Green Synthesis, Characterization of Silver Nanoparticles Using *Canna indica* and *Senna occidentalis* Leaf Extracts

Akinsiku, A.A, Ajanaku, K.O., Adekoya, J.A
Department of Chemistry,
Covenant University, Canaan Land
Nigeria
anu.akinsiku@covenantuniversity.edu.ng

Dare, E.O
Department of Chemistry,
Federal University of Agriculture Abeokuta,
Ogun State, Nigeria

***Abstract*— Green synthesis is now considered an alternative to chemical and physical synthetic procedures for nanoparticles by using sustainable and eco-friendly materials instead of harsh and toxic chemicals. This research aimed at synthesizing silver nanoparticles using locally- sourced leaf extracts of *Canna indica* and *Senna occidentalis.* The syntheses were monitored with double beam UV-Visible spectrophotometer. Aliquot samples were taken at time intervals (5, 10, 15, 20, 30 minutes) during bioreduction. Colour changes were observed in the process of Ostwald ripening in both syntheses. Again, excitation of surface plasmon resonance was obvious in the nanosilver formed by the biomass. Red shifting indicating particle size increase (400-430 nm), and blue shifting (350-380 nm) were evident in *Canna indica* and *Senna occidentalis* silver nanoparticles respectively. Energy dispersed analysis by X-ray (EDAX) indicated silver oxide peaks, and scanning electron microscopy (SEM) showed an amorphous phase of the nanoparticles as further proofs of nanosilver formation from both extracts.**

***key words*- Green synthesis, nanoparticles, nanosilver, *Canna indica, Senna occidentalis*, SEM, EDAX**

I. INTRODUCTION

Researchers are now focused on the use of sustainability ideas that use green chemistry for bioremediation in all scientific fields; as this will eliminate complex synthetic routes. Metal nanoparticles are of various uses- catalytic, electronics, biology and biomedical material science, physics and environmental remediation. Hence, there is a need for the development of cheap and eco-friendly nanomaterials, as nanoparticles synthesis is still on the high cost side [1-8]. Consequently, use of benign materials and biomass in the synthesis of nanoparticles is gaining widespread acceptance.

Microorganisms such as bacteria, actinomycetes, and fungi continue to be investigated in metal nanoparticles synthesis; the use of parts of whole plants in similar nanoparticles synthesis methodologies is an exciting possibility that is relatively unexplored and underexploited [9]. Even though gold nanoparticles are considered biocompatible, chemical synthesis methods may still lead to the presence of some toxic chemical species adsorbed on the surface that may have adverse effects in medical applications. Synthesis of nanoparticles using microorganisms or plants can potentially eliminate this problem by making nanoparticles more biocompatible. Using plants for synthesis of nanoparticles could be advantageous over other environmentally benign biological processes by eliminating the elaborate process of maintaining cell cultures. It can also be suitably scaled up for large-scale synthesis of nanoparticles [9, 10]. Hence, there is no need for hazardous chemicals, high-energy and wasteful purifications [11].

In recent times, biodiversified plant extracts that are peculiar to Nigeria for the synthesis of silver nanoparticles (SNPs) were reported by Dare *et al*., using the plant extracts of *Afromomum melegueta), Anacardium occidentale linn, Capsicum chinense, Citrus aurantifolia, Ocimum gratissimum, Newbouldia laevis, Piper guineense, Psidum guajava, Gangronema latifolum), Telfairia occidentalis, Xylopia aethiopica) and Vernonia amygdalina* [12]. Jha and Prasad also carried out nanoparticles synthesis using Eucalyptus hybrid [13]. Likewise, some selected alcoholic beverages [14] were employed for silver nanoparticles formation.

Recently, researchers have discovered that phytochemicals present in the plant extracts are responsible for metal ion reduction and capping of the newly formed particles during their growth processes [15, 16]. Alkaloids, flavonoids, terpenes etc. present in plants are good indicators for bioreduction process.

