Biosynthesis of Green Silver Nanoparticles and Its UV-Vis Characterization

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Abstract

In a recent time, silver nanoparticles (AgNPs) have attracted a lot of attention from researchers because of their special properties. In this paper green silver nanoparticles (AgNP) were synthetized from 2, 4 and 8 % w/v orange peel extracts. The synthesis was done by the process of chemical reduction in the presence of 1 mM silver nitrate ($AgNO_3$) solution at 23 °C at 400 rpm for 6 hours. Orange peel extracts were used as capping agent to reduce 1mM solution to silver nanoparticles. The biosynthesized AgNPs were characterized by UV- Vis spectroscopy in the wavelength range from 300 to 600 nm with maximum of absorption at 460 nm. The results have shown that by increasing the concentration of peel extract increase the formation of silver nanoparticles. The advantage of this green method of synthesis is the use of fruit waste to create new valuable materials with potential antibacterial activity.

Keywords: *Silver Nanoparticles, Biosynthesis, Orange Peel, UV-Vis spectroscopy.*

1. Introduction

Over the past few years, the interest of material scientists for metal and metal oxide nanoparticles (NPs) is increasing dramatically because of their unique physicochemical characteristics such as catalytic activity, magnetic, electronic, antibacterial, optical, and properties which depend on their size, shape, and chemical surroundings [1]. Nanomaterials have dimensions below 100 nm and usually exhibit different chemical and physical properties than macroscopic objects based on the same material [2]. Nanotechnology is necessarily a multidisciplinary field which encompasses and draws from the knowledge of several diverse technological fields of study including chemistry [3, 4], physics, molecular biology, material science, computer science, and engineering.

Over the past few decades, silver nanoparticles (AgNPs) have been investigated extensively due to their superior physical, chemical, and biological characteristics, and their superiority stems mainly from the size, shape, composition, crystallinity, and structure of AgNPs compared to their bulk forms. Different applications of nanomaterials and their impact on the environment have been published recently [5, 6].

AgNPs have made a substantial impact across diverse biomedical applications as antimicrobial agents, biomedical device coatings, drug delivery carriers, imaging probes, and diagnostic and optoelectronic platforms, since they have discrete physical and optical properties and biochemical functionality tailored by diverse size- and shape-controlled AgNPs [7-10]. Previous discoveries have shown that the physical, optical, and catalytic properties of AgNPs are strongly influenced by their size, distribution, morphological shape, and surface properties which can be modified by diverse synthetic methods, reducing agents and stabilizers [11-12].

Sang Hun Lee and Bong-Hyun Jun [13] have reported a comprehensive and contemporaneous view of the synthesis of AgNPs by various physio-chemical and biological methods, as well as the mechanism of action based on their unique properties. It has been reported that physical
and chemical synthesis tend to be more labor-intensive and hazardous, compared to the biological synthesis of AgNPs which exhibits attractive properties, such as high yield, solubility, and stability [14]. Finally, promising applications of AgNPs in the biomedical field from nanomedicine to optoelectronics, including their anti-cancer or anti-bacterial activity, made them very attractive in the new research challenges.

In 2016 Shet and co-workers [15] have synthetized AgNPs from banana and orange peel extracts and show that fruit peel biosynthesized AgNPs are effective against pathogenic strains of bacteria.

1.1 Methods of silver nanoparticles synthesis

1.1.1 Physical method
The physical synthesis of AgNP includes the evaporation–condensation approach and the laser ablation technique which are able to synthesize large quantities of AgNPs with high purity without the use of chemicals that release toxic substances and jeopardize human health
and environment. However, agglomeration is often a great challenge because capping agents are not used. In addition, both approaches consume greater power and require relatively longer duration of synthesis and complex equipment, all of which increase their operating cost.

1.1.2 Chemical methods
Chemical synthesis methods have been commonly applied in the synthesis of metallic NPs as
a colloidal dispersion in aqueous solution or organic solvent by reducing their metal salts. Various metallic salts are used to fabricate corresponding metal nanospheres, such as gold, silver, iron, zinc oxide, copper, palladium, platinum, etc. [16]. In addition, reducing and capping agents can easily be changed or modified to achieve desired characteristics of AgNPs in terms of size distribution, shape, and dispersion rate [17].

