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SYNTHESIS OF SILVER NANOPARTICLES USING HYDROALCOHOLIC EXTRACT OF PRUNUS MAHALEB (MAHALEB CHERRY) AND MALUS PURPUREA (BLUTAPFEL)

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Abstract: *The aim of the paper was to develop methods for obtaining environmentally friendly nanomaterials. The plant extracts used in this paper were characterized by spectroscopic methods (UV-Vis, FTIR and Raman). In this regard, it was used vegetal material at the optimal time and in the period of maximum maturity of the plant, from the geographical area of Dâmbovița County, and being processed in fresh / dry status. The nanomaterials formed with the help of these plant extracts (Ag) have also been characterized by various analytical techniques (UV-Vis, FTIR, Raman) analysis. The bioactive compounds existing in plant materials are responsible for the bio reduction of silver (Ag+ to Ag0) ions, as well as for the stabilization of silver nanoparticles.*

Keywords*: nanomaterials, silver nanoparticles, Prunus mahaleb (Mahaleb cherry), Malus Purpurea (Crab apple)*

1. INTRODUCTION

*Prunus mahaleb (*Mahaleb cherry*) and Malus Purpurea* (Crab apple) are shrubs that belong to the *Rosaceae family.*

Prunus mahaleb originates from Central and Southern Europe, Turkey, Persia, Irak and Syria. It is found in rocky places or in forests. It is a shrub with thick branches. Its fruits are a sort of cherry and the leaves are round with jagged edges. Its white flowers have a sweet and pleasant smell and open up during the spring in small bunches. The fruits are black, meaty, bitter. In South West Asia, its pips are known as „mahaleb" and are a highly appreciated spice [http://decostyle.mayra.ro/legume/mirodenii/dracila-rhus-typhina-si-visinul-turcesc/236/]

Malus Purpurea is an ornamental apple tree that has magenta coloured leaves during the spring, red flowers that blosson during aprilie and its fruits are small, of approximately 1,5cm in diameter and red. It's a hybrid obtained by crossing Malus atrosaguinea with Malus pumila Mill. The first description was made in 1910 by A. Barbier as a variety of wild japanese apple tree (Malus floribunda var Purpurea, basionim) after which, in 1920 was published by Alfred Rehder [1].

In this paper, taking into account our experience about the nanoparticles preparation in vegetal extracts, we intend to prepare the nanomaterials formed with the help of these plant extracts (Ag) and to characterize them by various analytical techniques (UV-Vis, FTIR, Raman). Also, for all of them, the determination of the phytochemical profile of extracts (polyphenols, flvonoids and antioxidant activity), have been determined as an important parameter for exploring potential practical applications.

2. EXPERIMENTAL PART

Materials

Silver nitrate (10^{-3} M $AgNO_3$), were provided by Sigma-Aldrich. DPPH (2, 2-diphenyl-1-picryl-hydrazyl-hydrate) was supplied by Sigma-Aldrich company.
Prunus mahaleb fruits was collected from Valea Voievozilor area and *Malus purpurea* fruits from Voinesti (private gardens).

The fruits of the two plants were dehydrated in a forced air circulation drying stove Venticell for 24 h at 30°C. 2 g of dried fruit were put in a Berzelius glass with a volume of 25 mL in which was added hydroalcoholic solution (ethanol:distilled water) after which it was boiled for 10 minute. The obtained extract was then filtered and left to cool to room temperature. Silver nitrate 10^{-3} M was used for the synthesis of the silver nanoparticles in aqueous solution. The prunus mahaleb and malus purpurea extract was mixed with the aqueous solution of silver nitrate (1: 1).

The phytochemical quantification procedures were used for the determination of total flavonoids, total polyphenols and antioxidant activity.

Equipments

The absorption spectra for the fruit extracts and the silver nanoparticles have been recorded with an Evolution 260 Bio UV-VIS spectrophotometer in the wavelength range of 190 –1100 nm.

The functional groups of the fruits extracts were determined by infrared spectroscopy Fourier transformed using a Vertex 80 spectrometer equipped with attenuated total reflection accessory (ATR), in the range of 8000-400 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were recorded as transmittance.

