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# Fast and Eco-friendly Microwave-Assisted Synthesis of Silver Nanoparticles using Rosemary Essential Oil as Renewable Reducing Agent.

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**Abstract:** A green and fast methodology was developed to synthesize silver nanoparticles using rosemary essential oil (EO) as a renewable reducing agent. The synthesis process was microwave (MW) assisted, using a coaxial dipole antenna immersed into the reaction medium. This configuration was used to promote both: i) rosemary EO extraction by hydrodistillation, and ii) silver nanoparticle synthesis in an aqueous solution at atmospheric pressure. The effect of two different silver salt substrates and the time reaction on the morphology of the silver nanoparticles was explored. The coaxial microwave-assisted hydrodistillation of rosemary yields 0.4% (w/w) in 30 min and contains ethers (17%), ketones (50%) and alcohols (15%). Silver nanoparticles with a tuneable particle size (from 7 to 18 nm) and morphology (from spherical to rod-like shapes) were obtained in reaction times ranging from 2 to 30 min. The nanoparticle formation was followed by UV-vis spectroscopy and SEM imaging.

## Introduction

Nanoscience research and technology developments have led to silver nanoparticles (AgNPs) being one of the most investigated classes of noble metal nanoparticles worldwide.[1] This is mainly due to the fact that AgNPs have been successfully used in many areas, particularly as antibacterial agents, catalysts, sensing components and in biomedical applications.[1,2]

Silver nanoparticles obtained by low-energy consumption, and environmentally-friendly and low-cost approaches are heavily in demand. The physicochemical properties of the nanoparticles also play a key role. Control of the geometry, particle size and surface character of the metal nanoparticles is mandatory to obtain successful applications. Several approaches to the synthesis, such as chemical, biological and physical methodologies, have therefore been proposed.[2]

The chemical synthesis involves both reducing agents and stabilizers to promote and control the size and geometric shape of the silver nanoparticles in a stable colloidal dispersion.[3] However, the use of some of these assisting compounds, such as $NaBH_4$, polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), and ethylene glycol among others, is highly undesirable in view of their cost, toxicity and the environmental harm they pose.

However, AgNPs can also be obtained by biogenic synthesis. This relatively new approach employs non-toxic reagents derived from natural renewable sources ranging from unicellular microorganisms to plant extracts.[4] Due to their chemical nature, they can also act as both reducing and functionalizing agents.[4,5] Silver nanoparticles that are synthesized using aqueous plant extracts have been widely reported.[6] Special attention has focused on the use of aromatic or medicinal plants as raw material to obtain the reducing and functionalizing agents.[6] Plants such as rosemary, sage, thyme are available worldwide, which makes them a non-expensive and accessible resource.

Rosemary can be exploited as a feedstock to obtain aqueous extracts as reducing agents for the synthesis of silver nanoparticles.[7-9] Silver reduction using rosemary aqueous extracts is feasible due to the broad type of bio-compounds obtained during water extraction, such as polyphenols, polysaccharides, alkaloids and alcoholic compounds.

On the other hand, the direct use of essential oils as reducing agents for metals nanoparticles has been scarcely investigated.[10] Moreover, the synthesis of silver nanoparticles using rosemary essential oil has not been reported to date.

In view of its chemical composition and its environmental benefits, rosemary essential oil is a promising and renewable reducing agent compared to the oil-based compounds used to obtain silver nanoparticles. In addition, its intrinsic antibacterial and antioxidant activities [11] may act in synergy to improve the performance of silver nanoparticles as antibacterial agents.[12]

Additionally, the silver salt precursor is another factor that can affect the physicochemical properties of the nanoparticles. While silver nitrate is usually the most common salt precursor for the synthesis of nanoparticles, silver acetate has recently been exploited in a biogenic synthesis using kiwi fruit juice as a green reducing agent.[13] Other studies consider the thermal decomposition of silver acetate in mild conditions [14] and also the use of formic acid in concentrated aqueous solutions.[15]

