GREEN SYNTHESIS OF SILVER AND GOLD NANOPARTICLES USING EXTRACTS OF *HERACLEUM SPP.*

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Abstract. *Heracleum mantegazzianum* and *Heracleum Sosnowskyi* are two invasive species in Slovakia and other countries of Central Europe. Both species are represented by variable morphology and their eradication is very problematic. The part of their metabolism is the production of different kind of secondary metabolites which protect themselves against local microbiota, fungi or herbivores. For instance, cumarin derivatives provide photodynamic effect after transmission to the human skin can be caused damages reminds „sun burn". This shows that *Heracleum spp.* is a source of compounds, which are the source of different kinds of interactions during the synthesis of metallic nanoparticles.
Our investigation focused on exploring the possibilities to use the extracts of *Heracleum spp.* for green synthesis of silver and gold nanoparticles (NPs). The products of green synthesis depend on different factors such as the external conditions of the reaction (e.g. temperature, concentration), as well as reaction time, pH and extract constituents, which permit the formation and stability of the nanoparticles. The formation of AgNPs and AgNPs was studied using UV-Vis and FTIR spectroscopy, and transmission electron microscopy.

Introduction. The remarkable electrical and optical properties of nanoparticles (AuNPs) have resulted in an increased interest of researchers in search of new methods and development of improved protocols for their fabrication. The traditional synthesis protocols used in wet chemistry involves the different chemicals which plays the role of the reducing agents and capping agents. Phytosynthesis (synthesis using plant extract) delivers new green approach in the search of new cost- a time-effective methods of NPs synthesis. If AgNPs are interesting due to their antimicrobial properties, the AuNPs are prospective because of optical properties. Thus, non-spherical AuNPs (nanotriangles, nanohexagons, nanostars, nanorods, etc.) recognized to be prospective for surface enhanced Raman spectroscopy.

The aim of this study was the synthesis and characterization of Ag- and Au-NPs prepared using extracts of widely distributed and easy invasive species of *Heracleum mantegazzianum* and *Heracleum Sosnowskyi*.

Experimental. Applied methods:
1. Water extracts of *Heracleum mantegazzianum* and *Heracleum Sosnowskyi* were prepared from air dry leafs at 60 °C.
2. Syntheses of AuNPs were carried out by direct interaction of plant extract (various concentrations) with aqueous solutions: 1 mM $HAuCl_4$, 1 and 10mM $AgNO_3$.
3. UV-Vis spectra were collected using Shimadzu UV-1800 spectrophotometer.
4. Infrared spectra were measured using Shimadzu FTIR Prestige-21 spectrometer with PIKE ATR accessory on Ge crystal.
5. Extract's dry matter contents was measured using Shimadzu MOC-120H moisture analyzer.
6. Transmission electron microscopy images were captured on a JEOL JEM-2100F transmission electron microscope at a maximum acceleration voltage of 200 kV.

Results and Discussion. Invasive plants, like *Heracleum spp.*, are easy accessible and cheap plant material (Fig. 1) which can be used for phytosynthesis of metal NPs. Some previous experiments were carried out for synthesis of silver [1] and platinum NPs [2]. However, there is no information about formation of AuNPs, especially irregular shaped (nanotriangles, nanohexagons etc.). In this work, we have examined the aqueous extracts of *Heracleum spp.* for synthesis of AgNPs and AuNPs. FTIR spectroscopy measurements of plant extract and NPs have shown the dramatic transformation of components of extracts (Fig. 2). Their showed the pronounced oxidation of components adsorbed on NPs. UV-Vis spectroscopy of AgNPs have shown the presence of SPR maximum at 437 nm) what clearly confirms the formation of stable spherical AgNPs (Fig. 3). However, the shape of AuNPs depends from the extract to Au^{3+} ratio (Fig. 4). Thus, at concentration of $HAuCl_4$ of 0.5 mM, the SPR maximum in NIR region occurs. This was confirmed by TEM (Figure 5).

