ANNONA SQUAMOSA LEAF EXTRACT AS AN EFFICIENT BIOREDUCING AGENT IN THE SYNTHESIS OF CHROMIUM AND NICKEL NANO Particles

Solomon A. Mamuru*, Abubakar S. Bello and Saminu B. Hamman
Electrochemical NanoLab, Department of Chemistry, Adamawa State University, PMB 25, Mubi, Nigeria
*Corresponding author’s email: almanto1@yahoo.com

Abstract
Biosynthesis is one of the rapid, reliable, and eco-friendly routes for the synthesis of metal nanoparticles in areas of nanotechnology research. The synthesis of chromium and nickel nanoparticles using Annona squamosa leaf extracts at neutral pH was studied. The formed metal nanoparticles were confirmed by colour changes from colourless to dark brown and it was characterized using UV-visible and Fourier transform infrared spectroscopy. UV-visible spectrums of the aqueous medium containing the metal nanoparticles show a surface Plasmon resonance at 285 nm. FT-IR analysis reveals that phytochemical groups of aromatic amine character might be responsible for the reduction to metal nanoparticles.

Keywords: Biosynthesis; Nanoparticles; Fourier transform infra-red spectroscopy; Annona squamosa

Introduction
Metal nanoparticles have received considerable attention in recent years because of their unique catalytic, electronic, optical and structural properties and subsequent technological applications as catalysts, sensors, nano electronic devices, biomedical tools and biosensors. The applicability as well as performance of these nanoparticles depends critically on their size, shape, composition and their fine structure, either as alloy or core–shell (Begun, Mondal, Basu, Laskar, & Mandal, 2009) therefore, the design and synthesis of nanoparticles with tailor made structural properties is a highly challenging problem for researchers working in the field of nanoscience and nanotechnology.

In the last decade, biosynthesis of metal nanoparticles has served as a growing need to the development of clean, nontoxic chemicals, environmentally benign solvents and renewable materials (Rai et al., 2009), hence the focus is now shifted towards ‘green’ chemistry and bioprocesses. In recent years several plant extracts have been studied in the utilization of their secondary metabolites (Gopinath et al., 2013; Gaware et al., 2012). This has emerged as a novel technology for the synthesis of various metal nanoparticles. The advantage of using plants for the synthesis of metal nanoparticles is that they are easily available, safe to handle and possess a broad variability of metabolites that may aid in reduction. The plant phytochemicals with anti-oxidant or reducing properties are usually responsible for reduction of metal compound into their respective nanoparticles. In this work we report for the first time the use of annona squamosa leaf extract in the synthesis of nickel and chromium nanoparticles. The use of annona squamosa fruit waste in the synthesis of palladium nanoparticles is the only known study for this plant. (Selvaraj et al., 2012)

Materials and Method

Materials
Annona squamosa leaves, Nickel oxide, Chromium (III) chloride, UV-visible spectrophotometer and Fourier transform infrared (FTIR) spectroscopy.

Method
Preparation of the extract
Adaptation of the synthesis process was from Gopinath et al (2013), and briefly explained. Annona squamosa collected within Mubi metropolis were used to make the aqueous extract. Fresh leaves of annona squamosa plant were cut, 10 g weighed and boiled in 200 mL distilled water for 10 minutes, this was allowed to cool under room temperature and then filtered with Whatman filter paper No.1 to obtain the extract.

Preparation of nickel and chromium nanoparticles
0.001M nickel oxide and the chromium (III) chloride solutions were prepared; 10 mL of the plant extracts was added drop wise with continuous stirring to 50 mL of each of the solutions for one hour until colour changes. The products were then centrifuged at 3000 rpm for 10 minutes, washed with ethanol and distilled water and allowed to dry at room temperature.
Solution characterization
The synthesized nickel and chromium nanoparticles were confirmed by sampling the aqueous component using UV-visible spectrophotometer. Distilled water was used as a blank. Various measurement of absorbance were carried out at a wavelength of 300-700 nm using Jenway 6400 UV-visible spectrophotometer at a scan interval of 5 nm; measurements were taken for nickel and chromium nanoparticles, the leaf extract, nickel oxide and chromium trichloride solutions. The biomolecule responsible for the reduction of nickel oxide and chromium chloride was determined using Perkin Elmer Fourier transform infrared (FTIR) spectrophotometer.

Results and Discussions

Optical Property
During the course of adding 10 mL of extract (Fig. 1A) to the flasks containing 0.001M nickel oxide and chromium trichloride respectively, there was no immediate change in the colour however at the end of 1 hour the colour of the solutions change from colourless for chromium trichloride (Fig. 1B) and light blue of nickel oxide (Fig. 1C) to dark-brown which indicates the formation of nanoparticles (Fig.1D). The difference in shade of colour is mostly likely due to the excitation of surface plasmon resonance effect in the metal nanoparticles (Lukman et al., 2011). It is known that metal surface plasma oscillation, and their optical properties, depends upon size and shape.