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The synthesis of green metal nanoparticles requires renewable and cheap reagents and also needs to be effective in terms of energy and time consumption. Microwave assisted technology (MW) is a promising tool to tackle these issues. MW assisted chemistry significantly reduces the processing time, energy costs and equipment size compared to conventional methods.[16] Other advantages, such as higher conversion in some reaction configurations where MW, ionic liquids (strong MW absorbers) and nanoparticles were simultaneously used have been recently reported.[17] Therefore, in order to develop a sustainable methodology, the use of MW to assist chemical processes is highly recommended. As a result, the Microwave-assisted biogenic synthesis of silver nanoparticles can lead to a greener methodology as an alternative to the traditional chemical, physical and biogenic approaches. Some publications have also reported the synthesis of biogenic silver nanoparticles using MW irradiation.[18-20]

In spite of the advantages of using MW and plant extracts simultaneously, these approaches employ MW oven-type devices. MW oven-type reactors have two main drawbacks: the cost of the equipment and a difficult process scale-up. As an alternative, the coaxial MW technology makes use of a coaxial dipole antenna to apply the electromagnetic energy inside the reacting medium. This technique is highly flexible, cheap, easily scalable and controllable since different reactor geometries are possible unlike conventional close-device MW oven reactors.[21,22]

The coaxial dipole antenna can be used not only to assist MW reactions but also to assist separation operation units such as the in-situ MW assisted hydrodistillation of essential oils from different plants [23] and feedstock.[24]

The rosemary EO extraction process assisted by MW has been widely investigated using a Clevenger apparatus coupled to MW oven-type devices.[25-29] The MW extraction approach plays an important role in the yield, extraction time and chemical composition.[30] These factors are also influenced by growth, environmental conditions and genetic variety of the plant sample.[31]

This work therefore presents a green and affordable methodology to explore the feasibility of rosemary essential oil as a renewable and environmentally-friendly reducing agent to synthesize silver nanoparticles. The isolation of the EO by MW assisted hydrodistillation (MWHD) was investigated using the highly efficient coaxial microwave-assisted Clevenger-type extractor. To the best of our knowledge, this is the first time rosemary EO has been used for this purpose. Rosemary was chosen since it is cheap, renewable and easily available.

In the development of the innovative green synthesis process of silver NP, several sustainable steps were involved: i) First, rosemary EO was obtained by a MW assisted hydrodistillation process, without the use of chemical solvents, and further characterized by means of GC and GC-MS. ii) Then, diluted rosemary EO was used as reducing agent in the MW assisted synthesis of silver nanoparticles in aqueous solution at atmospheric pressure and reflux conditions. This step was performed without the use of additional chemicals as capping and reducing agents. The effects of two different silver salt substrates on the time processing and morphology of the silver nanoparticles

were also explored. The synergy found during the silver salt reduction by the simultaneous use of coaxial MW and rosemary EO provides a fast and affordable methodology. We developed an ultrafast green synthesis of silver nanoparticles with a tuneable size and morphology, using a combined system of silver acetate, rosemary EO and MW.