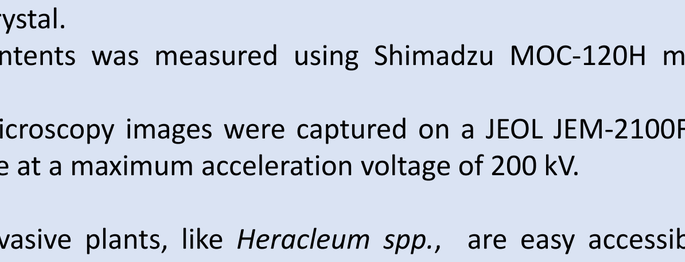

Figure 1. Images of *Heracleum spp.*

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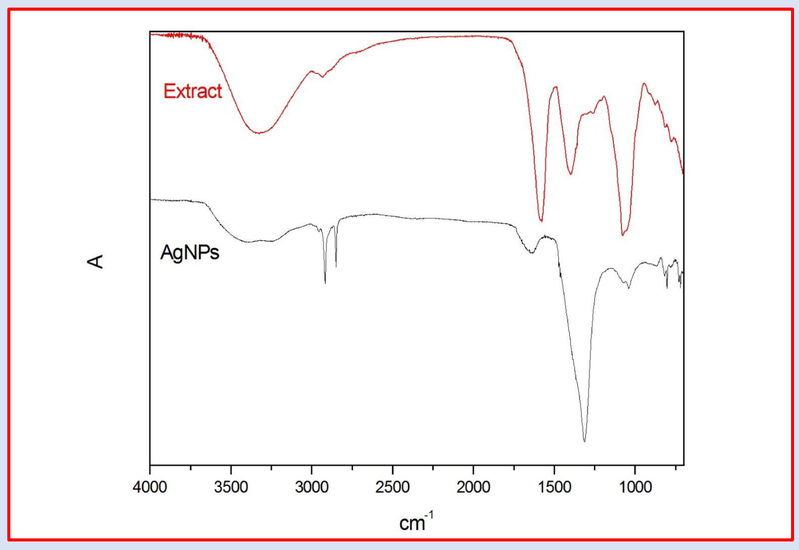
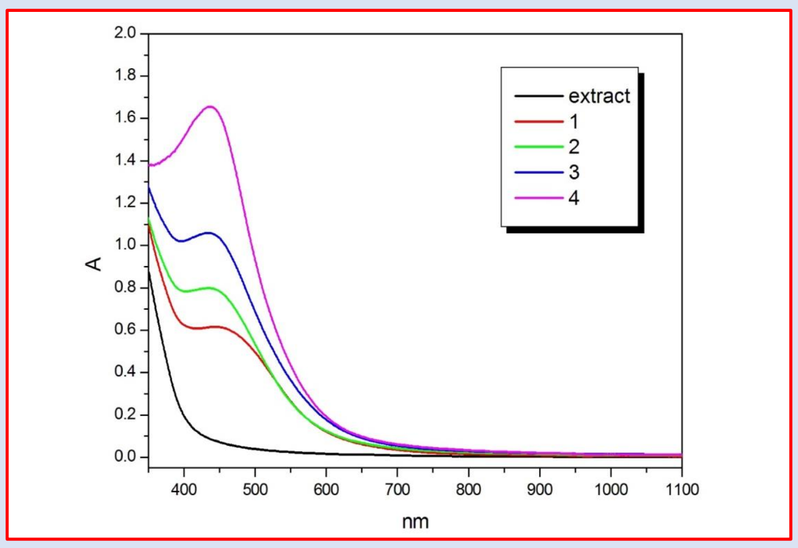


Figure 2. FTIR ATR spectra of *Heracleum Sosnowskyi* extract and AgNPs.

Figure 3. UV-Vis spectra of AgNPs solutions prepared by reaction of *Heracleum Sosnowskyi* extract (1mg/ml) and $AgNO_3$:
0 mM (extract);
0.25 mM (1);
0.50 mM (2);
0.75 mM (3);
1.00 mM (4).