However, *Canna indica* L. (Indian shot); the first plant considered for this research belongs to the family Cannaceae. Qualitative phytochemical analysis of *Canna indica* L. flower confirmed the presence of various alkaloids, carbohydrates, proteins, flavonoids, terpenoids, cardiac glycosides, steroids, tannins, saponins, phlobatinins [17]. Hence, these qualities are positive indicators for nanosilver formation, as the alkanoids, terpenoids, and carbohydrates are responsible for the reduction of silver metal ion (Ag^{+} to Ag^{0}), and capping of metal nanoparticles during nucleation and growth processes. The water extract of rhizomes of *C. indica* has been reported to have HIV-1 reverse transcriptase inhibitor activity [18], while its essential oil showed antibacterial activity [19]. Methanolic extract of aerial parts of *Canna indica* showed antioxidant activity [20]. The second plant- *Senna occidentalis* L.(Coffee senna) belongs to Caesalpiniaceae family. Its phytochemical screening revealed tannins, phlobatannins, flavonoids and alkaloids [21]. These biochemicals of course are expected to act as capping agent and bioreducing agent in the formation of nanosilver.

Moreover, growth of the syntheses is considered to be a diffusion controlled ripening process [22], as the final stage of the silver nanoparticles formation (new phase) is considered as Ostwald's ripening (OR). The Nanoclusters or nanocrystals (NCs) of the new phase regarded to have different sizes interact through the Gibbs-Thomson effect, which results in dissolution of small NC and growth of large ones. Diffusion growth of NC under matrix of volume diffusion has been fully studied by Lifshitz and Slyozov [23, 24].

This paper reports the green method for the synthesis of silver nanoparticles by bioreduction of Ag^+ with plant extracts of *Canna indica* leaves and *Senna occidentalis*, as reducing or stabilizing agents. The formation was monitored at time intervals with UV-Visible spectrophotometer. Energy dispersed analysis by X-ray (EDAX) and scanning electron microscopy (SEM) were also employed to characterize the silver nanoparticles.

II. Methodology

Materials

Leaf extracts of *Canna indica* and *Senna occidentalis*, $AgNO_3$ of analytical grade, purchased from Sigma-Aldrich, distilled-deionized water.

III. Preparation of Extracts

Fresh green plants of *Canna indica* L. and *Senna occidentalis* L. were collected from different gardens at Atan-Iju, Ogun state, Nigeria. The plants were identified and authenticated at Forest Research Institute of Nigeria (FRIN). *Canna indica* leaves were thoroughly rinsed with distilled water, and then finely cut. The plants were homogenized using mortar and pestle. The extraction was carried out at the ratio of 1:5 wt/v using distilled-deionized water. The mixture was then filtered using Whatman no. 1 filter paper, after which the collected filtrate was kept at 4 ^{0}Cfor the nanosilver synthesis [25]. The procedure was repeated for the preparation of extract from *Senna occidentalis* plant.

IV. Synthesis of Silver Nanoparticles Using the *Canna indica* and *Senna occidentalis* Extracts

Filtrate from each extract was added to varying concentrations of aqueous silver nitrate solution (0.5 - 3.0 mM), at ratio 1: 10 (v/v). The resulting mixture was heated at 70 ^{0}C for 30 minutes. The bioreduction of Ag^+ ions to Ag^0 was monitored by periodic sampling (5, 10, 20 and 30 minutes) using the UV-Vis spectrophotometer (Double beam thermo scientific GENESYS 10S model), in quartz cuvette operated at a resolution of 1 nm, to measure the absorbance, and the rate of nanoparticles formation evident by the appearance of surface plasmon resonance band, SPB [25].