## Results and Discussion

### Isolation of rosemary essential oil by coaxial MW-assisted hydrodistillation

The in-situ MW assisted extraction (MWHD) of rosemary EO obtained a yield of 0.4% (w/w) after an irradiation time of 30 min. This result is comparable with the yield and extraction time described in the literature [25-27,30] which ranges from 0.3% to 0.6% (yield weight percentage) using a MW irradiation time from 10 to 75 min in conventional oven-type reactors. Hydrodistillation (HD) using conventional heating was also performed as a reference method of essential oil extraction. A longer extraction time (180 min) was needed to achieve a similar yield percentage The chemical composition by GC and GC-MS analysis of rosemary EO led to the identification of the volatile compounds of the rosemary EO obtained by both MWHD and conventional HD. Figure 1 shows the quantitatively predominant compounds obtained by MWHD and HD. α-Pinene, verbenone, camphor, 1,8-cineole, borneol and camphene were obtained by both methodologies. Although a similar trend was observed for the essential oil obtained by conventional HD, a significant difference in the qualitative chemical composition was obtained. MWHD yielded oxygenated monoterpenes (more than 30% of the total composition), while conventional HD resulted in the production of hydrocarbon monoterpenes (more than 20% of the total composition). Only one main ether compound (1,8-cineole).
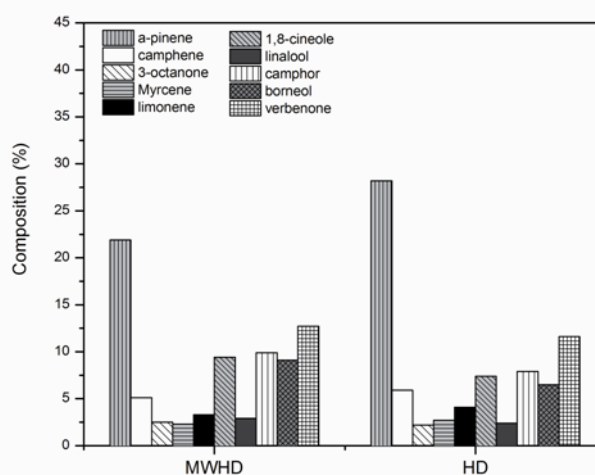


**Figure 1** Chemical composition of main compounds of rosemary essential oil obtained by microwave assisted (MWHD): α-Pinene (21.9%), verbenone (12.7%), camphor (9.9%), 1,8-cineole (9.4%), borneol (9.1%) and camphene (5.1%) and conventional hydrodistillation approaches (HD: α-Pinene (28.2%), verbenone (11.6%), camphor (7.9%), 1,8-cineole (7.4%), borneol (6.5%) and camphene (5.9%).
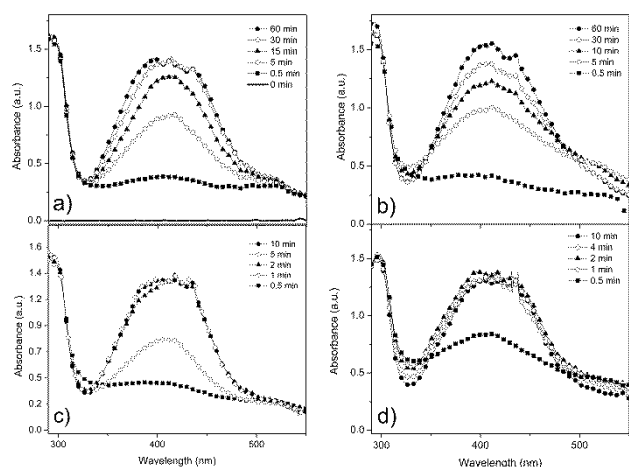
**Figure 2**. Uv-vis spectra of silver nanoparticle synthesis using rosemary EO as a reducing agent and thermal activation by: microwaves ((a) $AgNO_3$ and (c) $CH_3CO_2Ag$) and conventional heating ((b) $AgNO_3$-CH and (d) $CH_3CO_2Ag$).

was detected, which represents about 17% of the oxygenated monoterpenes. About 50% and 15% of the remaining compounds corresponded to ketones and alcohols, respectively.

The differences observed in the qualitative chemical composition (yielding a larger oxygenated monoterpene composition) obtained by the MWHD approach can be related to the MW interaction and the water solubility ($S_w$) of some essential oil compounds. The microwave interaction with a non-homogeneous material (such as a plant) is complex and can lead to a non-homogeneous heating of the material and an increase in the mobility of some chemical species more than others.

The energy transfer to the sample is carried out via three phenomena: i) dipolar heating; ii) Maxwell-Wagner effect at the surfaces between different materials; iii) Joule effect heating, due to the electrical conduction of the material.[32] The first effect is closely related to the permanent or induced dipole moment of the chemical species of interest. The heating also depends on the amount of water adsorbed into the material, since water shows a good absorbance of the microwave radiation at 2.45 GHz.