1.1.3 Biogenic (green) method
Recently, the biogenic (green chemistry) metal NP synthesis method that employs biological entities, such as microorganisms and plant extracts, has been suggested as a valuable alternative to other synthesis routes. The green synthesis of AgNPs with naturally occurring reducing agents could be a promising method to replace more complex physicochemical syntheses since the green synthesis is free from toxic chemicals and hazardous byproducts and instead involves natural capping agents for the stabilization of AgNPs [12].
In this paper the synthesis of AgNPs has been done by green synthesis method which is attributed as eco-friendly and economically acceptable.

2. Experiment

2.1. Materials and methods

2.1.1 Materials
About 10 kg of fresh oranges were collected in February 2018. The fruits were purchased at the same supermarket in Tuzla in Bosnia and Herzegovina. The origin of oranges were from Spain. The information about cultivar is missing. Fruit peel extracts were collected after consuming a certain type of fruit. The fruit was washed with the tap water before consumption. Each fresh fruit peel after consumption was weight and then cut in small pieces and dried in the air for seven days. After air drying, the samples were ground in a grinder AD 443, Adler Europe, 150 W, then the same sample was weight.
The silver nitrate ($AgNO_3$) employed was ACS reagent, ≥99.0% (Sigma-Aldrich).

2.1.2 Extraction from orange peel
Dried and milled orange peel was weight from 2, 4 and 8 g and put in the distilled water to warm up to 92 °C and keep it 10 min at that temperature under stirring at 500 rpm. After that the sample was filtered through LGG-Plain disc filter, qualitative, very slow. The extracts prepared in this way were stored at 4 °C until further use. The sample were named S1-PE which contain 2 g of orange peel, the next one is S1.1-PE containing 4 g of plant and the last one is named S1.2-PE containing 8 g of plant.

2.2 Biosynthesis of silver nanoparticles (AgNPs)
1 ml of orange extract (S1-PE) was added to 9 ml of $1x10^{-3}$M $AgNO_3$ and mixed using magnetic stirrer with temperature and velocity of stirring regulation (Tehtnica Rotamix SHP – 10) at room temperature at 23 °C at 400 rpm for 6 hours. The reaction took place in an acidic medium at pH 4.16. Then, UV spectrum was recorded. The absorption maximum was at 460 nm. The colour was changed during the reaction time from light yellow to light brown with formation of silver

nanoparticles. The name of the sample was S1-PN. The same procedure was followed for the synthesis of silver nanoparticles from S1.1-PE and S1.2-PE, with the name of nanoparticles S1.1-PN and S1.2 – PN.

2.3 pH and conductivity measurements

pH measurements were done by pH Meter Mettler Toledo MP220 and glass pH electrode Hanna Instruments HI 1053, 0-12 pH, temperature -5 to 70 °C in prepared fruit peel extracts, while conductivity measurements were done by conductometer Mettler Toledo MPC 227 pH/conductivity meter equipped with the electrode for conductivity measurements – Metler Toledo InLab 730 NTC, 0....1000 mS, 0 ... 100 °C.

2.4 UV/Vis measurements

For the UV-Vis characterization UV-Vis spectrophotometer, Perkin Elmer has been used. The absorbance spectra of AgNPs also could reflect changes in the shape of AgNPs as reported by Evanoff and Chumanov, 2005 [18].

3. Results and discussion

In Fig. 1 is shown the appearance of the orange peel extracts. These extracts were used for the preparation of silver nanoparticles. One may notice that by increasing the concentration of orange peel, the color of the samples becomes darker.