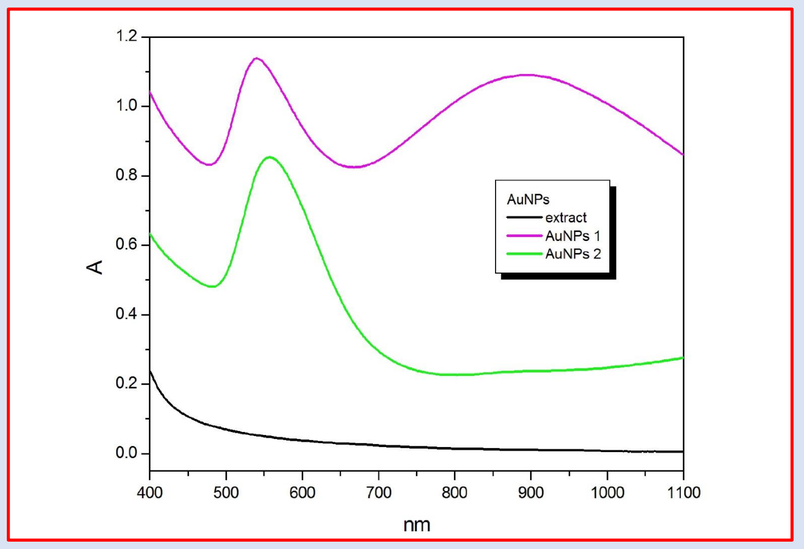


Figure 4. UV-Vis spectra of AuNPs solutions prepared by reaction of *Heracleum Sosnowskyi* extract (1mg/ml) and $HAuCl_4$:
0 mM (extract);
0.25 mM (AuNPs1);
0.50 mM (AuNPs2).

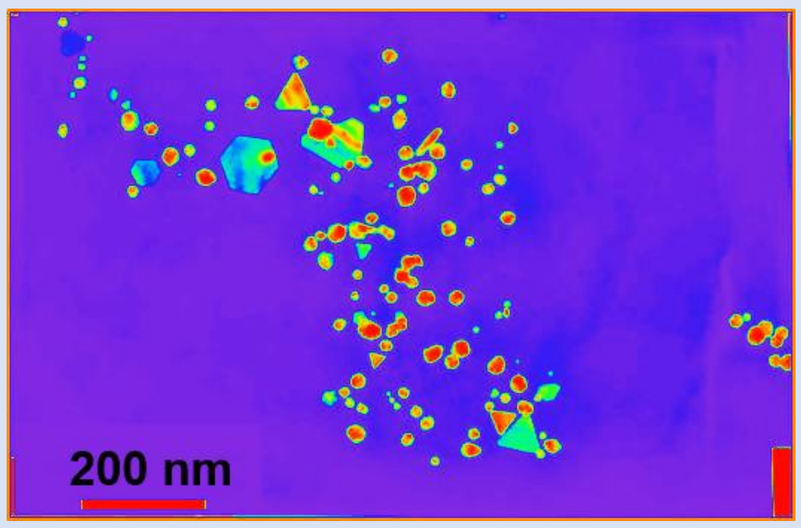


Figure 5. TEM images of AuNPs prepared using extract of *Heracleum Sosnowskyi*.

Conclusions. The green protocol for the room temperature synthesis of Ag and Au NPs using an aqueous extract of *Heracleum mantegazzianum* and *Heracleum Sosnowskyi* was investigated. The formation of stable AgNPs with SPR maximum of 437 nm was observed. However, multi-shaped (spherical, triangular, and hexagonal) AuNPs can be synthesized when using a concentration of $HAuCl_4$ over 0.5 mM.

References

[1] Mohammadi P., Heravi M.M., Sadjadi S. Green synthesis of Ag NPs on magnetic polyallylamine decorated g-C_3N_4 by *Heracleum persicum* extract: efficient catalyst for reduction of dyes (2020) *Scientific Reports*, 10 (1), art. no. 6579. DOI: 10.1038/s41598-020-63756-4
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