Thus, different compounds of the EO can be selectively heated regarding their dipole moment value, electric impedance and coordinated water.[33] During the extraction, once the temperature has increased, there is an increase in pressure within the exogenous glands caused by the expansion of the volatile compounds. This leads to cellular wall breakage and allows the essential oil to be released. The oxygenated compounds, such as 1,8-cineole and camphor, which have a highly complex permittivity, can be extracted more easily due to their strong MW interaction. On the other hand, the hydrocarbon monoterpenes, such as α-pinene and limonene, show less of an MW interaction, leading to a different release of the volatile compounds from exogenous secreting glands (washing and diffusion effects).[34] This possible mechanism is favoured since a high substrate/water ratio (1:5) was performed for both extraction approaches (MWHD and HD).

## Silver nanoparticle synthesis using rosemary essential oil as a reducing agent: the effect of microwave irradiation and the silver salt precursor

The rosemary EO obtained by the coaxial MWHD was used as a reducing agent in the green MW assisted AgNPs synthesis. Figure 2 shows the silver reduction followed by the in-situ monitoring of the plasmon extinction spectra measured by UV-vis spectroscopy of the silver salt precursor at the boiling temperature of the solution.

Two main absorption bands were detected once the silver nitrate solution achieved the boiling point temperature and the diluted rosemary EO was added. (see Fig. 2-a). The first absorption band below 300 nm can be assigned to the mixture of chemical compounds contained in rosemary EO. The second absorption band detected with a maximum absorption peak ($\lambda_{max}$) in the range 320 to 480 nm had a symmetric shape and appeared a few minutes after the rosemary EO had been added and grew continuously for 30 min (reaction time), while no significant changes were observed afterwards. This band corresponds to the surface plasmon resonance (SPR) of the growing silver nanoparticles.[35]

The shape of the SPR is sensitive to the size, shape and environment of metal nanoparticles.[35,36] In particular, symmetric and narrow shapes of the absorption peaks highlighted the presence of well-defined morphologies, such as spheres or ellipsoid particles without or with minimal intra-particle aggregation.[37] On the other hand a variation in the particle size distribution and aggregation results in a further broadening of the plasmon response. However, if the diameter increases, the peak plasmon resonance undergoes a red shift to longer wavelengths. Different particle shapes such as cubic, cylindrical or flat morphologies also led to an asymmetric peak plasmon resonance at longer wavelengths (up to 700 nm).[37]

The UV spectra of silver nitrate reduction using conventional heating as the thermal activation approach showed a symmetric and broad shape of the SPR absorption bands (see Fig. 2-b) and the reaction time to complete the silver reduction was longer (reaction time was explored up to 60 min) than the MW assisted synthesis.

Regarding savings in energy and processing time, clear advantages were shown by the MW assisted silver nanoparticle synthesis. First, not only was the time needed to achieve the water boiling temperature faster with the MW approach but also the reaction time was reduced by around 50%. The reduction in reaction time is directly related to savings in energy consumption leading to an overall less expensive process.

Silver acetate was also investigated as a different metal salt precursor (see Fig. 2-c and Fig. 2-d). Both in MW assisted and in conventional heating syntheses, the absorption band regarding EO was kept unchanged, the SPR absorption band, $\lambda_{max}$= 405 nm had a symmetric shape and the reaction time was 2 min. Silver acetate therefore produces a faster reaction both with a MW activation and conventional heating, however the MW approach provides energy saving in terms of the heating time needed to achieve the water boiling point.
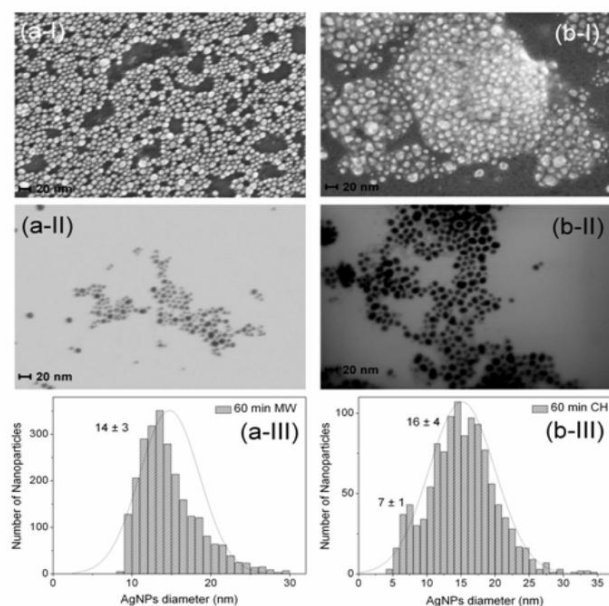
**Figure 3** Silver nanoparticles obtained using rosemary EO and silver nitrate: SEM (a), STEM (a-II) and Histogram (a-III) for the particle size distribution with average particle size obtained by MW (no. of counts: 2537). Same analysis for silver nanoparticles obtained using conventional heating in (b-(SEM image)), (b-II-(STEM image)) and (b-III-(Histogram, no. of counts: 1156)).

