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Synthesis and Growth of Spherical ZnO Nanoparticles Using Different Amount of Plant Extract; Characterization and Morphology of Structures

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ABSTRACT: The use of plant extracts has become an interesting ecofriendly method to synthesize and stabilize the different structures nanoparticles (NPs). This work investigated the effect of plant extract as a reducing and stabilizing agent on the growth and morphology of ZnO nanoparticles (ZnO-NPs). Green synthesis and growth of spherical ZnO-NPs was carried out by co-precipitation method using a Zinc acetate salt and various amounts of *Azadirachta indica* seed husk extract (20 ml and 40 ml). The synthesized ZnO-NPs were characterized by Fourier transform infrared (FTIR), scanning electron microscopy (SEM-EDX), and transmission electron microscopy (TEM). The FTIR analyses revealed the presence of Phenolic alcohol, amines and carboxylic acid groups and ZnO in synthesized NPs with more intense peaks at higher amount (40 ml) of *A. indica* extract. Also, structural morphology analyses using SEM revealed uniform spherical shaped particles with diameter from 25 to 60 nm (20 ml of extract) and 19 to 35 nm (40 ml of extract) for ZnO-NPs. The EDX spectral revealed that the required phase of Zn and O was present 69.54% (Zn) and 30.46% (O) at 20 ml of extract, also 73.71% (Zn), 26.26% (O) at 40 ml of extract respectively and confirmed high purity for the synthesized ZnO NPs. TEM revealed spherical shaped NPs with diameter ranging from 28 to 52 nm (20 ml of extract) and 8.2 to 11.9 nm (40 ml of extract) respectively, with a trend reduction in particle size of NPs at higher amount of *A. indica* seed extract (40 ml) and growth of more uniform particles with no agglomeration. The study showed successful growth of spherical ZnO-NPs with required properties at a higher amount of extract.

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Key words: *Azadirachta indica* seed husk extract, growth, morphology, Spherical, Zinc Oxide nanoparticles.

Nanotechnology involves the diverse applications of nanoparticles in various fields of science. Nanoparticles are a part of nanomaterials that are defined as a single particle at 1-100 nm in diameter. The various methods of synthesizing nanoparticles include physical, chemical, biological, or green approaches (Karanassios, 2018). Green synthesis of nanoparticles using plant extract is a cost-effective and eco-friendly process, eliminating the use of high energy and hazardous chemicals necessary in the conventional synthesis such as physical and chemical reduction of nanoparticles (Sorbiun *et al*., 2018). Plant parts are rich in various phytochemical constituents such as alkaloids, phenols, flavonoids, terpenoids, tannins, steroids and anthraquinones (Maria *et al*., 2018; Agarwal *et al*., 2017). The variation of compounds and the corresponding levels in plant extract renders green synthesis approach versatile. Crude plant extract containing various biomolecules with functional groups such as C=C (alkenyl), C=N (Amide), O-H (phenolic and alcohol), N-H (amine), C-H and COO^- (carboxylic group) are mainly responsible for the reduction and stabilization of metallic ions into metallic nanoparticles (Yadi *et al*., 2018; Nethavhanani, 2018). In the green synthesis of metallic nanoparticles using plant extracts, three important parameters required are metal salt (precursors), a reducing agent, and a stabilizing or capping agent (Husen, 2019). Reducing and capping agents such as plant extracts are frequently used in nanoparticle synthesis to prevent overgrowth and aggregation as well as to control the size of nanoparticle in a precise way (Haghighi *et al.,* 2018). Previous studies reported synthesis of ZnO-NPs with controlled sizes and shapes were achieved by only varying the concentration of the extract. Madan *et al.,* (2016) obtained a plant extract from the leaves of *A. indica*. They obtained nanoparticles of 9–40 nm by varying the concentration of the extract. With a higher concentration, they produced nanoparticles of smaller sizes. The shapes of nanoparticles could also be altered by changing concentration of extracts. In addition, they obtained different shapes such as hexagonal, spherical, and quasi-spherical, bullet, bud and cone. This study is aimed at investigating the influence of the amount of *Azadirachta indica* seed husk extract acting as the reducing and capping agent in the green

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synthesis of ZnO-NPs. The growth, control of particle size and structural morphology of ZnO-NPs.