For Raman spectroscopy it was used a portable IR Raman spectrometer Xantus-2 from Rigaku which is operated through software Micro 2020. The device can operate at two wavelengths 785 nm or 1064 nm. Fruit extracts were scanned at 1064 nm laser wavelength, 3000 ms exposure time and with an average of 3.

Malus purpurea	*Prunus mahaleb*

Figure 1. The photos of the plants

Determination of Total Flavonoid Content

The total flavonoid content (CTF) determination was carried out as follows: the preparation of the calibration curve, for which catechin was used as a standard and solutions of different concentrations were prepared (20, 40, 60, 80 and 100 mg/L) by dilution. In a volumetric flask of 10 mL were introduced: 1 mL sample + 4 mL distilled water + 0.3 mL NaNO2 5%. After 5 minutes 0.3 mL $AlCl_3$ 10% was added and after another 5 minutes 2 mL NaOH 1M. It was brought to the mark with distilled water and stirred in order to homogenize the solution. After homogenization, the solution was measured at λ= 510 nm, against blank (distilled water), and the results obtained (in mg C.E./L (catechin gram equivalents)) are given below.

Determination of the Total Polyphenol Content

The determination of the total polyphenol content (CTP) was carried out according to the method set out in SR ISO 14502-1 standard. Part 1.

1 mL of the sample was mixed with 5 mL Folin-Ciocâlteu solution, under continuous stirring, followed by a rest of 3-8 minutes. 4 mL Na_2CO_3 has been added and then kept at room temperature for 60 minutes. The solution was measured at λ = 765 nm, in relation to blank (distilled water), and the results obtained in mg GAE/L (equivalents gram gallic acid, for which a standard solution was prepared to perform the calibration curve).

Determination of the Antioxidant Activity

For this measurement DPPH (2,2-diphenyl-1-picril hydrate) was used, after the following procedure: over 0,5 mL extract from the plant was added 1 mL DPPH from the solution initially prepared (2 mg DPPH/100 mL methanol), then stirred the solution for 30 minutes after which it was left in the dark for another 30 minutes at room temperature. For the preparation of the reference sample (A_{blank}), the same was done as in the case of samples with vegetal extract (instead of vegetal extract, 0.5 mL of distilled water was used). The samples were analyzed by UV-Vis technique (Specord M 400, Analytic Jena, Germany), at wavelength λ = 517 nm, and the calculation of antioxidant activity was performed according to the formula:

$$AA\ \% = (A_{blank} - A_{extract} / A_{blank}) * 100$$

where:

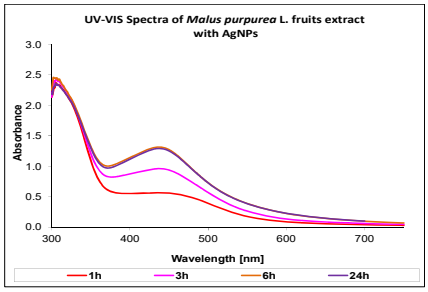
A_{blank} = 0.5 mL distilled water + 1 mL DPPH;
$A_{extract}$=0.5 mL sample + DPPH

3. RESULTS AND DISCUSSION

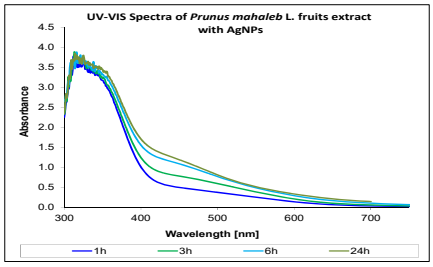
The UV-VIS spectroscopy was the first analyze used for the two extracts. Figures x and y show the UV-VIS spectra for *Prunus mahaleb* (a) *and Malus Purpurea* (b).

The wavelenght spectrum was recorded between 300-700 nm. The silver nanoparticles in the aqueous solution of *Malus Purpurea* fruits extract, showed a

maximum absorbtion at 440 nm [2,3] while the silver nanoparticles in the aqueous solution of *Prunus Mahaleb* fruits extract was slightly observed at the same wavelength as a large shoulder.



