *Eucalyptus hybrida*, but they do not attribute any effect to these compounds on the synthesis of silver nanoparticles mediated by these extracts. Weng *et al* [123] comment that the presence of alkaloids among other biomolecules present in *Eucalyptus* leaves could serve both as reducting and capping agents. Ali *et al* [88] proposed that the stability found in the synthesis of Ag-NP from extracts of *Eucalyptus globulus* was due to the presence of alkaloids, among other biocompounds.

Tannins

Tannins are compounds, generally polymeric, extracted from plants, with several hydroxyl groups in their structure. There are publications in which the effect of these compounds in the synthesis of nanoparticles has been studied. Kumar *et al* [124] studied the synthesis of Au-NP from extracts of *Terminalia chebula*, finding that the water-soluble tannins present in the extracts were responsible for the reduction and stabilization of the nanoparticles. In an additional work, Kumar *et al* [125] studied the effect of extracts of *Terminalia chebula* on the synthesis of Ag-NP, reporting that the hydrolyzable tannins present in the extracts act only as reducing agents. Edison *et al* [126] informed that the tannins found in extracts of *Terminalia chebula* used for the synthesis of Ag-NP act as both reducting and capping agents.

As far as we know, the participation of tannins from extracts of *Eucalyptus* has been very little addressed. Recently, Mo *et al* [82] proposed that the tannic acids present in extracts of *Eucalyptus urophylla*, *Eucalyptus citriodora,* and *Eucalyptus robusta* have reducing activity in the synthesis of Ag-NP.

Some of the publications that have used extracts of *Eucalyptus* in the synthesis of metal and metal oxides nanoparticles, their main features, and their application are summarized in Tables 5 and 6 respectively.

Mechanisms of nanoparticle formation

The mechanisms and the biomolecules responsible for the formation of nanoparticles mediated by plant extracts have not yet been fully established [24]. It has been reported that various biomolecules such as polyphenolic compounds, proteins, vitamins, organic acids, terpenoids, alkaloids, polysaccharides, and

Table 5. Synthesis of metallic nanoparticles by extracts of *Eucalyptus*.