The morphology and size distribution of AgNPs obtained by the silver nitrate and silver acetate salt reduction at different reaction times described above, were characterized more extensively by the SEM and STEM techniques. Table 1 reports the main properties (shape and size) of the AgNPs synthesized starting from silver nitrate and acetate under MW and conventional heating. The literature results obtained in the synthesis using rosemary aqueous extracts are also reported for comparison.

Figures 3 show the representative micrographs of the silver nanoparticles obtained when silver nitrate was used as a metal salt precursor.

The MW assisted synthesis of AgNPs using silver nitrate led above all to spherical shapes and aggregate structures. A mean particle size distribution with a small diameter of $14 \pm 3$ nm was found (see Fig. 3-(a-III)).

On the other hand, the AgNPs obtained using silver nitrate and conventional heating showed a similar spherical morphology with two very well defined particle size distributions. One group of particles with a main diameter of $16 \pm 4$ nm can be clearly observed in Figs. 3-(b-I) and 3-(b-II). This particle size is quite similar to the results obtained by the MW approach ($14 \pm 3$ nm). Another group of silver nanoparticles with a smaller diameter ($7 \pm 1$ nm) was also identified. The nanoparticles with different sizes tend to aggregate and they seem to remain aggregated according to the size distribution, see Fig. 3-(b-I). The use of silver acetate not only accelerated the formation of AgNPs but also had a different effect on the morphology and particle size, see Fig. 4.

Silver acetate reduced by rosemary EO and MW gave rise to nanoparticles with shapes from round ball-like to well-defined

spheres, with a main diameter of $21 \pm 7$ nm, Fig. 4-b. Some rod-shaped AgNps were also observed. The rod particle size is better described in terms of the aspect ratio, defined as R=L/d, where L is the length and d the diameter of the nanorods.[38,39] The average R value was $3 \pm 0.8$ for the nano-rods (with an average length of $46 \pm 10$ nm and diameter of $16 \pm 2$ nm) obtained by the rosemary-silver acetate-MW assisted approach. In the case of the silver acetate reduction using conventional heating, the morphology and particle size are shown in Figs. 4-c and 4-d. While the most predominant morphology obtained was round-like particles with an average size of $28 \pm 7$ nm, nanoparticles with a rod-like shape were also detected and their R average value was measured as $2.5 \pm 0.6$. The particular rod-like particle morphology obtained by the silver acetate reduction has not been reported in other studies that used the same salt precursor.[13-15]

Therefore, the synthesis methodology here reported, using rosemary essential oil and silver acetate constitutes a promising system that can be used to produce silver nanoparticles with a tuneable shape and with specific sizes and properties.