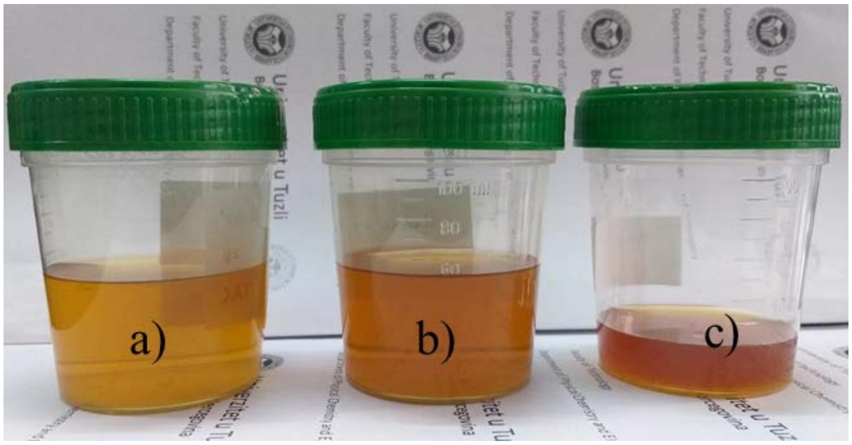

Figure 1. Orange peel extracts containing: a) 2% w/v - S1-PE;
b) 4% w/v - S1.2-PE; c) 8% w/v - S1.2-PE.

In Figure 2 is shown the formation of the silver nanoparticles from orange peel extract. The figure show that the colour change from colourless which comes from silver nitrate to light brown which confirms the formation of silver nanoparticles.
Actually, the silver ion (Ag^+) from $AgNO_3$ is reduced in aqueous solution, receiving an electron from a reducing agent (orange peel extract) to switch from a positive valence into a zero-valent state (Ag^0), followed by nucleation and growth. This leads to coarse agglomeration into oligomeric clusters to yield colloidal AgNPs. Nucleation and growth of AgNPs may be governed by various reaction parameters, including reaction temperature, pH, concentration, type of precursor, reducing and stabilizing agents, and molar ratio $AgNO_3$ and orange peel extracts. In this paper we will study only the influence of the mass of orange peel in extracts on the formation of AgNPs.

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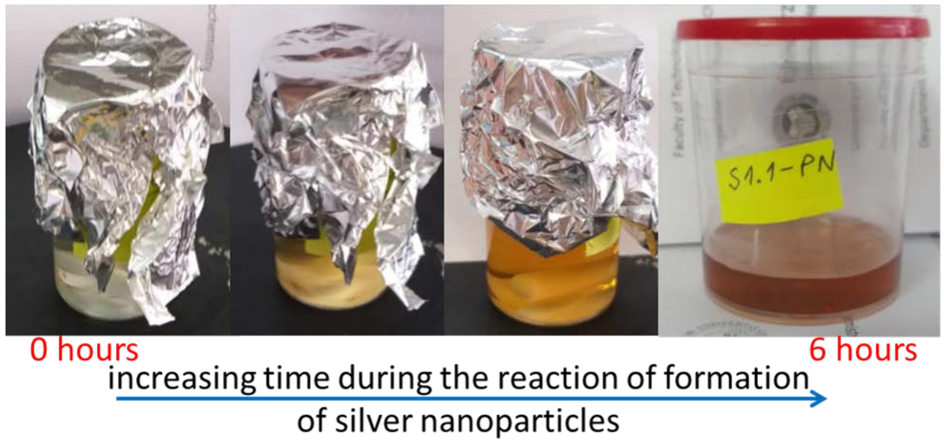

Figure 2. The reaction of formation of silver nanoparticles at 23 °C at 400 rpm during six hours.

3.1. pH and conductivity measurements

In table 1 are shown the experimental results of pH and conductivity of orange extracts.

Table 1. pH and conductivity of orange extracts

Sample	**pH**	**Conductivity (µS)**
S1-PE	4,16	525
S1.1-PE	4,08	840
S1.2-PE	3,93	1740

From table 1 we can see that all orange extract samples are weakly acid. By increasing the concentration of orange peel in the sample is evident decreasing the pH and increasing of conductivity. These results are reasonable, since the orange peel contain organic acids and amino acids which cuse decreasing the pH value by its higher presence in orange peel extracts.

3.2. UV-Vis characterization

In Figure 2 the UV-Vis spectrum of the orange peel extract were recorded.

