PLANT MEDIATED SYNTHESIS OF SILVER NANOPARTICLES USING EXTRACTS FROM Tilia cordata, Matricaria chamomilla, Calendula officinalis AND Lavandula angustifolia FLOWERS

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ABSTRACT

In this work, a simple, rapid and efficient green method for silver nanoparticles synthesis was developed by using extracts from four medicinal plants: flowers of Tilia cordata, Matricaria chamomilla, Calendula officinalis and Lavandula angustifolia, acting as reducing and capping agents. Silver nitrate was used as a precursor. The effect of the sunlight exposure and/or the sonication treatment on the synthesis process was investigated. The ultraviolet–visible spectroscopy (UV-Vis) studies showed surface Plasmon resonance peaks between 432 nm and 448 nm, characteristic of spherical silver nanoparticles. The morphology of the nanoparticles produced was investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The proposed method could be easily implemented for any kind of scientific or industrial application due to its cost effective nature.

Keywords: silver nanoparticles, green synthesis, Tilia cordata, Matricaria chamomilla, Calendula officinalis, Lavandula angustifolia.

INTRODUCTION

Silver nanoparticles (AgNPs) have attracted increased research interest in the recent years due to its unique optical [1], catalytic [2] electronic [3] and antibacterial properties [4]. Different approaches through physical, chemical or biological methods may be used for the synthesis of AgNPs [5]. Physical methods, generally including evaporation-condensation [6] and laser ablation [7] techniques, allow obtaining silver nanoparticles of no chemical contaminants and uniform size distribution. However, they have some disadvantages such as a low productivity and/or high energy consumption. Chemical reduction methods are the most commonly used ones. A solution containing silver ions is created by mixing a silver compound, for example silver nitrate, in an aqueous, a non-aqueous or a polyol solvent. The nanoparticles are formed by using stabilizers, capping agents or surfactants. Furthermore, reduction by using sonochemical approach offer several advantages over other conventional techniques such as rapid synthesis and higher yields [4]. However, all chemical methods involve the use of chemicals, some of which are harmful. Biological (green) approaches are proposed as a simple, cost effective and environmental friendly alternative for synthesis of AgNPs. One such promising method is the synthesis of silver nanoparticles using plant-based extracts. The review of the current literature, listed in Table 1, reveals the use of extracts from a large number of plants as sources of production of AgNPs compatible for biomedical or pharmaceutical applications. The plant leaves are the most commonly used parts, even though roots, seeds, pods and flowers can also be used. Biomolecules, such as proteins [30], amino acids [31], enzymes [32], flavonoids [33], polysaccharides [34], tannins [35], terpenoids [36] etc., present in the plant extracts act as reducing, capping and
stabilizing agents for the synthesis of silver nanoparticles. Nonetheless, the nucleation and the growth mechanisms of AgNPs by these techniques are complex and still remain not fully understood.

In this study, the main objective is to develop a rapid green method for plant-mediated synthesis of silver nanoparticle. The relationship between the operational conditions, as the sunlight or/and ultrasound irradiation, during the synthesis and the final size and shape of the nanoparticles is examined by using structural and morphological analysis.

**EXPERIMENTAL**

**Preparation of plant extracts**

Fresh *Tilia cordata*, *Matricaria chamomilla*, *Calendula officinalis* and *Lavandula angustifolia* flowers (Fig. 1) were collected from the local area of Sofia (Bulgaria) in June-July 2016, shade-dried at room temperature and powdered by hand crushing. Four aqueous extracts were prepared separately by placing 4 g of each plant material in 100 ml boiling distilled water under magnetic stirring (Boeco MMS-3000, Germany) for 15 min. The extracts were allowed to cool down and then filtered through Whatman No.1 filter paper followed by 0.22-µm microfiltration (Millex® filter).

