

# Synthesis and characterization silver nanoparticles using tomato pomace extract obtained by deep eutectic solvent



Vorobyova V.I., Vasyliiev G. S.

National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"  
Prosp. Peremohy-03056, 37, Kyiv, Ukraine.

E-mail: g.vasyliiev@kpi.ua

**Introduction.** Over the past years, most of the studies were focused on developing a vast variety of methods to green synthesized Ag nanoparticles (Ag-NPs). The results obtained by the authors showed that due to the physicochemical characteristics of the methods of synthesis to obtain certain properties, such as biocompatibility and antiradical activity and their successful application in specific industries (pharmaceutical) possible only with integrated use phytochemical methods of synthesis using the latest and environmentally friendly types of solvents as extractant of organic compounds from raw materials.

The current research is aimed at developing eco-friendly method for the synthesis of AgNPs using pomace extract obtained by ionic liquid. DESs are green and sustainable solvents having both hydrogen bond donors and acceptors.

**Methods.** Briefly, betaine and hydrogen bond donor HBD (1,2-Propanediol) were mixed in sealed 100 mL glass flasks in molar ratios. The mixtures were placed in a round-bottom flask and continuously stirred at 60 °C, 300 rpm in a magnetic stirrer until the mixture formed a clear solution. Water solvent (10%) was added to the mixture to get a better extraction yield. The tomato pomace powder was added into DES in a solvent/solid ratio of 20:1. The mixture was ultrasonic extracted in an ultrasonic bath with an ultrasonic input power of 100 W and a frequency of 30 kHz under the desired conditions. The extraction parameters were: temperature 65°C, duration 60 min. After the extraction, the solution was filtered through paper filter and used to synthesize AgNPs. Green synthesis process was applied according to the previously reported method published by us (1,2). The AgNPs were characterized by zeta-potential measurements and UV-Vis spectroscopy (absorption peak at 432 nm). The samples were diluted with deionized water and UV-visible spectra were recorded using 1 cm Quartz cuvette at 25 °C. Dynamic light scattering (DLS) and zeta potential measurements were performed on Malvern Zeta-sizer Nano-ZS, Malvern Instruments, UK.

**Results.** HPLC chromatograms (DAD: 280, 320 and 560 nm) showing the profiles of the main compounds obtained from a tomato pomace extract. Qualitative analysis of the extract by HPLC-DAD-MS/MS identified the phenolic acids, anthocyanins and flavanols was observed. A total of 9 different hydroxybenzoic and hydroxycinnamic acids were characterized, including gallic acid (RT: ~ 5.8 min); protocatechuic acid (RT: ~ 12.7 min); p-hydroxybenzoic acid (RT: ~ 18.0 min); coumaric acid (RT: ~ 20.8 min); caffeic acid (RT: ~ 23.4 min); syringic acid (RT: ~ 25.7 min); p-coumaric acid (RT: ~ 21.0 min); sinapic acid (RT: ~22.3 min) and ferulic acid (RT: ~ 22.9). A total of 4 anthocyanins were identified in tomato pomace extract including delphinidin 3-O-glucoside (retention time [RT] ~ 10.01 min), cyanidin-3-O-glucoside (RT: ~12.25 min); malvidin 3-O-glucoside (RT: ~16.98 min); peonidin 3-O-p-coumaroylglucoside (RT: ~ 20.10 min). The tomato pomace extract is characterized by being abundant of (+)-catechin and caffeic acid. The rich source of phenolic acids, anthocyanins and flavanols in a tomato waste extract might be responsible for reduction and capping of metal ions and efficient stabilization of synthesized nanoparticles. Phenolic acids, anthocyanins and flavanols have phenolic structures in addition to hydroxyl groups. The hydroxyl groups in these structures are essential for reducing the Ag<sup>+</sup> from the silver nitrate to the production of nanoparticles. The UV-Vis spectrum showed sharp absorption peaks at 452 nm (Fig.1), indicating the presence of as-prepared TPE-AgNPs.