(a)



(b)

Figure 2. UV-VIS spectra for Ag nanoparticles in *Malus Purpurea* (a) *and Prunus mahaleb* (b)

The FT-IR spectra of aqueous solution of fruits extract silver nanoparticles shows the presence of transmittance peaks at 3270, 1632, 1016, 316 cm^{-1} (*Prunus Mahaleb)* and 3270, 1634, 1010, 396, 373, 356 cm^{-1} (*Malus Purpurea*). The first peak are specific to O-H stretching (functional group of the phenols), second peak may belong to the C=C bonds of flavonoids; meanwhile the peak intensity at FT-IR spectral analysis of the fruits extracts of *Prunus Mahaleb* and *Malus Purpurea* showed the presence of –OH functional group [4,5].

Figure 3 shows the FTIR spectrum obtained for the colloidal solution of silver nanoparticles based on *Malus purpurea* fruit extract with a spectral maximum at the following wavelengths: 3300 cm^{-1} (possible OH, H2O bonds), 1640 cm^{-1} (possible C=C bonds, aromatic bonds) and 1020 cm^{-1} (OH bonds). This spectrum is similar with *Prunus mahaleb* spectral maxima.

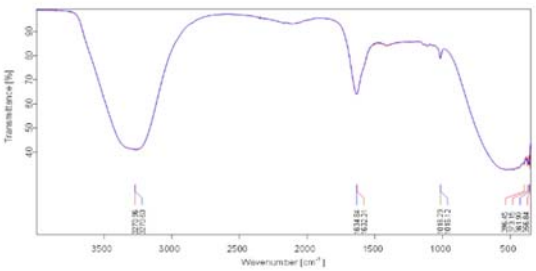
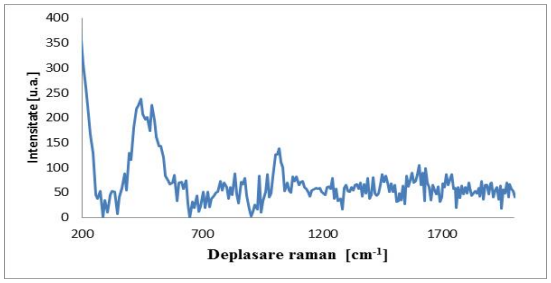
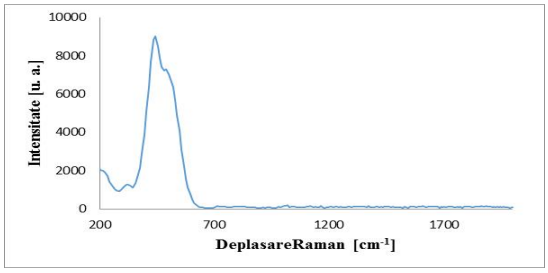


Figure 3. The FTIR spectra of Ag nanoparticels in *Malus Purpurea* and *Prunus Mahaleb*



(a)



(b)

Figure 4. The Raman spectra of Malus Purpurea (a) and Prunus Mahaleb (b) fruits extracts

The Raman spectra of Prunus Mahaleb and Malus Purpurea fruits extracts were recorded in the region 200 – 2000 cm^{-1} with 1064 nm stabilized laser. The Raman wavelengths for the same solution is shown in Figure 4, where spectral maximums are observed in the zones 442 cm^{-1} (possible bindings C=O, C(OH), 490 cm^{-1} (possible deformations C to O) and 1 019 cm^{-1} (aromatic bonds).

The Raman spectrum for the same solution is shown in Figure 4) where spectral maximums are observed in the zones 303 cm^{-1} (possibly amylose, amylopectin, pyranosic ring)), 442 cm^{-1} (possible C–O, C–OH bonds) and 490 cm^{-1} (possible C–O deformations).

It is well established that the phenolic compounds appeared in the phytochemicals such as flavonoids and polyphenols. Recent studies show that several plant products, including polyphenolic substances (e.g., flavonoids and tannins) and various herbal extracts, show antioxidant [6-10] activities.