Specie	Precursor	Capping and/or reducing agents	Conditions	Type of NP	Size (nm)	Morphology	Applications	References
Eucalyptus globulus	$AgNO_3$	Alkaloids, tannins, triterpenoids, flavonoids, proteins, carbohydrates and other metabolites	20 °C, pH 8.0, microwave	Ag	1.9–25	Spherical	Antimicrobial and anti-biofilm activity	[88]
Eucalyptus urophylla, Eucalyptus citriodora, eucaliptus robusta	$AgNO_3$	Polifenoles y proteinas	30 °C	Ag	4–60	Spherical	—	[82]
Eucalyptus oleosa	$AgNO_3$	-OH and -COO groups	100 °C, 24 h	Ag	10–30	Spherical	—	[91]
Eucalyptus globulus	$AgNO_3$	Phenolic compounds	30 °C, 24 h	Ag	30–50	Spherical, hexagonal y cubic	—	[127]
Eucalyptus leucoxylon	$AgNO_3$	—	27 °C	Ag	50	Irregular	—	[128]
Eucalyptus chapmaniana	$AgNO_3$	Flavanoid and terpenoid compounds	20 °C, 24 h	Ag	50–150	—	—	[129]
Eucalyptus	$AgNO_3$	—	75 °C	Ag	3–9	Spherical	Antibacterial activity	[130]
Eucalyptus macrocarpa	$AgNO_3$	—	24 °C, 10 min	Ag	10–50	Cubic	—	[131]
Eucalyptus globulus	$AgNO_3$	—	20 °C	Ag	30–36	Spherical, triangular and hexagonal	—	[132]
Eucalyptus citriodora	$AgNO_3$	Tannins	28 °C, 16 h	Ag	8–17	Spherical	Antibacterial activity	[133]
Eucalyptus chapmaniana	$AgNO_3$	—	50 °C	Ag	60	—	Antibacterial activity	[134]
Eucalyptus camaldulensis	$AgNO_3$	—	20 °C, 2 h	Ag	110–250	Spherical	—	[135]
Eucalyptus globulus	$AgNO_3$ $HAuCl_4$	Sugars and phenolic compounds	20 °C, 1 h	Ag Au	15–73 18	Spherical	—	[136]
Eucalyptus globulus	$HAuCl_4{\cdot}4H_2O$	Terpenos	20 °C	Au	12.8	Spherical	—	[137]
Eucalyptus globulus	$HAuCl_4{\cdot}3H_2O$	Phenolic compounds	20 °C, 24 h, pH 2.7	Au	20–100	Spherical	—	[89]
Eucalyptus oleosa	$HAuCl_4{\cdot}3H_2O$	—	20°C	Au	28	Spherical	—	[138]
Eucalyptus macrocarpa	$AuCl_4^-$	—	24 °C, 1 min	Au	20–100	Spherical and others	Antibacterial activity	[139]
Eucalyptus camaldulensis	$HAuCl_4$	—	15 min	Au	1.25–17.5	Spherical	—	[83]
Eucalyptus globulus	$CuCl_2{\cdot}2H_2O$	Phenolic compunds and sugars	2 h, 121 °C, 120 MPa	Cu	44–145	Nanowire	—	[140]
Eucalyptus sp.	$CuSO_4$	Phenolic compounds and carboxilic acids	20 °C, 8 h	Cu	27.65–48.19	Cubic	—	[141]
Eucalyptus	$FeSO_4{\cdot}7H_2O$	Phenolic compounds	20 °C, 30 min	α-Fe	20–80	Spherical	Wastewater treatment	[142]
Eucalyptus globulus	$FeSO_4{\cdot}7H_2O$	Phenolic compounds	20 °C, 1 min	Fe	50–80	Spherical	Cr(VI) adsorption	[143]
Eucalyptus	$FeCl_3$	Phenolic compounds, aldehydes, amines and alkanes	80 °C, 30 min, pH 4.0	Fe	95	Spherical	Cr(VI) adsorption	[144]
Eucalyptus globulus	$FeCl_3{\cdot}6H_2O$	Phenolic compounds	20 °C	Fe	38–47	Irregular, aglomerados	As(III) oxidation	[145]
Eucalyptus	$FeSO_4{\cdot}7H_2O$	Phenolic compounds	20 °C, N_2 atmosphere, 30 min	Fe	71.5	Spherical	Cr(VI) adsorption	[146]

Table 5. (Continued.)

Specie	Precursor	Capping and/or reducing agents	Conditions	Type of NP	Size (nm)	Morphology	Applications	References
Eucalyptus tereticornis	$FeCl_3$	Phenolic compounds	—	Ferric complex	40–60	Cubic	Dye adsorption	[104]
Eucalyptus tereticornis	$FeCl_3$	Phenolic compounds	—	Ferric complex	50–80	Spherical	Dye oxidation	[84]
Eucalyptus	$FeSO_4$	Phenolic compounds	20 °C	—	20–80	—	Cr(VI) and Cu(II) adsorption	[147]
Eucalyptus	$FeSO_4$, $Ni(NO_3)_2$	Aldehydes, phenols, amines, and alkanes	20 °C, 30 min, N_2	Fe/Ni	20–50	Spherical e irregular	Dye adsorption and oxidation	[123]

Table 6. Synthesis of metal oxide nanoparticles by extracts of *Eucalyptus*.

