

¹. Andra Sabina NECULAI-VĂLEANU, ¹. Adina Mirela ARITON,
¹.Bianca Maria MADESCU, ³.Gheorghe VAIDA, ^{1,2}.Steofil CREANGA

HARNESSING AGRI-WASTE FOR GREEN SYNTHESIS OF SILVER

¹Research and Development Station for Cattle Breeding Dancu-Iasi, ROMANIA

²University of Agricultural Science and Veterinary Medicine “Ion Ionescu de la Brad, Iasi, ROMANIA

³Academy of Agricultural and Forestry Sciences, “Gheorghe Ionescu-Sisesti”, ROMANIA

Abstract: This study aimed at using a green, rapid, and efficient method for silver nanoparticles synthesis using different types of agri-waste. Ag was reduced to Ag-NPs using the banana, apple and walnut waste extracts that served as both capping and reducing agent. Silver nitrate solution (1mM) was mixed with the vegetal extract (1:9 ratio) and sonicated in a cleaning bath, at 60C. The successful bio-reduction of silver nitrate into silver nanoparticles was confirmed by UV-Vis spectroscopy, a characteristic surface plasmon resonance (SPR) band being recorded for all the samples. Concluding, agri-waste may be harnessed to phyto-fabricate eco-friendly silver nanoparticles, with multiple applications in the agri-food sector.

Keywords: green synthesis, nanoparticles, agri-waste, circular economy

1. INTRODUCTION

Biological Synthesis (AgNPs), also called green synthesis, is a sustainable alternative to physical and chemical synthesis due to its low cost and environmental impact. The convergence of the concepts of green chemistry with nanotechnology has been a central field of nanoscience research and has attracted significant interest in recent years. Biological approaches are used to synthesize metallic nanoparticles of desirable size and morphology with improved characteristics.

Metallic nanoparticles are commonly known for their broad variety of uses, such as catalysis, telecommunications, optics, and nanodevice manufacture. Moreover, the development of greener synthesis alternatives has broadened the scope of applications to the biomedical and food industry fields, especially due to their improved biocompatibility and antimicrobial potential against common and antibiotics resistant pathogens (Wang *et al.*, 2017; Mousavi *et al.* 2018; Singh *et al.*, 2020).

Owing to the abundant biodiversity as well as its secondary metabolites, plants have increasingly been well used in the synthesis of a number of nanoparticles (Kuppusamy *et al.*, 2016). Plant extracts provide numerous natural compounds such as alkaloids, flavonoids, saponins, hormones, tannins and other nutrient compounds which may act as both reducing and stabilizing agents for the bioreduction of silver ions.

Walnut husk contain hydrojuglone, tannins, essential oil, chlorophyll, starch, pectins and organic acids. When exposed to air or other oxidizing substances, hydrojuglone, also called 5-hydroxy-1,4-naphthalenedione is converted to juglone. Walnuts are primarily grown mainly for the production of kernels. The outer, green, dense layer of walnut fruit is referred to as the husk and represents an abundant agri waste produced during fruit harvesting and processing (Jahanban-Esfahlan *et al.*, 2019).

Husk is a useful source of natural phenolic antioxidants or other beneficial bio compounds (Ghasemi *et al.*, 2011; Akbari *et al.*, 2012; Fernández-Agulló *et al.*, 2013), and besides being widely used in traditional medicines for the treatment of skin conditions and pain relief, has become of particular interest in other fields such modern pharmacology, cosmetics and textiles.

Presently, in spite of its potential, the green husk is barely used as an agricultural by-product. The use of husk as a source of phyto-chemicals or other natural compounds with antioxidant and antimicrobial effects may highlight the importance of walnut production and lead to a better valorisation of this plant.

Furthermore, the peels of a number of fruits have gained prominence as a natural source of antioxidants and phytochemicals abundant in free radical scavenging compounds. Banana peels, which are usually discarded after consumption, account for almost 33 % of the total fruit and, while being abundant in pectin, lignin, hemicelluloses and a wide variety of phenolic compounds, their use for purposes is limited. Similar, apples are eaten raw or used to prepare food products such as juice, shakes, and desserts. Peel and seed, containing different bioactive compounds such as pectin, phenols, may also be exploited for different purposes.

This study aimed at using a green, rapid, and efficient method for silver nanoparticles (AgNP) synthesis using different types of agri-waste: banana peel, walnut husk, apple peel.

2. MATERIALS AND METHODS

— Preparation of extracts

Fresh bananas, apples and green walnuts were purchased from a local market. The fruits were washed in abundance with distilled water to remove any residues and organic compounds. The apple, banana peel and walnut husk were removed, cut into small pieces and dried on paper towel. To prepare a 10%(w/w) aqueous extract, 10g of each agri food waste were grinded and transferred to 250 mL flask, mixed well with 100mL of deionized water and subsequently heated at 90°C for 10 min. Subsequently, filtration of the extracts was carried out using Whatman No.1 filter paper.