V. Characterization of the Synthesized Nanoparticles

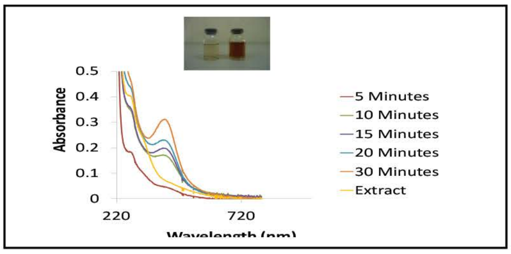
UV-Vis spectrophotometer was used to measure the optical absorbance, control the sizes and shapes of the nanoparticles formed [28, 29]. The reactions were monitored by taking aliquot samples at time intervals. The morphology and elements present in the prepared nanoparticles were confirmed using scanning electron microscope coupled with EDAX (TESCAN model), operated at 200 kV.

VI. Results and Discussion

Onset of nucleation and formation began as early as 5 minutes; as this showed the presence of adequate phytochemicals- alkaloids, terpenoids (found in *Canna indica*) and tannins in the *Senna occidentalis* [15], unlike most chemical syntheses in which nucleation can commence up to 2 hours. In this study, the reactions were fast. Overlap in the spectra indicated reaction completion, and of course, this took place within 30 minutes as observed in the nanoparticles formed from the two extracts considered for this experiment. Higher intensity of absorption observed can be related to the optical properties of the nanostuctures.

Red shifted absorbance peak (400-430 nm) for silver nanoparticles in Fig.1, likely indicates particle size increase. Also, capping by organics functional groups inherent in the bioextracts [12], was observed in the nanosilver formed by *C. indica* extract, while blue shift (340-380 nm), Fig. 2, was noticed in S. *occidentalis*. The wavelength values are typical of metallic silver nanoparticles (around 400 nm). Reaction mechanism is considered to be Ostwald's ripening, as this explains larger particle growth at the expense of smaller particles [28]. This is common in plant-mediated nanoparticles synthesis. It also depends mainly on diffusivity of the particles as this can be limited due to shape irregularity. The phytochemicals- alkaloids and flavaloids in the leaf extracts of *C. indica* and flavaloids with tannins in *S. occidentalis* leaf extracts acted as the reducing agent and capping agents in the nanoparticles formation reported in this work [15,16]; as this proved a better alternative to the use of harsh chemicals [29, 30, 31]. The observed colour change (light yellow to brown) when the extract was added to silver nitrate solution was an evidence of nanoparticles formation (Figs. 1 & 2). This can be attributed to the reduction of Ag^+ to Ag^0 excitation of surface Plasmon vibrations in the metal nanoparticles [32], and changes in electronic energy level [12].

The result of morphological characterization as prepared nanosilver mediated by plant extract is shown in Fig. 3 (*Canna indica* nanosilver) and Fig. 5 (*S.occidentalis* nanosilver). Novel nanoplate (from leaf extract) morphology was observed in the silver nanoparticles formed by *S. occidentalis* plant extract. The nanoparticles are amorphous. These further proved nanoparticles formation. Figs. 4 and 6 are the Energy Dispersive X-ray Analysis (EDAX) spectra of the plant-mediated silver nanoparticles. The spectra shows characteristics of Ag signal (3 kev), which is typical of the absorption of silver nanoparticles. Silver oxide peak is depicted in the spectra. Carbon is from the plant, and other elements are from the grid used.



ig. 1. Time resolved surface plasmon resonance of silver nanoparticles from *Canna indica* plant

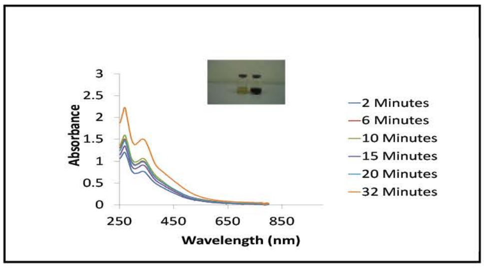


Fig. 2. Time resolved surface Plasmon resonance aof nanosilver from *Senna occidentalis* plant

Fig. 3. SEM image representative of silver nanoparticles from *Canna indica* plant