MATERIALS AND METHODS

Chemicals and Reagents: Zinc acetate dihydrate $[Zn(CH_3COO)_2].2H_2O$, sodium hydroxide (NaOH) pellets, deionized and distilled water of analytical grade were purchased and used without further purification.

Collection and preparation of A. indica Seed Husk: A. indica seed husk was collected from Zaria Local Government Area, Kaduna State and authenticated by a botanist at the herbarium of the Department of Plant Biology, Ahmadu Bello University Zaria, Nigeria (Shallangwa *et al.*, 2013). The seed husk was separated from the kernel and washed repeatedly with distilled water to remove particulate matter and other impurities on it, shade dried to constant weight, then pulverized into coarse powder using mortar and pestle and stored in air tight containers for further use.

Preparation of Aqueous A. indica Seed Husk: A. indica aqueous extract was prepared by slight modifications of the method described by Nava *et al.*, (2017). Briefly, about 50 g *A .indica* coarse powder were weighed and added into 250 ml beaker containing 50 ml of deionized water, and was stirred and heated for about 4 hours in water bath at 40ºC. After cooling, the extracts were filtered through muslin cloth and through Whatmann No.1 filter paper. The filtrate was collected in bottles and stored at 4ºC in a refrigerator until use.

Green synthesis of ZnO-NPs using A. indica Seed Husk Extract: All reagents were prepared according to standard procedures. The ZnO-NPs were green synthesized by following the co-precipitation method described by Africa *et al*., (2020). Zinc acetate dihydrate $[Zn\ (CH_3COO)_2].2H_2O$ and sodium hydroxide (NaOH) were used as precursors. Briefly, zinc acetate dihydrate (2M) was prepared in 50 ml of deionized water under constant stirring conditions. After complete dissolution of the mixture, 20-40 ml of seed husk extract was added. When the solution was heated up to 50ºC, 50 ml of 2M NaOH was added drop wise to the prepared solution of zinc acetate and seed extracts. The mixture was stirred continuously for 2h on magnetic stirrer resulting in white precipitate. The precipitate was filtered and washed repeatedly with distilled water followed by ethanol to remove the impurities. Finally, a white powder was obtained after overnight drying of the purified precipitate at 60℃ in oven over night, then annealed at 200ºC for 2h and kept for further characterization.

Characterization: The surface images, size and elemental composition of synthesized ZnO-NPs was captured by a scanning electron microscope/electron dispersion x-ray (Jeol JSM 7800F) and transmission electron microscope (Jeol, JSM2010). The surface functional groups of ZnO-NPs were analyzed by FTIR spectroscope (Agilent, Cary 630 2017 and FTIR-8400S Shimadzu, Japan). The spectral were recorded from 300 to 4000 cm^{-1} with a number of 30 scans.

FT-IR Spectral Analysis: Green synthesized ZnO-NPs using *A. indica* aqueous extract was within range of 400–4000 cm^{-1} to ascertain the possible phytochemical constituent which is implicated in capping and stabilization. The FTIR (figure 1) shows that synthesized NPs exhibit (broad, sharp) peaks at 3402.54 cm^{-1} (ZnO-NPs1 and ZnO-NPs2) corresponding to stretching bonds of primary O–H groups from phenols, polysaccharides, and protein. The peak at 3888.62 cm^{-1} corresponds to the O-H stretching vibration of the intra molecular hydrogen bond. The peaks at 2931.90 cm^{-1} (ZnO-NPs1), 2939.61 cm^{-1} (ZnO-NPs2) are attributed to the asymmetric and symmetric stretching vibrations of $–CH_2$ group, respectively.

The peak at 2260.65 cm^{-1} (ZnO-NPs1 and ZnO-NPs2) reveals the presence of C–H stretching vibrations of an aromatic aldehyde. The peaks of 1627.97 cm^{-1} (ZnO-NPs1), 1643.41-1589.40 cm^{-1} (ZnO-NPs2) correspond to C=O stretching vibration of primary amines (Nethahavanani, 2018). Absorption peaks in the region covering 1404.42–1141.90 cm^{-1} (ZnO-NPs1), 1419.66– 1141.90 cm^{-1} (ZnO-NPs2) imply the presence of an aromatic ring. An absorption peak found at 1018.45 cm^{-1} (ZnO-NPs2); 1026.42 cm^{-1} (ZnO-NPs1) corresponds to saturated primary alcohol C–O stretching. The above inference justifies the fact that the presence of phenols, polyphenols and primary amines in the plant extract could be implicated for capping and stabilization of ZnO-NPs.