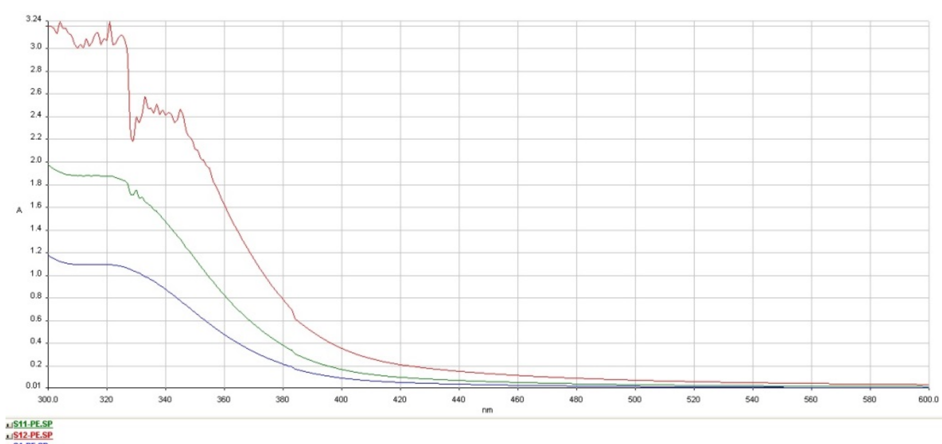

Figure 2. UV-Vis spectrum of the orange peel extract for 2, 4 and 8 % w/v.

In figure 2 the peak in the wavelength range from 400 – 600 nm is not present confirming the absence of silver nanoparticles in orange peel extracts.

The formation of silver nanoparticles (AgNPs) is confirmed in the figure 3 with blue line. In Figure 3 the overlay of UV-Vis spectrum of orange peel extract (red line) and silver nanoparticles (blue) is present.

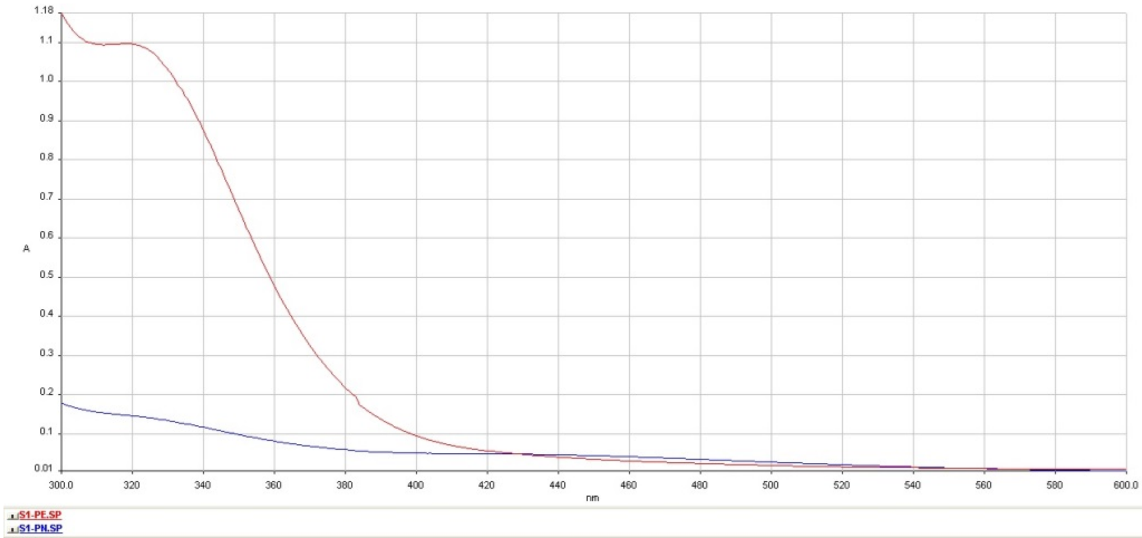

Figure 3. Overlay of UV-Vis spectrum of S1-PE and S1-PN samples.

From figure 3 is possible to observe slight differences between two spectra, S1-PE (red curve) which correspond to orange extract and S1-PN (blue curve) which correspond to silver nanoparticles formed. Silver absorb at 460 nm. In the wavelength range from 400 to 600 nm is possible to see slight increase in the broad peak. For recording of UV-Vis spectrum, both samples were diluted 20 times. The total concentration of silver in nanoparticles formed was $9x10^{-4}$M.

