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Green synthesis of silver nanoparticles in oil-in-water microemulsion and nano-emulsion using geranium leaf aqueous extract as a reducing agent

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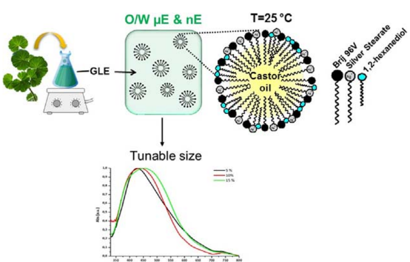
GRAPHICAL ABSTRACT



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ABSTRACT

A green synthesis of silver nanoparticles was developed, using a low-toxic system of microemulsion and nano-emulsion with castor oil as the oily phase, Brij 96 V and 1,2-hexanediol as the surfactant and co-surfactant respectively. Geranium (*P. hortorum*) leaf aqueous extract was employed as a reducing agent. The content and concentration of a metallic precursor and geranium leaf extract (GLE) in the systems used makes it possible to obtain different sizes of silver nanoparticles from 25 to 150 nm. The characterization by FTIR and Z potential shows that the biomolecules of the plant extract act as a reducing and capping agent, giving negative charges to the nanoparticle surface. The present study represents a contribution to the green synthesis of silver nanoparticles that can be extended to other metals.

1. Introduction

Several methods for noble metal (Au, Ag, Pt and Pd) nanoparticle synthesis are reported in the literature [1]. Silver nanoparticles (AgNPs) are one of the most popular materials among noble metal nanoparticles due to their unique chemical and physical properties and versatile applications in many fields (medicine, electronic devices, catalysis, antimicrobial agent, inks, sensors and many others [2,3]). Usually AgNPs are prepared by physical or chemical methods, ultrasound-assisted processes, laser ablation, electrochemical and thermal decomposition, chemical reduction, etc. [2]. One of the easiest and lowest-cost processes is the chemical method, which is based on a redox reaction. The right choice of the reducing agent and control in synthesis parameters guarantees the production of nanoparticles. However, alternatives to these chemical methods have been developed recently, substituting the common reducing agents with natural antioxidant compounds. These methods are called "green synthesis" because they follow the green chemistry principles.

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Green synthesis of silver nanoparticles using microorganisms and plant extracts has been studied, the latter method being the best alternative to obtain these nanomaterials due to the ease and efficacy in the reduction of metal ions by the biomolecules present in plant extracts [4]. Consequently, the process involves no chemicals that are hazardous for the environment and living organisms. The *Pelargonium hortorum* plant, better known as geranium or storksbill, is widely distributed around the world due to its adaptability to different climates. For this reason, *P. hortorum*, is an excellent option for consideration as a source of reducing agents for silver nanoparticle synthesis. Jafarizad et al. [5] reported the use of mint and *P. hortorum* extracts for producing gold nanoparticles with sizes in the interval of 10–100 nm. The characterization of these extracts showed that the main reducing agents are Isoeugenol and Spathulenol, present in mint; and flavonoids, phenols and tannins from the *Pelargonium* extract. Sastry et al. [6] report the use of *Pelargonium graveolens* for synthesizing silver nanoparticles, with sizes ranging from 16 to 40 nm. Mirończyk et al. [7] obtained gold nanoparticles (2–80 nm) by using extract of *P. hortorum* leaves, but multiple morphologies were obtained (spherical, triangular and hexagonal particles). When the sonocatalytic effect is added to the reducing effect of the *P. hortorum* extract, gold nanoparticles measuring between 8 and 20 nm, can be obtained [8]. Thus, extracts obtained from *Pelargonium* species have proven effective in obtaining nanomaterials. However, one of the great disadvantages is the polydispersity of sizes of the nanoparticles obtained because the dependency of the medium conditions [9]. Emulsion systems have been reported as template for nanoparticle production. Sivakumar et al. [10,11] formulated a W/O emulsion composed by natural oil (rapeseed oil) without the use of surfactants using the ultrasound assisted emulsification method, in the case of the synthesis of nanocrystals of zinc and manganese ferrites. The use of microemulsions as nano-reactors has proven to be an effective method to avoid or diminish the polydispersity in the size of nanoparticles synthesized [12]. This method presents advantages compared with the emulsion system since low energy input is needed for the nanoparticle formation. Reports indicate that the concentration of the metallic precursor, the reducing power of the reducing agent, and the amount of phase dispersed in these systems are the keys to controlling size and obtaining monodisperse nanoparticle populations [13]. Water-in-oil (W/O) and oil-in-water (O/W) microemulsions are used for production of metal nanoparticles [14,15] and interestingly it has been reported that O/W microemulsions are advantageous in obtaining stable nanoparticle dispersions and also represent a more eco-friendly way for nanoparticle production because the aqueous phase is the major component [16]. In recent years, nano-emulsions have shown their effectiveness as templates for the production of nanoparticles [17], solid lipid nanoparticles [18], polymeric nanoparticles [19], metallic nanoparticles [20–23] and other nanomaterials [24]. Nevertheless, to the best of our knowledge this paper is the first report where a plant extract is used as a reducing agent in a microemulsión and nano-emulsion system to synthesize silver nanoparticles, because the systems used up to now for preparing metallic nanoparticles have been composed mostly of organic solvents with high volatility and surfactants that are not environmentally friendly [3]. New studies are emerging in which these petroleum-based oils are replaced by vegetable oils and surfactants with low or no toxicity for the environment, thus offering new options in microemulsion formulation [25,26]. Vegetable oils are made up of mixtures of long-chain triglycerides, and until now it has been a challenge to find systems with a large microemulsion zone due to the structural complexity of natural oils compared with common microemulsion systems where linear hydrocarbons are used as the oil phase; because the interphases are stabilized better due to a greater structural compatibility between the surfactant and the oil. De Castro Dantas et al. [27] have reported the formation of microemulsions using vegetable oils as oily phases. The microemulsion zone reported in the corresponding phase diagram is very small, due mainly to the structural complexity of oils used. The study of microemulsion formation in systems with vegetable oils and plant extracts is important for the development of new and green reaction media for the production of metal nanoparticles with controlled size in an ecofriendly way and using soft reaction conditions.