The use of rosemary EO (where the bio-compounds are ketones, ethers and alcohols) and silver nitrate to synthesize silver nanoparticles produced smaller (from 7 to 18 nm) nanoparticles compared to their counterparts synthesized by aqueous extracts (see Table 1). On the other hand, the use of silver acetate and rosemary EO produced different shapes such as rods and spherical NPs. These findings are very important, since during the development of biogenic approaches to synthesize silver nanoparticles, research has mainly focused on using water extracts of plants. Essential oils produce smaller, functionalized and tuneable shape nanoparticles due to their different chemical and molecular composition compared to aqueous extracts used in traditional biogenic synthesis.
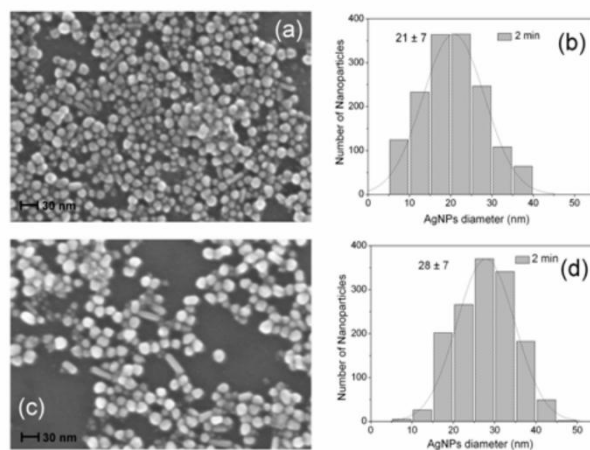


**Figure 4** Silver nanoparticles obtained using rosemary EO and silver acetate: Microwave approach (a-(SEM image), b-(Histogram, no. of counts: 1455), and conventional heating (c-(SEM image) and d- (Histogram, no. of counts: 744)).

**Table 1.** Main properties (shape and size) of the AgNPs synthesized starting from silver nitrate and acetate under MW and conventional heating. The literature results obtained in synthesis employing rosemary aqueous extracts, are also reported for comparison.

| | | Sulaiman, et al (2013)[8] | J. Das and P. Velusamy (2013)[9] | R. C. Fierascu et al. (2014)[7] | This work | | | |
|---|---|---|---|---|---|---|---|---|
| Silver Salt | | AgNO$_3$ | AgNO$_3$ | AgNO$_3$ | AgNO$_3$ | | CH$_3$CO$_2$Ag | |
| Rosemary extracts | | Aqueous extracts | Aqueous extracts | Aqueous extracts | Essential oil | | Essential oil | |
| Heating approach | | Conventional heating | Conventional heating | Conventional heating | Microwave irradiation | Conventional heating | Microwave irradiation | Conventional heating |
| Reaction time (min) | | 30 | 70 | 720 | 30 | 60 | 2 | 2 |
| Particle size and morphology | Spherical shape d$_{mean}$ (nm) | 60 | 42 | 76 | 12±2 | 7±1 16±4 | 21±7 | 28±7 |
| | Rod like (R) | Not observed | Not observed | Not observed | Not observed | Not observed | 3±0.8 | 2.5±0.6 |

## Conclusions

Rosemary essential oil was successfully used as a green and versatile reducing agent to synthesize silver nanoparticles in rapid MW assisted water dispersion. The use of a versatile coaxial MW technology for renewable reducing agent extraction and silver nanoparticle synthesis was a key factor in successfully developing a fast and cheap methodology with a minimal environmental impact. Figure 5 shows the green methodology developed in this work to obtain silver nanoparticles.

Silver nanoparticles with a tuneable particle size (from 7 to 28 nm) and morphology (from spherical to rod like shapes) can be obtained by a combining MW, rosemary EO and silver salt precursor. Morphology changes are linked to the silver salt precursor and time processing, while the particle size distribution and aggregation pattern are more influenced by the heating activation protocol, both enhanced by the use of microwaves irradiation.

Besides its greener advantages, the use of rosemary essential oil obtained smaller silver nanoparticles than those obtained from its aqueous extracts. The combined use of silver nitrate with MW produced smaller NPs with a narrow size distribution, and silver acetate and MW led to a faster approach.

The silver nanoparticles obtained by the combined use of silver acetate and rosemary EO led to an ultrafast methodology with rapid time processing (2 min) and considerable energy savings compared with methodologies that make use of the same salt precursor (silver acetate) namely the biogenic synthesis with reaction times ranging from 30 to 180 min,[13] the thermal decomposition (60 min),[14] the use of aqueous formic acid mixtures (processing times ranging from 150 to 350 min) [15] or a different salt precursor such as silver nitrate. In addition, rosemary EO and silver acetate produce different NP morphologies, such as rod NPs without the use of other assisted chemicals. On the other hand, the use of silver nitrate as a salt precursor produced less intra-particle aggregation than when using silver acetate.