Specie	Precursor	Capping and/or reducing agents	Conditions	Type of NP	Size (nm)	Morphology	Applications	References
Eucalyptus camaldulensis	$Cu(NO_3)_2$	—	80 °C, 10 min	CuO	21.1	—	Antibacterial activity	[148]
Eucalyptus globulus	$CuSO_4 \cdot 7H_2O$	Terpenoids	60 °C, 3 h	CuO	16.78–22.50	Spherical, oval and hexagonal	Antibacterial activity	[90]
Eucalyptus globulus	$Cu(CH_3COO)_2$ $Zn(CH_3COO)_2$	—	150 °C, 12 h	CuO ZnO	12.29 10.16	—	Photodiode	[149]
Eucalyptus	$FeSO_4 \cdot 7H_2O$	Phenolic compounds	20 °C, 30 min	α-Fe-iron oxide-polyphenols	20–80	Spherical (core shell structure)	Nitrate adsorption	[100]
Eucalyptus globulus	$FeSO_4 \cdot 7H_2O$	Phenolic compounds	50 °C, 30 min, pH 6	α-FeOOH, γ-FeOOH, α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4,	5.37–36.51	Spherical	Photocatalysis activity	[150]
Eucalyptus	Laterite	Phenolic compounds, aromatic amines, aliphatic amines	60 min	Fe, Fe_2O_3, Fe_3O_4	20–70	Spherical	Herbicide oxidation	[151]
Eucalyptus	$FeCl_3 \cdot 6H2O$	—	70 °C, 2 h	Fe_3O_4	80–90	Spherical	Phosphate adsorption	[152]
Eucalyptus	$FeCl_3$	Phenolic compounds	70 °C, 2 h	Fe_3O_4	80	Spherical	Phosphate adsorption	[153]
Eucalyptus globulus	$Fe(NO_3)_3 \cdot 9H_2O$	—	25 °C	Fe_3O_4, γ-Fe_2O_3, γ-FeOOH, α-Fe_2O_3	<100	—	As(V) adsorption	[154]
Eucalyptus	$FeSO_4 \cdot 7H_2O$	—	80 °C, 1 h	Fe(II) and Fe(III) oxides	57.6	Agglomerates	Dye adsorption	[155]
Eucalyptus globulus	$FeCl_3$	—	20 °C, 3 min	β-Fe_2O_3	100	Agglomerates	—	[156]
Eucalyptus globulus	$NiNO_3 \cdot 6H_2O$	Phenolic and terpenoid compounds	70 °C, 4 h, pH 8	NiO	3–23	Polymorphic	Antibacterial activity	[87]
Eucalyptus globulus	$Mg(NO_3)_2 \cdot 6H_2O$	Terpenoids, Phenolic compounds, and flavonoids	80 °C, 20 min	MgO	6–9	Nanorods	—	[17]
Eucalyptus globulus	$Zn(NO_3)_3 \cdot 6H_2O$	Phenolic and terpenoid compounds	3 h, pH 5.2	ZnO	11.6	Spherical	Adsorption and photocatalytic activity	[157]
Eucalyptus	Graphite oxide	—	80 °C, 8 h	Reduced graphite oxide	0.807–1.129	Nanocables	—	[158]
Eucalyptus	Graphite oxide	Eucalyptols, aldehydes, terpineols, alcohols, amides, and ethers	80 °C, 8 h	Reduced graphite oxide	—	Spherical	Dye adsorption	[159]
Eucalyptus	Graphene oxide	Phenolic compounds	—	Graphene and gold nanocomposite onto carbon brush	—	Rod-shaped	Energy recycle	[160]

heterocyclic compounds are responsible for the reduction of metal ions, as well as being able to act as capping and stabilizing agents [22]. In this way, considering that different mechanisms have been reported to explain the formation of nanoparticles depending on the species of plant [161], defining a single mechanism responsible for the formation of nanoparticles from plant extracts seems to be a difficult task.

The phenolic compounds present in the extracts of *Eucalyptus* play a key role in the synthesis of metallic nanoparticles. Thus, the synthesis of metallic nanoparticles can be explained based on the phenolic compounds ($Ar–(OH)_n$). For example, different mechanisms have been proposed to explain the formation of iron nanoparticle (equations (1)–(4)).

$$\mathrm{nFe^{3+}} + 2\mathrm{Ar} - (\mathrm{OH})_n \ \rightarrow \mathrm{nFe^{2+}} + 2\mathrm{nAr} = \mathrm{O} + 2\mathrm{nH^+} \tag{1}$$

$$\mathrm{nFe^{2+}} + 2\mathrm{Ar} - (\mathrm{OH})_n \ \rightarrow \mathrm{nFe^0} + 2\mathrm{nAr} = \mathrm{O} + 2\mathrm{nH^+} \tag{2}$$

$$2(x+1)\mathrm{Fe^0} + 2\mathrm{Ar} = \mathrm{O} + \mathrm{yO_2} \rightarrow 2(\mathrm{Fe^0} - \mathrm{Fe}_x\mathrm{O}_y - \mathrm{Ar} = \mathrm{O}) \tag{3}$$

$$\mathrm{Fe^{3+}} + 3[\mathrm{Ar} - (\mathrm{OH})_2] \rightarrow [\mathrm{Fe(ArO_2)_3}]^{3-} + 6\mathrm{H^+} \tag{4}$$