The peak at 663.53 cm^{-1}, 624 cm^{-1} (ZnO-NPs1), 648.10 cm^{-1} (ZnO-NPs2) indicates the stretching vibrations of ZnO-NPs which is consistent with previous reports on similar studies (Bhuyan *et al.*, 2015; Nethahavanani, 2018).

The FTIR spectrum, absorption at 400 cm^{-1} to 600 cm^{-1} identifies the absorption peaks of metal oxide and the presence of ZnO (Bhuyan *et al.,* 2015; Nethahavanani, 2018) which further confirms the formation of ZnO-NPs by using plant extracts. The peaks at 439.78 cm^{-1} (ZnO-NPs1), 455.22 cm^{-1} (ZnO-NPs2) indicates the presence of ZnO-NPs (Elumalai *et al.,* 2015).

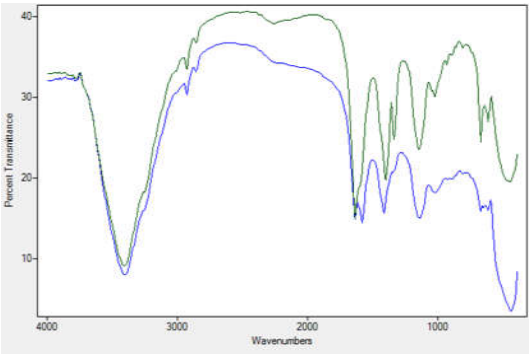

Fig 1: FTIR spectral of synthesized ZnO NPs1 (blue) and ZnO-NPs2 (green) spectral lines using 20-40 ml of *A. indica*

Scanning electron microscopy analyses: The particle size distribution of the nanoparticles was estimated from the Image J software by treating the nanoparticles as spheres and thus calculating the particle size distribution from the deduced area. SEM micrographs in Figure 2 revealed the shape of ZnO-NPs1 was spherical with agglomeration of particles with size ranging from 25 to 60 nm and ZnO-NPs2 (figure 3) were more uniform spherical shaped particles with size ranging from 19 to 35 nm. The morphology of structures indicated a reduction in size of particles and more uniform larger surface area with synthesis at higher amount of *A. indica* seed husk extract.