— Synthesis of silver nanoparticles

An aqueous solution of 1 mM AgNO₃ (Chemical, Romania) was prepared at room temperature. To this solution (90 ml), 10 ml from each filtrate was pipetted dropwise (1:9 ratio) and the mixture was sonicated using an ultrasound bath (Elmasonic, Germany), at 60°C, for 10 minutes.

— Characterization of silver nanoparticles

The characterization of silver nanoparticles was performed by determining the absorption spectra of the AgNPs solutions using a UV – Visible spectrophotometer (T90+ UV VIS, PG Instruments Ltd,Uk), at a wavelength ranging between 300-600 nm, and a resolution of 1 nm.

3. RESULTS

This study aimed at using a green, rapid, and efficient method for silver nanoparticles (AgNP) synthesis using different types of agri-waste. The formation of AgNPs was analyzed firstly by visual observation, a color change of the initial solution, from pale yellow for banana and apple, respectively brown in walnut husk being noticeable.

The presence of a reddish brown color, respectively dark reddish brown indicated the phyto-synthesis of AgNPs (Figure 1). This change of color of the reaction solution is determined by the excitation of the surface plasmon resonance (SPR) exhibited by the synthesized nanoparticles.

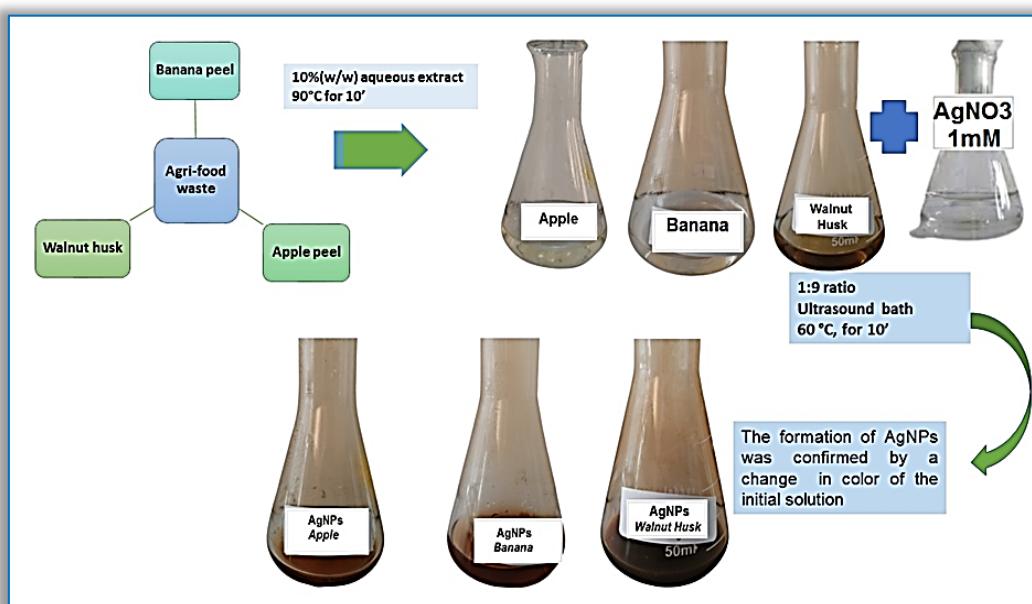


Figure 1 - The flow diagram of the green synthesis of nanoparticles from agri-waste

Growth and progressive formation of nanoparticles was confirmed by UV – vis spectroscopy, as peaks of absorbance were recorded in the wideband characteristic to silver, respectively 300-600 nm. In the present study, Ag ion (silver nitrate dissolved in distilled water with concentration 1mM) is reduced to Ag-NPs using the banana, apple and walnut waste extracts that served as both capping and reducing agent. For walnut husk, the surface plasmon resonance (SPR) was observed at 428 nm, while for banana and apple, at 421, respectively 420 nm (Figure 2).

According to previous studies, the presence of a single peak signifies that the NPs are smaller compared to the mean free path of conduction electrons (50 nm for Ag) and present a spherical form, since forms other than spheres usually generate multiple peaks (Alameen, 2015). The size of the nanoparticle determines the characteristics of Plasmon Resonance, which include the ratio of absorption to scattering, the number of SPR modes, as well as the peak location. Thereby, the size of the nanoparticles may be determined based on the Surface Plasmon Resonance (SPR) peak, using the correlation equations introduced by Dalal *et al.*, 2019.