The values of the total flavonoid content (C.T.F.) obtained for hydroalcoholic extracts using different component parts of the plant material (mg C.E./L) are: 380.25 for *Malus purpurea* and 137.50 for *Prunus mahaleb*.

The values of the total polyphenol content (C.T.P.) obtained for hydroalcoholic extracts using different parts of the plant material (mg GAE/L) was 380.25 for *Malus purpurea* and not detected for Prunus mahaleb.

The values of antioxidant activity obtained for hydroalcoholic extracts using different component parts of plant material (AA %)) are: 99.45% for *Malus purpurea* and 56.09% for *Prunus mahaleb*.

We concluded that the highest polyphenols, flvonoids concentrations and antioxidant activity, the highest yields for silver nanoparticles.

4. CONCLUSIONS

In this work, the following objectives were achieved: (1) harvesting the vegetal material, at the optimal time and in the period of maximum maturity of the plant, from the local therapeutic vegetal source, both from the natural environment and from its own ecological cultures, from the geographical area of Dâmbovița County, Romania; (2) obtaining natural hydroalcoholic extracts from native plants by non-invasive extraction methods (maceration); (3) determination of the phytochemical profile of extracts (polyphenols, flvonoids and antioxidant activity), important for exploring potential practical applications; (4) the generation of nanoparticles by fast, environmentally friendly and low-cost methods; (5) Physico-chemical characterisation of nanomaterials obtained by different analytical techniques (UV-Vis, FTIR, Raman).

REFERENCES

[1] Rehder, A. (1919). New Species, Varieties And Combinations From The Herbarium And The Collections Of The Arnold Arboretum. *Journal of the Arnold Arboretum*, *1*(1), 44–60.

[2] Ion R-M, Nyokong T, Nwahara N, Suica-Bunghez I-R, Iancu L, Teodorescu S, et al. Wood preservation with gold hydroxyapatite system. *Heritage Science*. 2018;6(1):1-12.

[3] Huang J., Qingbiao Li., Sun D., Lu Y., Su Y., Yang X., Wang H., Wang Y., Shao W., He N., Hong J., Chen C. (2007), Biosynthesis of silver and gold nanoparticles by novel sundried *Cinnamomum camphora* leaf, *Nanotechnology*, 18(10):105104.

[4] Chandran S. P., Chaudhary M., Pasricha R., Ahmad A., Sastry M. (2006), Synthesis of gold nanotriangles and silver nanoparticles using *Aloe vera* plant extract, *Biotechnology Progress*, 22(2):577–583.

[5] Gardea-Torresdey J. L., Gomez E., Peralta-Videa J. R., Parsons J. G., Troiani H., Jose-Yacaman M. (2003), *Alfalfa sprouts*: a natural source for the synthesis of silver nanoparticles, *Langmuir*, 19(4):1357–1361.

[6] Subhankari J., Nayak P. (2013), Synthesis of copper nanoparticles using *Syzygium aromaticum* (Cloves) aqueous extract by using green chemistry, *World Journal of Nanoscience and Nanotechnology*, 2(1):14–17.

[7] Iravani S., Zolfaghari B. (2013), Green synthesis of silver nanoparticles using *Pinus eldarica* bark extract, *BioMed Research International*, 2013:639725-1–639725-5.

[8] Song J. Y., Kim B. S. (2009), Rapid biological synthesis of silver nanoparticles using plant leaf extracts *Bioprocess and Biosystems Engineering*, 32(1):79.

[9] K. Jha, Prasad K. (2010), Green synthesis of silver nanoparticles using Cycas leaf, *International Journal of Green Nanotechnology*, 1(2):P110–P117.

[10] Suica-Bunghez I. R., Covaliu I. C., Sorescu A. A., Nistor L. C., Constantin M., Raut I., Ion R. M., Silver nanoparticles obtained by eco-friendly method using *Galanthus nivalis* plant for wood conservation, *Optoelectronics And Advanced Materials – Rapid Communications* Vol. 16, No. 1-2, January-February 2022, p. 79 - 89