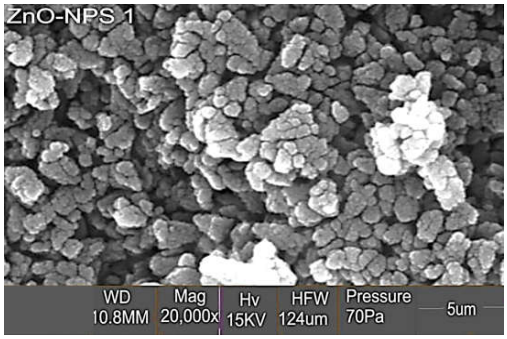

Fig 2: SEM micrograph of synthesized ZnO-NPs1 using 20 ml of *A. indica* extract

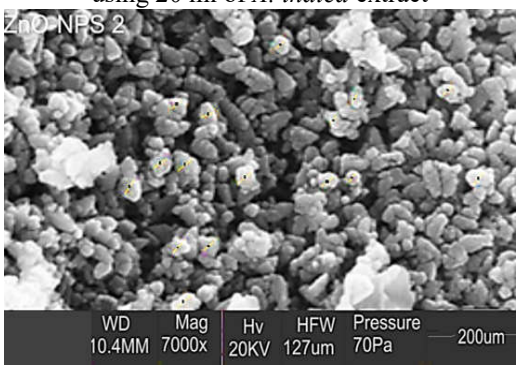

Fig 3: SEM micrograph of synthesized ZnO-NPs2 using 40 ml of *A. indica* extract

Electron Dispersive x-ray Analyses: The EDX studies shown in figure 4 and 5 reveal the elemental composition of the different ZnO-NPs samples, where it can be observed that all the samples presented similar chemical composition. The EDX analysis of the green synthesized ZnO-NPs using *A. indica* seed husk extract confirms the presence of pure ZnO-NPs. The EDX spectrum of ZnO-NPs show only emission of strong signals of zinc and oxygen elements, which confirm ZnO-NPs prepared is essentially free from impurities and it is seen in the limit of the EDX (figure 4, 5). Additionally, the values shown by these EDX studies corroborate the presence of zinc oxide in all samples. Similar kinds of observations have been reported by Madan *et al.*, (2016) indicating that increases in the amount of plant extract leads to a decrease in the particle size of nanoparticles (Fakhari *et al*., 2019). It is evident that the morphology of ZnO-NPs is spherical shaped and well distributed particles on the matrix with aggregation indicating the presence of biological material observed which is very similar to earlier studies of biosynthesized ZnO-NPs by Bhuyan *et al*., (2017), Haghighi *et al*., (2018). This agglomeration maybe due to polarity and electrostatic attraction of ZnO NPs rising from the biological material (*A. indica* seed husk extract).

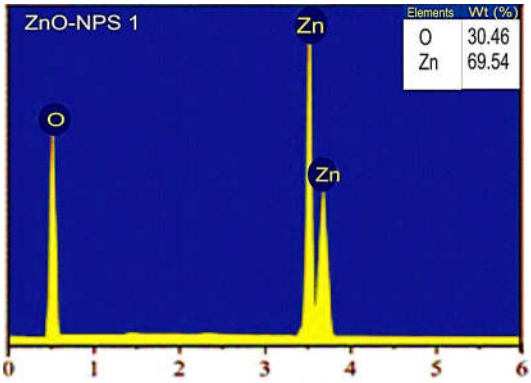

Fig 4: EDX spectral of synthesized ZnO-NPs1 using 20 ml of *A. indica* extract

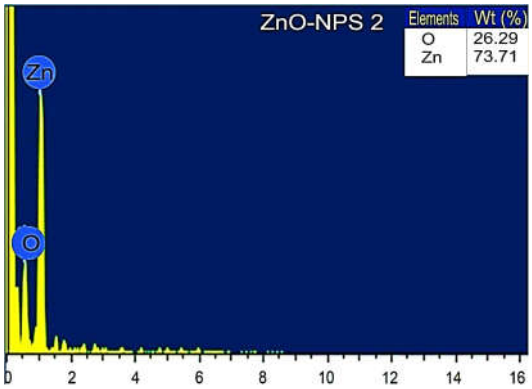

Fig 5: EDX spectral of synthesized ZnO-NPs2 using 40 ml of *A. indica* extract

Theoretically, the expected stoichiometric mass percent of Zn and O are 80.3% and 19.7% respectively. The EDX of ZnO-NPs1 was observed as 69.54% (Zn) and 30.46% (O). The emission peaks for ZnO-NPs2 were 73.71% (Zn), 26.26% (O) was obtained. The EDX analyses in our study show similar results for all the synthesized nanoparticles and in close agreement especially the values for ZnO-NPs1with reports by Elumalai *et al*., (2015) in previous studies of ZnO-NPs synthesis using *A. indica* leaf extract with atomic and weight percent values of Zn and O observed as 67.39, 32.61, respectively without impurities, also our study proved to have higher elemental composition of zinc and oxygen than the reported 57.16% and 14.87% of Zn and O by Bhuyan *et al*., (2015). It can be noted that ZnO-Nps2 has the highest mass percent of Zn and O. This study results further confirms that an increase in the amount of extract has significant effect on the nanoparticles yielded.

Transmission electron microscopy analyses: The growth of the ZnO-NPs was analyzed through TEM, as shown in Figure 6 and 7. TEM micrograph for ZnO-NPs1, 2 was digitized using image J software treating particles as spheres revealed the particles are discreet and spherical in nature and poly dispersed with size ranging from 28 to 52 nm and the mean particle size of 45.38 ± 12.15nm. The ZnO-NPs2 revealed the particles are distinctly spherical with size ranging from 8.2-11.9 nm and the mean particle size of 10.288 ± 1.066. The synthesized ZnO-NPs present different shapes and a reduction in the particle size of each sample related to the higher amount of *A. indica* seed husk extract used, which could be `attributed to the polyphenolic content of the *A. indica* seed husk extract as described by Nava *et al*., (2017).