Liu *et al* [144] proposed that the phenolic compounds, as well as the functional groups of other biomolecules present in plant extracts, are capable of forming iron nanoparticles in three stages: (1) the compounds form complexes with Fe^{3+} and simultaneously reduce it to Fe^{2+} (quation (1)); (2) the compounds present in the extracts continue to reduce iron, now from Fe^{2+} to Fe^0 (equation (2)); and (3) the phenolic compounds and other ligands terminate the reaction, surrounding the nanoparticles and helping to their stability. Wang *et al* [142] and Rama *et al* [145] obtained iron nanoparticles from extracts of *Eucalyptus*, and suggest that the formation of nanoparticles from Fe^{2+} ions is produced by the reduction of Fe^{2+} to Fe^0 by means of the phenolic compounds present in the extracts (item 2). It has been proposed that phenolic compounds are also capable of forming metal oxide nanoparticles with a core of Fe^0 and Fe_xO_y, and a layer of biomolecules (equation (3)) [100, 144]. Additionally, Wang *et al* in two publications 84, 104] and Markova *et al* [103] have reported the formation of nanoparticles consisting of stable complexes of phenolic compounds and Fe^{3+} (equation (4)).

Similar mechanisms have been proposed for the formation of metal oxide nanoparticles. Saleem *et al* [87] established that the formation of NiO-NP from Ni^{2+} and extracts of *Eucalyptus globulus* occurred by phenolic compounds able to reduce Ni^{2+} ions to Ni^0, whereas the phenolic compounds on the surface of the nanoparticles would cause the formation of NiO. On the other hand, Jeevanandam *et al* [17] stated that the main phenolic compounds in extracts of *Eucalyptus globulus* were able to form nanoparticles of MgO, acting as chelating and stabilizing agents of the Mg^{2+} ions, to then form the nanoparticles of MgO.

Applications of nanoparticles

The nanoparticles obtained by green methods have been applied in various fields, such as adsorbant/antioxidants [162], chemocatalytic reactions [163–169], oxidative desulfurization [170], dyes degradation [96, 171–175], degradation of organochlorine compounds [176], sensors development [177, 178], electrodes development [179, 180], antibacterial agents [164, 181–189], antiviral agents [190], antifungal agents [191], cytotoxic agents [192, 193], larvicidal agents [190, 194], photocatalysts [187, 195–197], anti-cancer agents [186, 189, 198–202], α-amylase inhibitors [203] and as components of solar cells [204].

On the other hand, the nanoparticles obtained by extracts of different species of *Eucalyptus* have been widely studied in environmental applications. For example, Sangami and Manu [151] studied the degradation of Ametryn, a well-known herbicide, by using iron nanoparticles as Fenton-type catalysts obtained from Laterite and extracts of *Eucalyptus*. Gan *et al* [152] reported the removal of phosphate ions using nanoparticles of iron oxides obtained by extracts of *Eucalyptus*. Jin *et al* [146] synthesized iron nanoparticles using extracts of *eucalyptus* for the removal of Cr(VI). Madhavi *et al* [143] described the Cr(VI) adsorption by zero-valent iron nanoparticles obtained by extracts of *Eucalyptus globulus*. Wang *et al* [100] synthesized iron nanoparticles by extracts of *Eucalyptus*, and showed their application in the treatment of swine wastewater. In other work, Wang *et al* [142] used iron nanoparticles obtained from extracts of *Eucalyptus* in the treatment of eutrophic wastewater. Wang *et al* [100] also worked on the synthesis of iron nanoparticles by extracts of *Eucalyptus*, applying them in the removal of nitrate ions from swine wastewater. Weng *et al* [205] reported the synthesis of a hybrid material formed by iron and reduced graphene oxide nanoparticles, synthesized from extracts of *Eucalyptus*. This hybrid nanomaterial was successfully used for the removal of methylene blue. In other work Weng *et al* [147] used extracts of *Eucalyptus* for the synthesis of iron nanoparticles for the Cr(VI) and Cu(II) removal. Siripireddy and Mandal [157] obtained ZnO-NP using extracts of *Eucalyptus globulus*. These nanoparticles were used as photocatalysts in the methyl orange and methylene blue degradation. Besides, Martinez-Cabanas *et al* [154] reported the application of iron oxide nanoparticles obtained from extracts of *Eucalyptus globulus* in the As(V) removal.