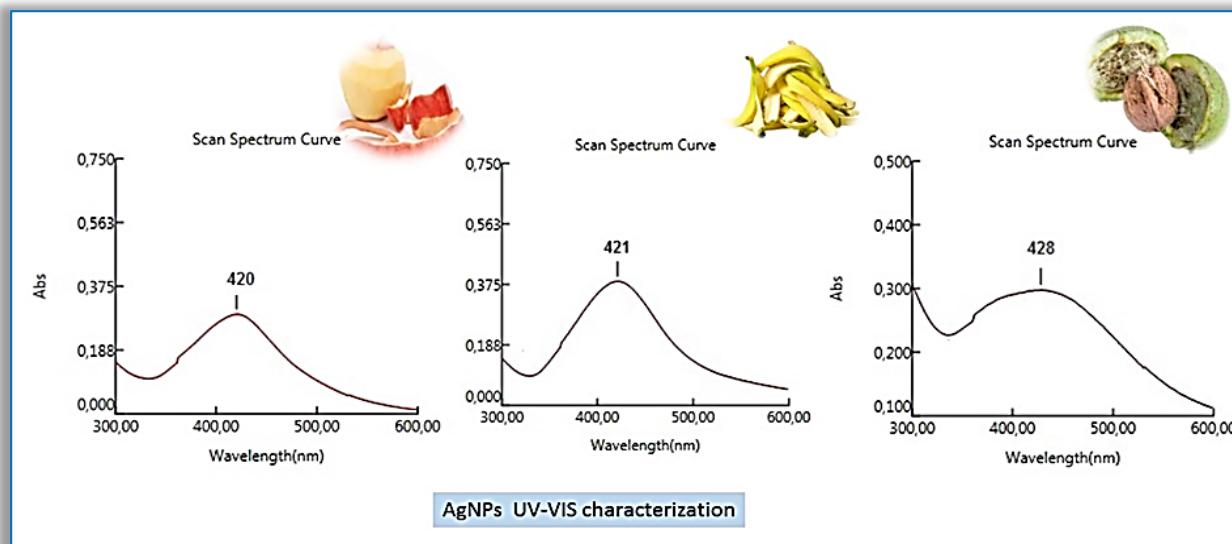


Figure 2 - Surface plasmon resonance (SPR) peaks recorder for silver nanoparticles synthesized using apple peel, banana peel and walnut husk

According to Dalal, the size of AgNPs may be express as: $S_s = (0.84 * X_s) - 310$ (approximate), where:

≡ S_s = the size of the silver nanoparticles

≡ X_s = the SPR wavelength.

In our case, we established that the green synthesized nanoparticles using agri-food waste exist in ~40–60 nm range, which means that their use would be suitable for both biomedical and food applications, such as antimicrobial biofilms. The European Union produces more than 2.5 billion tonnes of agri-food waste annually. Furthermore, very commonly, these wastes have low nutritional quality and may also contain anti-nutrients that hinder their use as animal feeds. Thus, the E.U is currently updating its waste management legislation to promote the transition to a more sustainable model known as the circular economy (Wurzel et al., 2019; IPCC, 2020; Giordano et al., 2020; Weishaupt et al., 2020).

A series of biotechnological strategies have been designed aiming at improving the nutritional content of agri-waste and processing of biogas (Zhang et al., 2014). Further attempts are now made to expand the use of agri-wastes as a source of basic material in green nanotechnology for the phyto-fabrication of metallic nanoparticles.

4. CONCLUSIONS

The physical characteristics of grist intermediate products determine the functional characteristics of Agri-food waste is generated in huge amounts and disposed of without any oversight, generating a detrimental environmental impact.

Therefore, by identifying potential applications for agri-food waste products that are produced in high quantities, the environmental impact may be diminished. Green chemistry approach to nanoparticle synthesis has many benefits, such as the simplicity at which the procedure may be scaled up and the economic viability, since agri-waste may be harnessed to phyto-fabricate eco-friendly silver nanoparticles, with multiple applications in the agri-food sector.

Note:

This paper is based on the paper presented at ISB-INMA TEH' 2020 International Symposium (Agricultural and Mechanical Engineering), organized by Politehnica University of Bucharest – Faculty of Biotechnical Systems Engineering (ISB), National Institute of Research–Development for Machines and Installations Designed to Agriculture and Food Industry (INMA Bucharest), Romanian Agricultural Mechanical Engineers Society (SIMAR), National Research & Development Institute for Food Bioresources (IBA Bucharest), National Institute for Research and Development in Environmental Protection (INCDPM), Research–Development Institute for Plant Protection (ICDPP), Research and Development Institute for Processing and Marketing of the Horticultural Products (HORTING), Hydraulics and Pneumatics Research Institute (INOE 2000 IHP) and “Food for Life Technological Platform”, in Bucharest, ROMANIA, 30 October, 2020.

