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Green Reduction of Silver Ions to Silver Nanoparticles Using Aqueous Plant Extracts †

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Abstract: Silver nanoparticles are used in numerous scientific fields due to their versatile properties and because their surface can be functionalized with different biological molecules. Their synthesis follows both conventional and unconventional routes and, in recent years, the methods that start from plants are constantly detaching from the hazardous, time consuming chemical methods. This paper presents the green synthesis of silver nanoparticles from St. Benedict's herb (*Geum urbanum*) and its corresponding aqueous extracts via two different temperature conditions: room temperature, for 24 h with no additional stirring and 50^{0}C, for 30 min under a constant stirring of 600 rpm. Silver nanoparticles were then characterized using UV-Vis spectroscopy at well—established time intervals in the range of 250–650 nm and FTIR spectra were recorded to show the presence of different functional groups. DLS technique was used to investigate the particle size and zeta potential was also measured to analyze the stability of the green synthesized silver nanoparticles. TEM microscopy revealed a spherical—shape profile of the green synthesized silver nanoparticles and optical microscopy images were also recorded. Also, the antioxidant activity was determined using the DPPH method and compared to that of the crude aqueous extracts.

Keywords: green synthesis; silver nanoparticles; *Geum urbanum*; antioxidant activity

1. Introduction

Metallic nanoparticles are at the leading edge of nanotechnology, a scientific field that in constantly and rapidly growing ever since the physicist Richard P. Feynman, a Nobel Prize laureate, first visualized it in 1959. Practically, metallic nanoparticles can be considered a bridge between bulk materials and molecular structures and, therefore, they exhibit unique physical-chemical properties that allows their use in numerous applications [1,2].

St. Benedict's herb (*Geum urbanum*) is an astringent herb, used mainly for the treatment of different problems affecting the mouth, throat and the gastro-intestinal tract. It helps heal mouth ulcers and reduces irritation of the stomach and gut.

The phytochemicals that naturally occur in *Geum urbanum* such as saponins, flavonoids, carbohydrates or polyphenols have anti-inflammatory and antioxidant properties and can reduce the metal ions to metallic nanoparticles in a one - pot environmentally friendly synthesis [3,4].

Silver nanoparticles (AgNPs) due to their antibacterial, antioxidant and antifungal properties, have various applications in medicine, different industry branches, biology, as sensors, drug delivery systems, etc. [5,6].

This paper presents the green synthesis of silver nanoparticles from St. Benedict's herb (*Geum urbanum*) and its corresponding aqueous extract via two different temperature conditions: room temperature and 50 °C. Silver nanoparticles are then characterized using UV-Vis and FTIR spectroscopy and their antioxidant activity is determined using the DPPH method. TEM microscopy revealed a spherical—shape profile of the green synthesized silver nanoparticles and optical microscopy images were also recorded.

2. Materials and Methods

2.1. Materials

Silver nitrate ($AgNO_3$), DPPH, (2,2-diphenyl-1-picryl-hydrazyl-hydrate stable free radical). The distilled water used in all our experiments was freshly prepared in the laboratory.

Geum urbanum was purchased from the local natural shop as dried plant (tea).

2.2. Preparation of Aqueous Plant Extracts

St. Benedict's herb (*Geum urbanum*) was purchased ready dried and used as such for the preparation of the aqueous extract as follows: 25 g of dried plant were weighted, transferred into a "French press" type extractor and 250 mL distilled water was added; the mixture was left for 24 h, at 4 °C (in a refrigerator) to infuse so that all the active ingredients were released into the aqueous extract; the resulted aqueous extract was filtered and a clear aqueous extract was obtained.

2.3. Green Synthesis of Silver Nanoparticles

An aqueous 1×10^{-3} M solution of silver nitrate ($AgNO_3$) was freshly prepared and used for the phytosynthesis of AgNPs from Geum urbanum as follows: 5 mL aqueous extract was mixed with 50 mL 1×10^{-3} M $AgNO_3$ solution and left for 24 h in the dark, at room temperature. After 24 h, the Geum urbanum—AgNPs (GU—AgNPs) was agitated in an ultrasound bath, for 30 min, at 50 rpm. At 500 C, 5 mL aqueous extract was mixed with 50 mL 1×10^{-3} M $AgNO_3$ solution, heated under continuous stirring (500 rpm) for 30 min. The heat was turned off and the GU–AgNPs suspension was stirred at room temperature for 30 min and left for 24 h in the dark.

2.4. Characterization Methods

The absorption spectra for Geum urbanum aqueous extract and AgNPs were recorded using a M 400 Carl Zeiss Jena UV–Vis spectrometer in the wavelength range of 250–800 nm. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a Vertex 80 FT-IR spectrometer equipped with high-resolution Hyperion 3000 microscope, in the range of 8000–400 cm^{-1}.

Dynamic light scattering (DLS) spectra were recorded using a Zetasizer Nano SZ–Malvern instrument with a computer connected and preinstalled Zetasizer software that controls the measurements. Antioxidant activity for Geum urbanum aqueous extract and AgNPs was measured using a standard method: a DPPH solution was prepared in ethanol and 0.5 mL aqueous extract was mixed with 1 mL 0.02 mg/mL DPPH solution.