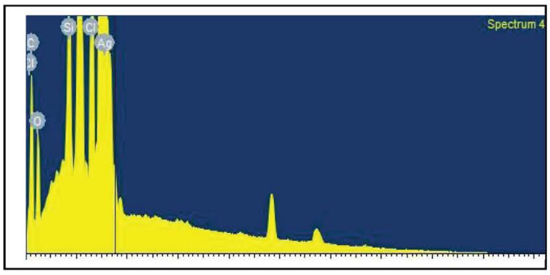


Fig. 4. EDAX spectra of *Canna indica* nanosilver

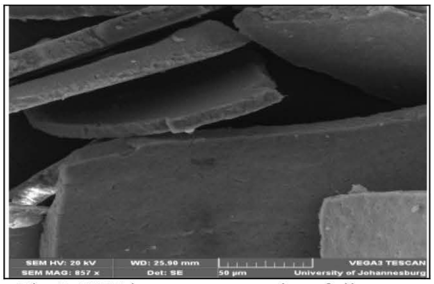


Fig. 5. SEM image representative of silver nanoparticles from *Senna occidentalis* plant

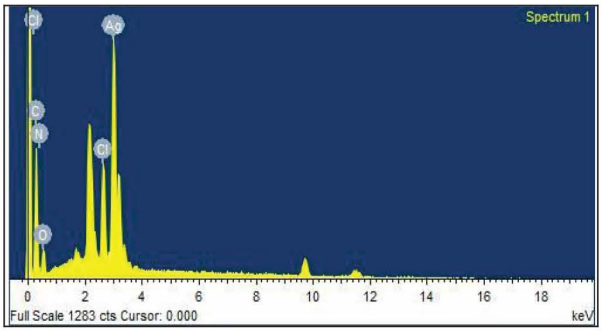


Fig. 6. EDAX spectra of S*enna occidentalis* nanosilver

Reaction of formation

$AgNO_3 \rightarrow Ag^+ + NO_3^-$

$Ag^+ + \text{phytochemicals} \rightarrow Ag^0 + R \quad (E^0 = +0.80\ V)$

VII. CONCLUSION

In this work, a facile one-pot 'green' synthesis of silver nanoparticles had been successfully carried out with the leaf extract of *C. indica* and *S. occidentalis.* The extracts initiated nucleation and growth of the nanoparticles. Alkaloids, flavaloids and tannins present in the plant extracts have been considered to be responsible for the bioreduction process. The two plants considered have found use in the field of nanotechnology. The application of the synthesized nanoparticles is underway. The synthesis is cheaper and faster than the conventional methods.

ACKNOWLEDGMENT

We acknowledge the assistance of Mr. Samson Alayande at the University of Johannesburg, South Africa for SEM-EDAX characterization.

REFERENCES

[10] A.L. González and C. Noguezm, "Influence of morphology on the optical propertieof metal nanoparticles," Journal of Computational and Theoretical Nano- science, Vol. 4, No. 2, pp. 231-238, 2007.

[11] M. Gross, M. A. Winnacker and P. J. Wellmann, "Electrical, optical and morphological properties of nanoparticle indium-tin-oxide layers," *Thin Solid Films*, Vol. 515, No. 24, pp. 8567-8572, 2007. doi:10.1016/j.tsf.2007.03.136

[12] J. Y. Kim, M. Kim, H. M. Kim, J. Joo and J. H. Choi, "Electrical and optical studies of organic light emitting

devices using SWCNTs-Polymer nanocomposites," *Optical Materials*, Vol. 21, No. 1-3, pp. 147-151, 2003. doi:10.1016/S0925-3467(02)00127-1

[13] W. J. Parak, D. Gerion, T. Pellegrino, D. Zanchet, C. Micheel, S. C. Williams, R. Boudreau, M. A. Le Gros and C. A. Larabell and A. P. Alivisatos, "Biological applications of colloidal nanocrystals," *Nanotechnology*, Vol. 14, No. 7, pp. 15-27, 2003. doi:10.1088/0957-4484/14/7/201