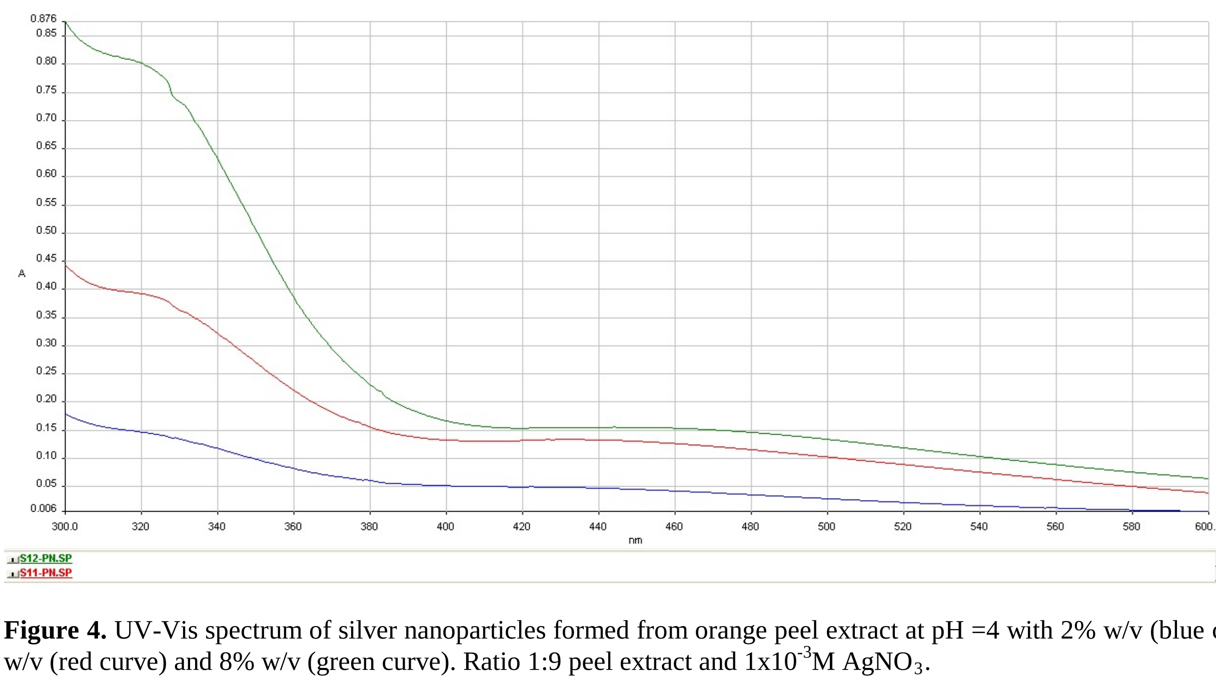

Figure 4. UV-Vis spectrum of silver nanoparticles formed from orange peel extract at pH =4 with 2% w/v (blue curve), 4% w/v (red curve) and 8% w/v (green curve). Ratio 1:9 peel extract and $1x10^{-3}$M $AgNO_3$.

From Figure 4 is evident that by increasing the concentration of peel extract increase the formation of silver nanoparticles.

4. Conclusion

In this paper is shown that orange peel as a very well known fruit, widely available in countries around the world can be used as a good natural capping agent for the stabilization of silver nanoparticles in biosynthesis. This green method of synthesis is attributed as eco-friendly and economically acceptable. From one side it is a very good way of recycling food waste with sustainable development, making environmental, social and economic sense by production new nanoparticles which may be used as antimicrobial agents. The experimental results showed very promising green way of the synthesis of silver nanoparticles with minimal environmental impact. One can see that by increasing the concentration of peel extract, the formation of silver nanoparticles is increased.

References

[1] Amra Bratovcic (February 21st 2020). Synthesis, Characterization, Applications, and Toxicity of Lead Oxide Nanoparticles [Online First], IntechOpen, 2020. DOI: 10.5772/intechopen.91362. Available from: https://www.intechopen.com/online-first/synthesis-characterization-applications-and-toxicity-of-lead-oxide-nanoparticles

[2] A. Bratovcic, Degradation of micro- and nano-plastics by photocatalytic methods, *Journal of Nanoscience and Nanotechnology Applications,* 2019, *3,* 206.