References

- [1] Akbari V., Jamei R., Heidari R., Jahanban Esfahan A. (2012), Antiradical activity of different parts of Walnut (*Juglans regia L.*) fruit as a function of genotype. *Food Chemistry*. Volume 135, pp 2404–2410. doi: 10.1016/j.foodchem.2012.07.030, Norwich/Uk;
- [2] Alameen AGM, 2015. Green Synthesis of Silver Nanoparticles Using Cinnamon Extract. Dissertation Thesis. Riyadh/Saudi Arabia;

- [3] Fernández-Agulló A., Pereira E., Freire M.S., Valentão P., Andrade P.B., González-Álvarez J., Pereira J.A. Influence of solvent on the antioxidant and antimicrobial properties of walnut (*Juglans regia L.*) green husk extracts, (2013), *Industrial Crops and Products*. Vol. 42, pp 126–132, North Dakota/USA
- [4] Ghasemi K., Ghasemi Y., Ehteshamnia A., Nabavi S.M., Nabavi S.F., Ebrahimzadeh M.A., Pourmorad F., (2011), Influence of environmental factors on antioxidant activity, phenol and flavonoids contents of walnut (*Juglans regia L.*) green husks. *Journal of Medical Plant Research*, Volume 5, pp 1128–1133, Lagos, Nigeria;
- [5] Giordano C., Falasconi L., Cicatiello C., Pancino B., (2020), The role of food waste hierarchy in addressing policy and research: A comparative analysis, *Journal of Cleaner Production*, 252, 119617, Brno/Czech Republic;
- [6] Intergovernmental Panel on Climate Change (IPCC), (2020), Climate Change and Land. An IPCC Special Report on Climate Change, Desertification, Land Degradation, Sustainable Land Management, Food Security, and Greenhouse Gas Fluxes in Terrestrial Ecosystems; Summary for Policymakers; IPCC Secretariat, Geneva/Switzerland;
- [7] Jahanban-Esfahlan A., Ostadrahimi A., Tabibazar M., Amarowicz R., (2019), A Comprehensive Review on the Chemical Constituents and Functional Uses of Walnut (*Juglans spp.*) Husk. *International journal of molecular sciences*, Vol 20, Issue 16, pp 3920-3930, Basel, Switzerland;
- [8] Kuppusamy P., Yusoff M.M., Maniam G.P., Govinda N., (2016), Biosynthesis of metallic nanoparticles using plant derivatives and their new avenues in pharmacological applications – an updated report. *Saudi Pharmacology Journal*, Vol. 24, pp 473–484, Riyadh/Saudi Arabia;
- [9] Mousavi S.M., Hashemi S.A., Ghasemi Y., Atapour A., Amani A.M., Dashtaki A.S., Babapoor A., Arjmand O., (2018), Green synthesis of silver nanoparticles toward bio and medical applications: review study. *Artificial Cells, Nanomedicine, and Biotechnology*, 46 :sup3, S855-S872, DOI: 10.1080/21691401.2018.1517769, London/Uk;
- [10] Singh A., Gautam P.K., Verma A., (2020), Green synthesis of metallic nanoparticles as effective alternatives to treat antibiotics resistant bacterial infections: A review. *Biotechnology Reports*, 25:e00427, London/Uk;
- [11] Wang L., Hu C., Shao L., (2017), The antimicrobial activity of nanoparticles: present situation and prospects for the future. *International Journal of Nanomedicine*, Vol.12, pp 1227-1235, Texas/USA;
- [12] Weishaupt A., Ekardt F., Garske B., Stubenrauch J., Wieding J., (2020) Land Use, Livestock, Quantity Governance, and Economic Instruments—Sustainability Beyond Big Livestock Herds and Fossil Fuels, *Sustainability*, Vol. 12, 2053-2068, Basel/Switzerland;
- [13] Wurzel R., Zito A., Jordan A., (2019), Smart (and Not-So-Smart) Mixes of New Environmental Policy Instruments. Ed. Cambridge University Press, Cambridge/Uk, 2019;
- [14] Zhang, C.; Su, H.; Baeyens, J.; Tan, T., (2014), Reviewing the anaerobic digestion of food waste for biogas production. *Renewable Sustainable Energy Revue*. Vol. 38, pp 383–392, Belfast/Uk.



ISSN 1584 – 2665 (printed version); ISSN 2601 – 2332 (online); ISSN-L 1584 – 2665

copyright © University POLITEHNICA Timisoara, Faculty of Engineering Hunedoara,

5, Revolutiei, 331128, Hunedoara, ROMANIA

<http://annals.fih.upt.ro>