[14] D. A. Schultz, "Plasmon resonant particles for biological detection," *Current Opinion Biotech*, Vol. 14, No. 1, pp. 13-22, 2003. doi:10.1016/S0958-1669(02)00015-0

[15] A. M. Smith, H. Duan, M. N. Rhyner, G. Ruan and S. Nie, "A systematic examination of surface coatings on the optical and chemical properties of semiconductor quantum dots," *Physical Chemistry Chemical Physics*, Vol. 8, No. 33, pp. 3895-3903, 2006. doi:10.1039/b606572b

[16] G. H. Wei, Z. Zhou and Z. Liu, "A simple method for the preparation of ultrahigh sensitivity surface enhanced raman scattering (SERS) active substrate," *Applied Surface Science*, Vol. 240, No. 1-4, , pp. 260-267, 2005. doi:10.1016/j.apsusc.2004.06.116

[17] H. Y. Wang, Y. F. Li and C. Z. Hua, "Detection of ferulic acid based on the plasmon resonance light scattering of silver nanoparticles, special issue on China- Japan-Korea environmental analysis," *Talanta*, Vol. 72, No. 5, pp. 1698-1703, 2007.

[18] J.L. Gardea-Torresdey, J.G. Parsons, E. Gomez, J. Peralta-Videa, H.E. Troiani, P. Santiago, M. Jose-Yacaman, *Nano Letter*. Vol. 2, pp. 397, 2002.

[19] J.L. Gardea-Torresdey, E. Gomez, J.R. Peralta-Videa, J.G. Parsons, H. Troiani, M. Jose-Yacaman, *Langmuir*, Vol. 19, pp. 1357, 2003.

[20] A.M. Awwad, M.S. Nida, and O.A. Amany, "Green synthesis of silver nanoparticles using carob leaf extract and its antibacterial activity." *Int. J. Ind. Chem*. Vol. 4, pp. 1–6, 2013.

[21] E. O. Dare, C. O. Oseghale, A. H. Labulo, E. T. Adesuji, E. E. Elemike, J.C, Onwuka, J. T. Bamgbose, " Green synthesis and growth kinetics of nanosilver under bio-diversified plant extracts influence", *J. Nanostruct Chem,* 2014.DOI 10.1007/s40097-014-0139-5.

[22] A.K. Jha and K. Prasad, "Green synthesis of silver nanoparticles using Cycas leaf. Int. J. Green Nanotechnology Phys. Chemistry, Vol. 1 (2), pp. 110–117, 2010.

[23] E.T. Adesuji, E.E. Elemike, A. Chuku, A.H. Labulo, M.C. Owoseni , C.O. Oseghale, R. Mfon and O.E. Dare, "Synthesis of silver nanoparticles using some alcoholic beverages from Nigeria market," *Int. J. Nano Mater. Sci*, Vol. 2(1), pp. 25–35, 2013.

[24] B. Harekrishna, K.B. Dipak, P.S. Gobinda, S. Priyanka, P. Santanu and M. Ajayi, "Green synthesis of silver nanoparticles using seed extract of Jatropha curcas," *Colloids Surf. A Physicochem. Eng. Asp.*, Vol. 348,pp. 212–216, 2009.

[25] S.Y. He, Z.R. Guo, Y. Zhang, S. Zhang, J.Wang and N. Gu, "Biosynthesis of gold nanoparticles using the bacteria Rhodopseudomonas capsulate," *Mater. Lett.* Vol. 61, pp. 3984, 2007.

[26] G. Lamaeswari and T. Ananthi, P.G and Research Department of Biochemistry, S.T.E.T Women's College, Mannargudi, India, *Int. J. Pharm. Sci. Rev. Res.,* Vol.*14*(2),pp. 76-79, 2012.