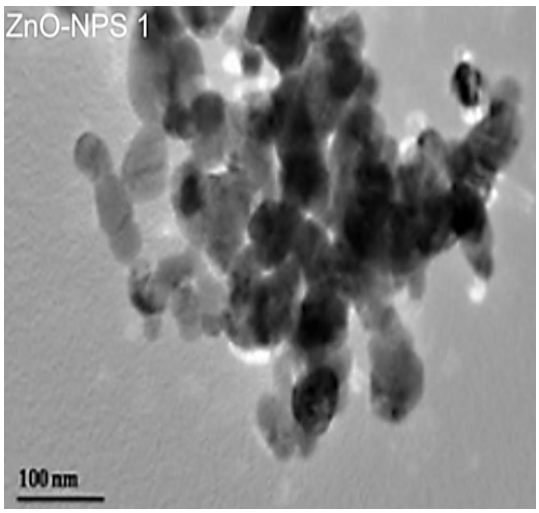

Fig 6: TEM micrograph of synthesized ZnO-NPs1 using 20 ml of *A. indica* extract

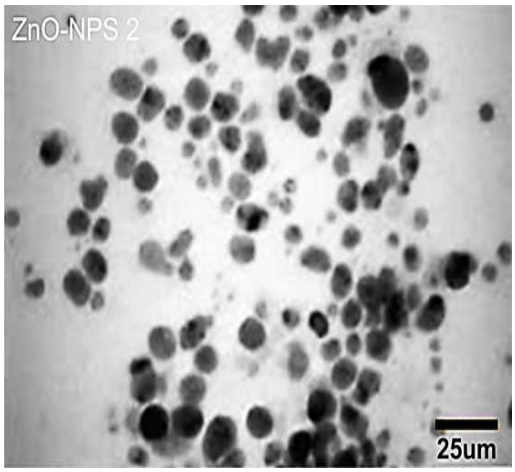

Fig 7: TEM micrograph of synthesized ZnO-NPs2 using 40 ml of *A. indica* extract

The effect of the *A. indica* seed husk extract used in the synthesis of the nanoparticles is largely noticeable. The smaller amount in sample ZnO-NPs1 presents non-homogenous ragged particles of very irregular sizes and shapes, with an average diameter of 45.38 ± 12.15nm. On the other hand, the larger amount of *A. indica* seed husk extract in sample ZnO-NPs2 shows a more homogeneous material that has very well defined spherical particles, almost all of which are of a similar size and shape, with an average diameter of 10.288 ± 1.066 nm which is in close agreement with reports of Bhuyan *et al*., (2017). Luque *et al*., (2018) carried out biosynthesis of purely spherical and hexagonal ZnO-NPs and different size and shape homogeneity depending on the amount of extract used.

Conclusion: The green synthesis and growth of small, stable, spherical and pure ZnO-NPs using various amount of *A. indica* seed husk extract as a reducing agent was successful. The study confirms that the growth of Spherical ZnO-NPs is supported by the presence of phytochemicals in the plant extract, thereby has significant effects on the growth, stabilization and control of the size and shape of synthesized nanoparticles. This research reveals *A. indica* seed husk extract as an effective reducing agent and significantly influences the surface morphology and structure of the ZnO-NPs.

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REFERENCES

Africa, NS; Dallatu, YA; Shallangwa, GA (2020). Biosynthesis and Characterization of ZnO

Nanoparticles using Azadirachta Indica Seed Husk Extract. *Nig. Res. J. Chem. Sci.* 8(1), 115-128

Agarwal, H.; Kumar, SV; Rajeshkumar, S (2017). A Review on Green Synthesis of Zinc Oxide Nanoparticles–An Eco-Friendly Approach. *Resource-Effic. Technol*. *3*(4), 406-413.

Bhuyan, T; Mishra, K; Khanuja, M; Prasad, R; Varma, A (2015). Biosynthesis of Zinc Oxide Nanoparticles from A*zadirachta Indica* for Antibacterial and Photocatalytic Applications. *Mater Sci Semicond Process*. *32*, 55-61.