Other applications of the nanoparticles obtained by extracts of *Eucalyptus* are in the energy field. In a recent work Senthilkumar *et al* [206] used Ag-NP prepared from extracts of *Eucalyptus glopus*, *Azadirachta indica,* and *Coriandrum sativum*. These Ag-NP were used as anti-reflecting agents, improving the efficiency of Si solar cells. Cheng *et al* [160] obtained from extracts of *Eucalyptus*, biocompatible anodes of reduced graphene and gold obtained, which were successfully tested for efficient energy recycling.

It is also possible to find works dealing with the synthesis of nanoparticles with antimicrobial activity from extracts of *Eucalyptus*. For example, Mohammed [207] described the synthesis of Ag-NP from extracts of *Eucalyptus camaldulensis* with antimicrobial activity. Likewise, Sulaiman *et al* [134] reported the antimicrobial activity of Ag-NP synthesized from extracts of *Eucalyptus chapmaniana*. Moreover, Poinern *et al* [139] synthesized Au-NP from extracts of *Eucalyptus macrocarpa* and showed their antimicrobial activity. Paosen *et al* [133] obtained Ag-NP by extracts of *Eucalyptus citriodora* with antimicrobial activity. Torabi *et al* [208] reported the synthesis of Au-NP by extracts of *Eucalyptus camaldulensis* for the treatment of cutaneous zoonotic leishmaniasis caused by *Leishmania major* (MRHO/IR/75/ER). Saleem *et al* [87] studied the effect of NiO-NP synthesized from extracts of *Eucalyptus globulus* in the growth inhibition and biofilm formation of isolated clinical bacteria.

Conclusions and future perspectives

This review has summarized recent research in the field of synthesis of metallic and metal oxides nanoparticles mediated by plant extracts, especially extracts of *Eucalyptus*. The use of non-toxic plant extracts in the synthesis of metallic and metal oxides nanoparticles is considered a method friendly to the environment and inexpensive. In particular, the use of extracts of different species of *Eucalyptus* seems to be an interesting way to synthesize metallic and metal oxides nanoparticles. The fact that leaves and bark of *Eucalyptus* are considered disposable plant material, along with the massive availability of plantations of *Eucalyptus* species, would support the synthesis of metallic and metal oxides nanoparticles on an industrial scale. In future investigations, it is necessary to pay more attention to the role of the different components of the extracts of *Eucalyptus* in the different stages of synthesis of metallic and metal oxides nanoparticles. Although there are many reports in the literature regarding the mechanisms that govern the synthesis of metallic and metal oxides nanoparticles by plant extracts, including extracts of *Eucalyptus*, they are hypothetical. Thus, further research is necessary to fully understand the reaction steps behind the synthesis processes. Since the composition of the extracts depends on the extraction methods, the effect of the type of *Eucalyptus* species and the part of the plant used should be optimized to favor the extraction of the components involved in the different metallic and metal oxides nanoparticle synthesis. Additionally, it is necessary to scale the synthesis of metallic and metal oxides nanoparticles by extracts of *Eucalyptus* from laboratory to industrial scale. The scale-up of the chemical methods is not such a trivial process and requires a fully understanding of the involved steps. The use of metallic and metal oxides nanoparticles in various forms of environmental remediation, energy applications, and antimicrobial activity have been addressed. In order to achieve a more secure implementation of metallic nanoparticles and metal oxides in biomedical and environmental applications, it is necessary to increase the study and characterization of these materials in terms of their toxicity, biocompatibility and action mechanisms of the nanoparticles. Due to the constant efforts to improve and optimize the efficiency of the synthesis of metallic and metal oxides nanoparticles, it is expected that these approaches will allow expanding their applications in the field of medicine and agriculture in the coming years.

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