In conclusion, the use of rosemary EO and silver acetate coupled with MW thermal activation represents a greener approach and leads to a very promising scale up process.

Further investigations applying the coaxial MW assisted continuous reaction on AgNPs and other metal nanoparticles (copper and zinc oxide) synthesis using different essential oils and are currently carried out.

## Supporting Information Summary

The Experimental Section is reported in the Support information.
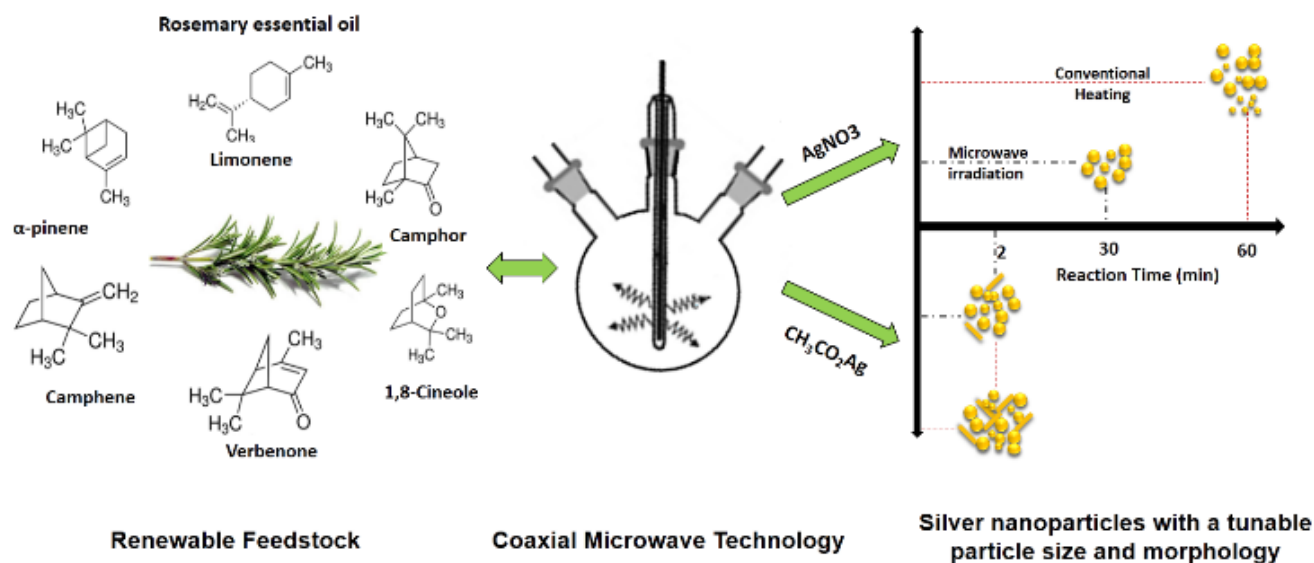
## Acknowledgements

**Figure 5** Method used to synthesize silver nanoparticles.

**Keywords:** Essential oil • Microwave • Nanoparticles • Silver

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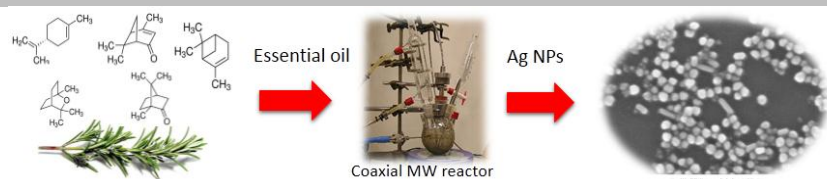


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**Fast and eco-friendly microwave-assisted synthesis of silver nanoparticles using *Rosemary* essential oil as renewable reducing agent**

An ultrafast green synthesis of silver nanoparticles with a tuneable size and morphology, using a combined system of silver salts, rosemary EO and MW is shown. The new reduction agent is available worldwide, non-expensive and it poses intrinsic antibacterial and antioxidant activities that it may act in synergy to improve the performance of silver nanoparticles as antibacterial agents.