**Silver nanoparticles synthesis**

An accurate concentration of 5 mM silver nitrate was prepared by dissolving AgNO₃ (> 99.8 %, Valerus Co., Bulgaria) in distilled water under magnetic stirring (Boeco MMS-3000, Germany) at room temperature. Different samples (containing extract of *Tilia cordata*, *Matricaria chamomilla*, *Calendula officinalis* or *Lavandula angustifolia* respectively) were prepared separately through a slow addition of 0.5 ml of the aqueous extract to the silver salt solution at constant stirring. The volume of each sample was adjusted to 100

<table>
<thead>
<tr>
<th>Plant</th>
<th>Used part of the plant</th>
<th>Particle shapes</th>
<th>Particle size (nm)</th>
<th>References</th>
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<tr>
<td><em>Arbutus unedo</em></td>
<td>leaves</td>
<td>spherical</td>
<td>&lt; 30</td>
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<td>spherical</td>
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<tr>
<td><em>Azadirachta indica</em></td>
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<td>&lt; 20</td>
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<tr>
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<td>17 – 61</td>
<td>[12]</td>
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<td>20 – 30</td>
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<td>spherical</td>
<td>25 – 40</td>
<td>[29]</td>
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Table 1. Various biological sources for nanoparticle synthesis.
Then, the samples were exposed to natural sunlight irradiation for 1 h. At this stage, the colorless solution of the mixture turned to an intense yellow-brown color, characteristic of silver nanoparticles. Another series of samples were prepared following the same procedure. Then an active carbon (AC) was added to the solutions which were further evaporated at 85°C and constant stirring. These samples were used for the X-ray powder diffraction (XRD) measurements. In order to study the effect of sonication on the AgNPs synthesis process, another set of experiments was performed by placing the samples first for 6 min in a conventional ultrasonic bath (Siel UST 2,8-100, 120 W, Siel Ltd. Bulgaria), followed by 54 min of sunlight exposure.

The time-dependent evolution of the obtained solutions containing silver nanoparticles was studied by UV-Vis spectrophotometry (Varian Cary 100, Varian Inc. USA). The high-resolution transmission electron microscopy (TEM) analysis (JEOL JEM 2100, 80–200 kV, Jeol Ltd. Japan) was carried out on samples prepared by placing a drop of the solution on a carbon-coated copper grid subsequently dried in the air. The X-ray powder diffraction (XRD) data of the composites (Active carbon / silver) were collected on Philips APD 15 X-ray diffractometer fitted with a mounted graphite monochromator using CuKα radiation (λ = 1.54178 Å) over the 2θ range of 10° - 90°. The samples’ XRD patterns were identified using standards from the Inorganic Crystal Structure Database (ICSD).

RESULTS AND DISCUSSION

The sunlight irradiation of the reaction mixture containing 5 mM silver nitrate and 0.5 ml plant extract for 1 h at room temperature results in color changes of the samples from transparent to yellow-brown as the time duration increases. It is found that the aqueous solution is cloud, turning rapidly (after few minutes) dark brown. A black precipitate is formed in case a plant extract greater than 0.5 ml is used for a mixture of 100 ml. Photographs of the samples prepared with *Tilia cordata*, *Matricaria chamomilla*, *Calendula officinalis* and *Lavandula angustifolia* and 1 h sunlight irradiation are presented in Fig. 2. The corresponding UV-Vis absorption spectra (Fig. 3) show a surface plasmon absorption bands with maxima at ca 436 nm, 448 nm, 440 nm and 432 nm, respectively. They correspond to the typical surface plasmon resonance (SPR) of the conducting electrons from the silver nanoparticles.
Furthermore, the evolution of the AgNPs colloidal solutions is studied by measuring the UV-Vis spectra for 24 h reaction time. As shown in Fig. 3, the peak absorbance is increased indicating that the amount of silver nanoparticles increases. No obvious change in the peak position is observed for the samples prepared with *Tilia cordata* and *Lavandula angustifolia*. The stable peak position suggests that the nanoparticles do not aggregate. However, the shifting of the peak to higher wavelength for samples synthetized with *Matricaria chamomilla* and *Calendula officinalis* indicates that AgNPs agglomeration takes place in the solutions.

The obtained results suggest that the synthesis of AgNPs is driven by the sunlight irradiation. Indeed, neither yellow-brown color, nor a plasmon resonance peak is observed for a silver nitrate solution mixed with a plant extract under dark conditions. Fig. 4 shows the results obtained for AgNPs synthesized with *Tilia cordata*. Similar results are found with the rest of the plant extracts used in this work. The dark control

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**Fig. 2.** Photographs of the colloid solutions containing silver nanoparticles obtained with *Tilia cordata*, *Matricaria chamomilla*, *Calendula officinalis* and *Lavandula angustifolia* flowers extract after 1 hour of sunlight irradiation.