This paper proposes a new methodology for producing silver nanoparticles in a greener way using microemulsions and nano-emulsions formulated with low-toxic components for the environment and living organisms. Thus, in the present research a new microemulsion and nano-emulsion system was used as a nano-reactor for synthesizing silver nanoparticles, with castor oil, Brij 96 V and 1,2-hexanediol as the surfactant and con-surfactant respectively and geranium leaf aqueous extract as the reducing agent. Microemulsion and nano-emulsion formation was determined by means of phase diagrams. The nanoparticles obtained were characterized by UV–vis, FT-IR, zeta potential and dynamic light scattering (DLS). The sizes of the nanoparticles obtained have been related to those of the template microemulsions and nano-emulsions, taking into account the amount of aqueous phase in the system.

2. Material and methods

2.1. Materials

Castor oil (commercial sample), silver stearate from MP Biomedicals, 1–2 hexanediol (purity ≥98.0%) and Brij 96V® were obtained from Sigma Aldrich. Dry leaves of *Pelargonium hortorum* (geranium) were used to prepare the extract. The aqueous phases were prepared using Milli-Q water from a Millipore system with a resistivity of 18.2 MΩ cm^{-1}.

2.2. Ternary phase diagram

The phase behavior was studied by means of a ternary phase diagram to determine the monophasic zone of the system corresponding to microemulsions and also a delimited zone in the multiphasic zone corresponding to nano-emulsions. The titration of defined mixtures of oil and surfactant with the aqueous phase was performed using vortex mixing. All the samples were kept in a bath at a temperature of 25 °C. The aqueous phases used contained Milli-Q water and geranium leaf extract (GLE).

2.3. Conductivity

Conductivity measurements were performed with a Crison conductometer GLP31 with a cell constant of 1 cm^{-1} and with controlled temperature. The conductivity was measured along the dilution line of surfactant:oil (S:O) weight ratio of 35/65 adding the aqueous phase drop by drop to the mixture S:O in order to study the microstructure of the system (Water/1,2-hexanodiol:Brij 96 V 1:1/castor oil).

2.4. Preparation of *P. hortorum* leaf aqueous extract

P. hortorum plant was purchased in a local market. The leaves were rinsed with deionized water and then put in the oven to dry at 60 °C for 12 h. 2 g of dry geranium leaves were put in contact with 50 mL of boiling Milli-Q water for five minutes. Once the mixture reached room temperature, it was centrifuged at 5000 rpm for 15 min and then filtered with a nylon membrane with a pore size of 0.22 µm to obtain a cell free aqueous extract. The GLE was stored in a freezer (0 °C) until use.

2.5. Nanoparticle synthesis and characterization

The syntheses were carried out in oil-in-water (O/W) microemulsions and nano-emulsions by mixing the right amounts of the reagents to obtain the desired composition. The silver stearate was used at 1 and 2.5 mM. This compound was solubilized in oil. The nano-emulsions were made by a low-energy emulsification method [28] consisting of