UV-visible spectroscopy analysis
More information on the metal nanoparticles by reduction of aqueous metal ions during exposure with Annona squamosa extract was observed by UV-visible spectroscopy. The UV-visible absorption spectrum of nickel and chromium nanoparticles is shown in Fig. 2. The spectrum shows the characteristic surface plasmon resonance (SPR) with absorbance at approximately 280-295 nm and peak maxima at 285 nm, for nickel and chromium nanoparticles this can be ascribed to the formation of the metal nanoparticles. The shape of the plasmon bands was almost symmetrical, suggesting that the nanoparticles are well-dispersed and uniform. If the particles are not uniform, then it leads to a broad absorption peak at higher wavelength and the splitting of a plasmon band into two bands (Baia et al., 2007; Smitha et al., 2008).

Fig. 2: The UV-visible absorption spectrums of Annona squamosa extract, chromium and nickel nanoparticles

Fourier transform infrared spectroscopy analysis
The Fourier transform infrared analysis was perform to identify the possible biomolecules responsible for the reduction of nickel oxide, chromium chloride and capping of the reduced metal nanoparticles synthesized using Annona squamosa leaf extract.

Fig. 3: The FTIR spectrums of annona squamosa extract, chromium and nickel nanoparticles

This paper can be downloaded online at http://ijasbt.org & http://nepjol.info/index.php/IJASBT
The bands which appeared at 3217 cm\(^{-1}\) and 2918 cm\(^{-1}\) correspond to aliphatic R-NHR and amine salt; primary NH\(_3^+\), respectively, the bands at 1574 cm\(^{-1}\) and 1379 cm\(^{-1}\) are due to primary amine; aliphatic and tertiary bicyclic alcohols; phenols, respectively. The FT-IR bands observed at 1039 cm\(^{-1}\), and 584.9 cm\(^{-1}\) may be ascribed to aliphatic RCH\(_2\)-NH\(_2\) and amide, C-C(=O)-NH\(_2\), respectively (Patnaik, 2004).

The band at 1606 cm\(^{-1}\) which was absent in the spectra of the metal nanoparticles (indicated with the red arrow in Fig. 3) and assigned to aryl amine group may be responsible for the reduction of nickel oxide and chromium chloride to nickel and chromium nanoparticles respectively.

**Conclusion**

Chromium and nickel nanoparticles were successfully synthesized using plant leaf extract of *Annona squamosa*. Initial synthesis was confirmed by colour changes from light blue of nickel oxide and colourless of chromium chloride to different shades of brown of the metal nanoparticles. The metal nanoparticles were characterized using UV-visible spectroscopy. The surface plasmon resonance was at 285 nm indicating that the particles are of small sizes. Fourier transform infrared analysis was used to identify the possible biomolecules responsible for the reduction of nickel oxide and chromium chloride to their metal nanoparticles using *Annona squamosa* leaf extract. The band at 1606 cm\(^{-1}\) which was absent in the spectra of the synthesized material which belongs to aryl amine group might be responsible for the reduction.

**Acknowledgement**

We would like to thank Adamawa State University and TET Fund for providing all the resources used in carrying out this research.

**References**

Baia L, Muresan D, Baia M, Popp J and Simon S (2007) Structural properties of silver nanoclusters-phosphate glass composites. *Vibrational Spectroscopy* 313-318.

Begun N, Mondal A, Basu S, Laskar RA and Mandal D (2009) Biogenic synthesis of Au and Ag nanoparticles using aqueous solution of Black Tea leaf extract. *Colloids and Surfaces B: Biointerfaces* 113-118.

Gaware, U., Kamble, V., and Balaprasad, A. (2012). Ecofriendly synthesis of anisotropic gold nanoparticles: A potential candidate of SERS studies. *International Journal of Electrochemistry*, 6-12.

Gopinath, K., Gowri, S., and Arumugam, A. (2013). Phytosynthesis of silver nanoparticles using *Pterocarpus santalinus* leaf extract and their antibacterial properties. *Journal of Nanostructures in Chemistry*, 1-7.

Lukman I, Audra G, Marjo, E, Roessier U and Harris T (2011) Facile synthesis, Stabilization and anti bacterial performance of discerete silver nanoparticle using Modica sativa seed exudates. *Colloids and Surfaces*, 433-444.

Patnaik P (2004) *Deans Analytical Chemistry Hand book*, New York: McGraw Hill.

Rai M, Yadav A and Gade A (2009) Silver nanoparticles as a new generation of antimicrbials. *Biotechnology Advances* 76-83.

Selvaraj M, Annadurai B, Rajendran K, Venkatesh GK and Arunachalam P (2012) Acaricidal, insecticidal, and larvicidal efficacy of aqueous extract of *Annona squamosa* L peel as biomaterial for the reduction of palladium salts into nanoparticles. *Colloids and Surfaces B: Biointerfaces* 209-212.

Smitha S, Nissamudeen K, Philip D and Chopchandran K (2008) Studies on surface plasmon resonance and photoluminescence of silver nanoparticles. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 186-190.