**Fig. 3.** Evolution of the UV-Vis spectra of AgNPs synthesized by using 5 mM silver nitrate and *Tilia cordata*, *Matricaria chamomilla*, *Calendula officinalis* or *Lavandula angustifolia* flowers extract, for 1 hour of sunlight irradiation and after 24 hours.
experiments are performed in glass vessel wrapped by four layers of aluminum under conditions identical with those applied to the samples irradiated by sunlight.

Furthermore, the effect of sonication during the synthesis of silver nanoparticle is investigated. The reaction mixtures are treated in an ultrasonic water bath for 6 min. Subsequently they are subjected to sunlight irradiation for 54 min. However, no color change is observed during the sonication. No significant difference is also found by comparing the absorbance spectra of the AgNPs prepared by sonication and sunlight irradiation with those formed only by sunlight irradiation. Fig. 5 shows the UV-Vis spectra of AgNPs synthesized with *Tilia cordata* extract. Similar results are found for the rest of the plant extracts used. No change in the color is noted for solutions sonicated for more than 6 min. However a black precipitate (probably silver oxide) is formed, indicating that the reduction process is negatively influenced, leading therefore to a poor capping process. The results reported verify that the plant-mediated AgNPs formation and growth are induced by the sunlight.

The AgNPs size, shape and degree of agglomeration are quite evident from the TEM images of different magnifications (Fig. 6). These results show that the particles are spherical with an average size of ~ 20 nm. There are also some particles of a size in the range of 5 nm - 10 nm. It is seen that some AgNPs are agglomerated into small aggregates. When AgNPs are synthetized with *Tilia cordata*, the aggregates are coated with a thin organic layer, which probably acts as a capping organic agent (Fig. 6a). The Selected Area Electron Diffraction (SAED) patterns show concentric rings, indicating that the nanoparticles are crystalline in nature.

Fig. 7 shows the XRD patterns of all synthesized samples juxtaposed to active carbon (AC) as well as standards for Ag (ISCD 44387) [37] and graphite (ISCD 52230) [38]. The silver nanoparticles are deposited onto the surface of active carbon for these measurements. The main motive of using AC as a substrate is to prevent the subsequent oxidation of Ag in the course and following the synthesis. Another one refers to the pattern which is predominantly amorphous featured by two halos (20 of 18° - 30° and 40° - 46°, correspondingly). There is a single peak (20 of 26.6°) marking the graphite form [38] of the AC but this peak does not overlap with any silver reflections. All synthesized samples display peaks (20 of 37.9°, 44.1°, 64.5°, 77.8° and 81.5°) corresponding to Ag with a face centered cubic (fcc) lattice and a space Fm-3m group. The AC’s halos and peak are well observed in the samples diffractograms suggesting that there is no chemical transformation of the active carbon during the synthesis. There are small unidentified peaks (marked by asterisks in Fig. 7) at 20 of 20.9°, 32.1° and
Fig. 6. TEM images and corresponding SAED patterns of silver nanoparticles synthesized with a) *Tilia cordata*, b) *Matricaria chamomilla*, c) *Calendula officinalis* and d) *Lavandula angustifolia* flowers extract.

Fig. 7. XRD patterns of the as-synthesized composites, active carbon and Ag standard (ICSD 44387).
50.1° for almost all samples, most likely caused by the plant extracts.

The as-prepared AC–Ag composites are a subject of interest to future investigation in respect to their catalytic activity and possible application in an air-metal electrochemical system.

CONCLUSIONS

Four plant flower extracts show a reduction and stabilization ability for silver nanoparticles synthesis at room temperature. The results suggest that the growth of AgNPs is driven by the sunlight irradiation. The TEM observations show a spherical nature of the particles of a size ranging from 5nm to 30nm. The X-ray diffraction patterns are assigned to the face-centered cubic (fcc) structure of AgNPs.

REFERENCES

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37. Inorganic Crystal Structure Database #44387.