[27] W. Woradulayapinij, N. Soonthornchareonnon, C. Wiwat, " In vitro HIV type 1reverse transcriptase inhibitory activities of Thai medicinal plants and Canna indica L. rhizomes," *Journal of Ethnopharmacology,*Vol. 101,(3), pp. 84-89, ,2005.

[28] A. K. Indrayan, N. K. Bhojakb, N. K. Shatru and A. Gaur, "Chemical composition and antimicrobial activity of the essential oil from the rhizome of Canna indica Linn**,"** *Indian journal of chemistry,* Vol. 50B (08) , pp.1136 – 1139, 2011.

[29] Y. M. Joshi,V. J. Kadam and P. R. Kaldhone, "In-vitro antioxidant aActivity of methanolic extract of aerial parts of Canna indica L," *Journal of Pharmacy Research*, Vol. 2(11),pp. 1712- 1715, 2009.

[30] H.O. Egharevba, A.C. Odigwe, M.S. Abdullahi, S.K. Okwute and J.I. kogun, "Phytochemical analysis and broad spectrum antimicrobial activity of *Cassia Occidentalis* L. (whole plant)," *New York Science Journal*.Vol. 3 (10),pp. 74-81, 2010.

[31] E.O. Dare, C.O. Oseghale, A. H. Labulo, E. T. Adesuji, E. E. Elemike, J. C. Onwuka and J. T. Bamgbose, "Green synthesis and growth kinetics of nanosilver under bio-diversified plant extracts influence," *Journal of Nanostructure Chemistry.* 2014. DOI 10.1007/s40097-014-0139-5

[32] I. M. Lifshits andV.V. Slyozov, "Onkinetics of diffusion decay of oversaturated solid solutions," *JETP*, vol. 35, pp. 479–492, 1958.

[33] I. M. Lifshitz and V. V. Slyozov, "The kinetics of precipitation from supersaturated solid solutions," *Journal of Physics and Chemistry of Solids*, vol. 19, no. 1-2, pp. 35–50, 1961.

[34] N. Ahmad and S. Sharma, "Green synthesis of silver nanoparticles using extracts of *Ananas comosus*," *Green and Sustainable Chemistry*, Vol. 2, pp.141-147, 2012.

[35] R. Swarnalathan, R.S Christina and B. Payas, "Evaluation of in vitro antidiabetic activity of Sphaeranthus amaranthoides silver nanoparticles," *Int. J. Nanomaterials Biostructures,* Vol. 2(3),pp. 25–29, 2012.

[36] B.J. Wiley, S.H, McLellan, J. Siekkinen, A and Y. Xia, " Manoeuvring the surface plasmon resonance of silver nanostructures through shape-controlled synthesis," *J. Phys. Chem. B* , Vol.110, pp. 15666–15675, 2006.

[37] B. V. Ivanskii, A.V. Moskalyuk, S. V. Yarema, I. I. Panko, and M.O. Stasyk, "Wagner-Vengrenovich Distribution," Nanomaterials, Vol. 2013, Article ID 651576, 8 pages, 2013. doi:10.1155/2013/651576

[38] M. Sui, X. Chen and L.Y. Wang, "Capping effect of CTAB on positively charged Ag nanoparticles," *Physica E*, Vol. 33,(2), pp.308–314, 2006.

[39] Y. Moon, T. Kusunose and T. Sekino, "CTAB-assisted synthesis of size- and shape-controlled gold nanoparticles in SDS aqueous solution," *Materials Letters*,Vol. 63,(23), pp. 2038–2040, 2009.

[40] C. Boca and S. Astilean, "Detoxification of gold nanorods by conjugation with thiolated poly(ethylene glycol) and their assessment as sers-active carriers of raman tags" *nanotechnology*, vol.21, pp. 23, 2010.

P. Mulvaney, "Surface plasmon spectroscopy of nanosized metal particles," *Langmuir*, Vol. 12, pp. 788, 1996