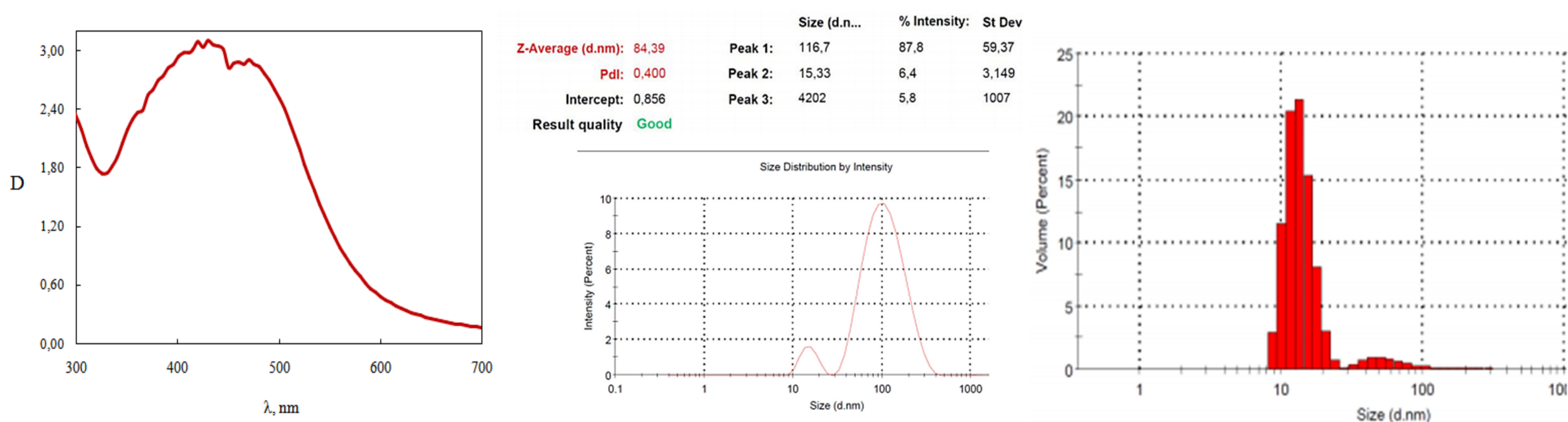


Fig.1 UV-Vis spectra, Dynamic light scattering distribution (DLS) of TPE-AgNPs, particle distribution diagram of the system

The DLS and zeta-potential analysis were used to determine the hydrodynamic particles size and stability of the TPE-AgNPs. Particle size distribution of AgNPs determined by dynamic light scattering (showed a normal bimodal distribution of particles with effective diameter of 84.39 nm (peak intensities at approximately 15 and 100 nm are recorded) with polydispersity index of 0.400. The value of IP values less than 0.4 correspond to populations with monodisperse size distribution. The data obtained correlate with the results of the bimodal distribution of nanoparticles. The DLS analysis showed that the zeta potential of nanoparticles is  $-24.5 \pm 1.0$  mV. Negative values of zeta potential were measured which confirm the presence of the anionic phenolic compounds and/or flavanoids at the surface of the particles. The stabilization of AgNPs most likely can be due to an electrostatically mechanism. The presence of carbonyl groups on the surface of the AgNPs creates an electrostatic shell, which promotes the repulsion between charged NPs, during their growing stage.

**Conclusions.** Silver nanoparticles were prepared by green chemical reduction with tomato pomace extract. It is believed, this is the first time that tomato pomace extract that obtained by DESs has been used as capping and reducing agents for reduction of metal ions and efficient stabilization of synthesized nanoparticles. The synthesized TPE-AgNPs exhibit a spherical shape with small size (15 and 100 nm), uniform dispersion, and high stability.

**Funding.** This work was supported by the Ministry of Education and Science of Ukraine [grant no. 2403, 2021].

## References

1. Vasyliiev G., Vorobyova V., Skiba M., Khrokalo L. 2020. Green Synthesis of Silver Nanoparticles Using Waste Products (Apricot and Black Currant Pomace) Aqueous Extracts and Their Characterization. *Advances in Materials Science and Engineering*. 2020, 4505787. DOI: [10.1155/2020/4505787](https://doi.org/10.1155/2020/4505787)
2. Vorobyova V, Vasyliiev G., Skiba M. 2020. Eco-friendly "green" synthesis of silver nanoparticles with the black currant pomace extract and its antibacterial, electrochemical, and antioxidant activity, *Appl. Nanosci.* 1-12. DOI: [10.1007/s13204-020-01369-z](https://doi.org/10.1007/s13204-020-01369-z).