Elumalai, K; Velmurugan, S (2015). Green Synthesis, Characterization and Antimicrobial Activities of Zinc Oxide Nanoparticles from the Leaf Extract of *Azadirachta Indica* (L.). *Appl. Surf. Sci*. *345*, 329-336.

Fakhari, S; Jamzad, M; Fard HK (2019). Green Synthesis of Zinc Oxide Nanoparticles: A Comparison. *Green Chem. Lett. Rev*. *12*(1), 19-24.

Haghighi, M; Nikoofar, K; Ahmadvand, Z (2018). Growth of Wurtzite ZnO Nanorods using Different Capping Agents: Characterization, Morphology, and Investigation the Catalytic Activity in Some Oxindoles and Indolyl Organics. *Nanochem. Res*. *3*(2), 131-141.

Husen, A (2019). Natural Product-Based Fabrication of Zinc-Oxide Nanoparticles and their Applications. In Husen, A., Iqbal, M. (Eds.), Nanomaterials and Plant Potential. *Springer*, *Cham,* pp. 193–219.

Jafarirad, S; Mehrabi, M; Divband, B; Kosari-Nasab, M (2016). Biofabrication of Zinc Oxide Nanoparticles using Fruit Extract of Rosa Canina and their Toxic Potential Against Bacteria: A Mechanistic Approach. *Mater. Sci. Eng. C. 59*, 296-302.

Karanassios, V (2018). Brief Introduction to Nanoscience and Nanotechnology. *Nanosci. J. 1*(1), 1-6.

Luque, PA; Soto-Robles, CA; Nava, O; Gomez-Gutierrez, CM; Castro-Beltran, A; Garrafa-Galvez, HE., Olivas, A (2018). Green Synthesis of Zinc Oxide Nanoparticles using Citrus Sinensis Extract. *J. Mater. Sci: Mater. Electron*. *29*(12), 9764-9770.

Madan, HR; Sharma, SC; Suresh, UD; Vidya, YS; Nagabhushana, H; Rajanaik, H Anantharaju KS, Prashantha SC and Sadananda Maiya,, P (2016). Facile Green Fabrication of Nanostructure Zno Plates, Bullets, Flower, Prismatic Tip, Closed Pinecone: their Antibacterial, Antioxidant, Photoluminescent and Photocatalytic Properties. *Spectrochim. Acta A*. *152*, 404-416.

Maria, R; Shirley, M; Xavier, C; Jaime, S; David, V; Rosa, S; Jodie, D (2018). Preliminary Phytochemical Screening, Total Phenolic Content and Antibacterial Activity of Thirteen Native Species from Guayas Province Ecuador. *J. King Saud Univ-Sci*. *30*(4), 500-505.

Nava, OJ; Luque, PA; Gómez-Gutiérrez, CM; Vilchis-Nestor, AR; Castro-Beltrán, A; Mota-González, ML; Olivas, A (2017). Influence of Camellia Sinensis Extract on Zinc Oxide Nanoparticle Green Synthesis. *J. Mol. Struct. 1134*, 121-125.

Nethavhanani, T; Diallo, A, Madjoe, R, Kotsedi, L; Maaza, M (2018). Synthesis of Zinc Oxide Nanoparticles by a Green Process and the Investigation of their Physical Properties. *AIP Conf. Proc.* 1962(1), 040007.

Shallangwa, GA; Jibrin, GP; Haliru, M; Hamidu, AA; Dallatu, YA; Abba, H; Moyosore, AA (2013). In Vitro Evaluation of Aloe Vera and Camellia Sinensis Aqueous Extracts Effect on Protein Denaturation During Acute Inflammation. *Biointerface Res. Appl. Chem. 3*(3), 7-19.

Sorbiun, M.; Shayegan Mehr, E.; Ramazani, A.; Mashhadi Malekzadeh, A (2018). Biosynthesis of metallic nanoparticles using plant extracts and evaluation of their antibacterial properties. *Nanochem. Res. 3*(1), 1-16.

Yadi, M; Mostafavi, E; Saleh, B; Davaran, S; Aliyeva, I; Khalilov, R; Nikzamir, N; Akbarzadeh, A; Panahi, Y; Milani, M (2018). Current Developments in Green Synthesis of Metallic Nanoparticles using Plant Extracts: A Review. *Artif. Cells Nanomed. Biotechnol*. *46*(3), 336-343.