[3] A. Bratovcic and I. Petrinic, Carbon based aerogels and xerogels for removing of toxic organic compounds. *In: Karabegović I. (eds) New Technologies, Development and Application III. NT 2020*. Lecture Notes in Networks and Systems, vol 128. Springer, Cham, (2020).

[4] Bratovcic, A. New Solar Photocatalytic Technologies for Water Purification as Support for the Implementation of Industry 4.0. In Karabegović, I., Kovačević, A., Banjanović-Mehmedović, L., & Dašić, P. (Eds.), *Handbook of Research on Integrating Industry 4.0 in Business and Manufacturing*. IGI Global. 2020, (pp. 385-412) http://doi:10.4018/978-1-7998-2725-2.ch017

[5] Bratovcic, A. Different Applications of Nanomaterials and Their Impact on the Environment, *SSRG* International Journal of Material Science and Engineering (IJMSE) – 2019, 5(1)

[6] Bratovcic, A. Nanocomposite Hydrogels Reinforced by Carbon Nanotubes, International Journal of Engineering Research and Application, 2020, 10(5), Series IV, 30-41

[7] Syafiuddin, A.; Salmiati; Salim, M.R.; Kueh, A.B.H.; Hadibarata, T.; Nur, H. A Review of silver nanoparticles: Research trends, global consumption, synthesis, properties, and future Challenges. J. Clin. Chem. Soc. 2017, 64, 732–756.

[8] Kumar, A.; Vemula, P.K.; Ajayan, P.M.; John, G. Silver-nanoparticle-embedded antimicrobial paints based on vegetable oil. Nat. Mater. 2008, 7, 236–241.

[9] Desireddy, A.; Conn, B.E.; Guo, J.; Yoon, B.; Barnett, R.N.; Monahan, B.M.; Kirschbaum, K.; Griffith, W.P.; Whetten, R.L.; Landman, U.; et al. Ultrastable silver nanoparticles. Nature 2013, 501, 399–402.

[10] Sun, Y.; Xia, Y. Shape-controlled synthesis of gold and silver nanoparticles. Science, 2002, 298, 2176–2179.

[11] Atwater, H.A.; Polman, A. Plasmonics for improved photovoltaic devices. Nat. Mater. 2010, 9, 205–213.

[12] El-Nour, K.M.M.A.; Eftaiha, A.; Al-Warthan, A.; Ammar, R.A.A. Synthesis and applications of silver nanoparticles. Arab. J. Chem. 2010, 3, 135–140.

[13] Sang Hun Lee and Bong-Hyun Jun, Silver Nanoparticles: Synthesis and Application for Nanomedicine, Int. J. Mol. Sci. 2019, 20, 865; doi:10.3390/ijms20040865

[14] Zhang, X.-F.; Liu, Z.-G.; Shen,W.; Gurunathan, S. Silver nanoparticles: Synthesis, characterization, properties, applications, and therapeutic approaches. Int. J. Mol. Sci. 2016, 17, 1534.

[15] A.R Shet, S. Tantri, A. Bennal, Economical biosynthesis of silver nanoparticles using fruit waste, Journal of Chemical and Pharmaceutical Sciences, 2016, 9(3), 2306-2311.

[16] Kinnear, C.; Moore, T.L.; Rodriguez-Lorenzo, L.; Rothen-Rutishauser, B.; Petri-Fink, A. Form follows function: Nanoparticle shape and its implications for nanomedicine. Chem. Rev. 2017, 117, 11476–11521.

[17] Pillai, Z.S.; Kamat, P.V. What factors control the size and shape of silver nanoparticles in the citrate ion reduction method? J. Phys. Chem. B 2004, 108, 945–951.

[18] Evanoff, D.D., Jr.; Chumanov, G. Synthesis and optical properties of silver nanoparticles and arrays. Chem. Phys. Chem. 2005, 6, 1221–1231.

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