The solutions were tested by recording and noting the absorbance at 517 nm. A blank probe was prepared in parallel by mixing 0.5 mL distilled water with 1 mL 0.02 mg/mL DPPH solution and the spectrum was recorded at the same wavelength [7,8].

The antioxidant activity (AA%) was calculated using the formula:

$$AA\% = [(A_{Control} - A_{Sample})/A_{Control}] \times 100, \quad (1)$$

where:

- $A_{Control}$ is the absorbance of the blank DPPH solution and
- A_{Sample} represents the absorbance *Geum urbanum* aqueous extracts mixed with 0.02 mg/mL DPPH solution.

3. Results and Discussions

3.1. Ultraviolet—Visible (UV—Vis) Results

An absorption at a wavelength around 270 nm and 370 nm is characteristic for phenolic acids and/or their derivatives (flavones or quinones) [9]. In the case of the aqueous extract from *Geum urbanum,* the phenolic acids and flavonoids were identified at 273 and 374 nm respectively. The bioreduction of silver ions was first visually observed by a change of color of the colloidal solutions from light green to yellow-greenish whatever the temperature conditions used for the green synthesis of AgNPs and then it was confirmed by the UV–Vis recordings (Table 1). For AgNPs, the specific absorbance is situated between 430 nm–450 nm.

Table 1. UV—Vis absorptions for the green synthesized AgNPs.

Aqueous Extract	AgNPs Room Temperature	AgNPs 50 °C
St. Benedict's herb *(Geum urbanum*)	445 nm	448 nm

3.2. Fourier Transform Infrared Spectroscopy (FTIR) Results

FTIR spectra allows the identification of different functional groups at different wavelengths. All the FTIR spectra were recorded using dried samples. The strong band observed around 3300 cm^{-1} for the aqueous extract of St. Benedict's herb (Geum urbanum) and its AgNPs shows the presence of alkynes while in the region of 1600 cm^{-1} C=O bonds were present. The medium absorption bands recorded in the range of 2800–3000 cm^{-1} are characteristic for alkyl-methyl bonds and the clear band around 1460 cm^{-1} in Geum urbanum aqueous extract is characteristic for the imidazole ring. The absorptions between 1300–1500 cm^{-1} regions are a results of base sugar vibrations.

A very important result is the peak at 1200 cm^{-1} present only in the aqueous extract of Geum urbanum, correspondent to amides, proteins and enzymes and absent in the FTIR spectra of GU–AgNPs, thus explaining the Ag^+ reduction.

3.3. Antioxidant Activity Results

Antioxidant activity was evaluated using the DPPH method and the results are presented in Table 2. It is clear that, for GU–AgNPs, AA (%) has higher values that the one specific to the aqueous extract, with a slight increase in the case of GU–AgNPs green synthesized at room temperature. AA (%) for the Geum urbanum aqueous extract was calculated at 56.77%.

Table 2. Antioxidant activity for the green synthesized AgNPs.

Crt. no.	AA (%) Room Temperature	AA (%) 50 °C
Antioxidant activity	92.56	90.26

3.4. Dynamic Light Scaterring (DLS) Results

Dynamic light scattering (DLS) recordings (Figure 1) were used to determine the size distribution profile of the GU–AgNPs in suspension and the Zeta potential was allows a proper analyze of the stability of the colloidal suspensions (Table 3).

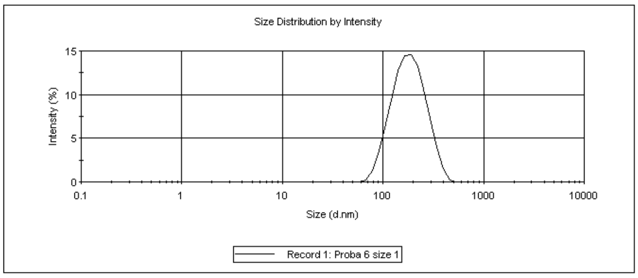

Figure 1. DLS spectrum for the RA–AgNPs at 50 °C.

Table 3. DLS measurements and zeta potential.

Sample	Dm (d.nm)	$P_{1 \ldots i}$ (d.nm)	PdI	PZ (mV)
GU–AgNPs room temperature	178	P_1 = 180	0.178	−17
GU–AgNPs 50 °C	185	P_1 = 176	0.168	−15

4. Conclusions

This original research presents the green synthesis of silver and gold nanoparticles from aqueous extracts of St. Benedict's herb (*Geum urbanum*), a medicinal plant recognized for its numerous health benefits. The aqueous extract of St. Benedict's herb (*Geum urbanum*) was prepared after a 24 h cold infusion at 4 °C, using commercially available tea. Silver nanoparticles (AgNPs) were prepared at room temperature, in the dark, for 24 h and at 50 °C, under continuous stirring at 500 rpm, for 30 min. The formation of GU–AgNPs was at first visually observed by the change of the color of the colloidal solutions and then confirmed by UV-Vis recordings. The characteristic absorption for GU–AgNPs was observed at 427 nm. The antioxidant activity showed a considerable increase for AgNPs as compared to plain *Geum urbanum* aqueous extract and Dynamic light scattering (DLS) measurements prove the presence of GU–AgNPs in the tested samples. Also, the bioactive compounds found in *Geum urbanum* act as reducing and capping agents, preventing the agglomeration of the particles and stabilizing the nanoparticles.

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Conflicts of Interest: The authors declare no conflict of interest.

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