Spectrophotometric Evaluation of Biosynthesized Copper Nanoparticles using *Allium cepa*, *Azadirachta indica* And *Moringa oleifera* Plant Extracts

Mamuru, S A., John S., Samuel P. and Edam, E
Electrochemical NanoLab, Department of Chemistry, Adamawa State University, Mubi
Contact: *almanto1@yahoo.com*

ABSTRACT

Development of eco-friendly process for the synthesis of nanoparticles is one of the main steps in the area of nanotechnology research. The biological synthesis of copper nanoparticles using *Allium cepa*, *Azadirachta indica* and *Moringa oleifera* plant leaf extracts at pH 12 was studied. The synthesized nanoparticles are confirmed by color changes from light blue to green and it was characterized using UV-visible spectroscopy with average surface Plasmon resonance (SPR) at 307-315 nm and peak maxima at 310 nm for *Allium cepa* and average SPR absorbance at 301-310 nm and peak maxima at 305 nm for *Azadirachta indica* and *Moringa oleifera*. The shapes of the SPR are almost symmetrical and at lower wavelength suggesting that the nanoparticles are of small size, monodispersed and uniform.

KEYWORDS: Nanoparticles, Biosynthesis, Spectrophotometric, *Allium cepa, Azadirachta indica*, and *Moringa oleifera*

Introduction

Generally, metal nanoparticles are synthesized and stabilized by using chemical methods such as chemical reduction, electrochemical techniques, photochemical reactions in reverse micelles and now days via green chemistry route. Use of plants in synthesis of nanoparticles is quite novel leading to truly green chemistry which provide advancement over chemical and physical method as it is easily available, safe to handle and possess a broad variability of metabolites that may aid in reduction and in this method there is no need to use high pressure, energy, temperature and toxic chemicals (Saxena, Tripathi & Singh, 2010). Moreover, shape, size and nature can be controlled by these biological approaches through just modifying pH, temperature and nutrient media composition. A number of plants are being currently investigated for their role in the synthesis of nanoparticles (Zaheer, Javed & Athar, 2012).

Biosynthesis of metal nanoparticles is a kind of bottom up approach where the main reaction occurring is reduction/oxidation (Narayanan & Sakthivel, 2011). The microbial enzymes or the plant phytochemicals with anti oxidant or reducing properties are usually responsible for reduction of metal compounds into their respective nanoparticles. This study comes to highlight on biosynthesis of copper nanoparticles using *Allium Cepa* (onion), *Azadirachta Indica* (neem) and *Moringa Oleifera* (drumstick) which can be effective alternatives to nanoparticles synthesis from plant secondary metabolites.

Materials and Methods

Materials

Allium Cepa, Azadirachta Indica and *Moringa Oleifera,* were obtained locally from Mubi, copper nitrate (79.57%), Fisher Scientific Company, USA; sodium pellets (99%) Sigma-Aldrich; ethanol (99.7%) Guangdong Guanghua Chemical Factory Co. Ltd China; Jenway pH meter, Jenway 6405 UV- visible spectrophotometer

Preparation of extracts

The methods of extraction and nanoparticles preparation are adopted from (Gaware, Kamble, & Balaprasad, 2012). *Allium cepa, Azadirachta indica,* and *Moringa oleifera* were used to make the aqueous extract. Fresh leaves of the plants were cut, 10 g weighed and boiled in distilled water for 10 minutes; these were allowed to cool under room temperature and then filtered with Whatman filter paper No. 1 to obtain the extracts. The pH of the extracts was also adjusted to 12 using 0.1 M NaOH. Figures 1A, B and C show the extracts of *Allium cepa, Azadirachta indica,* and *Moringa oleifera,* respectively.

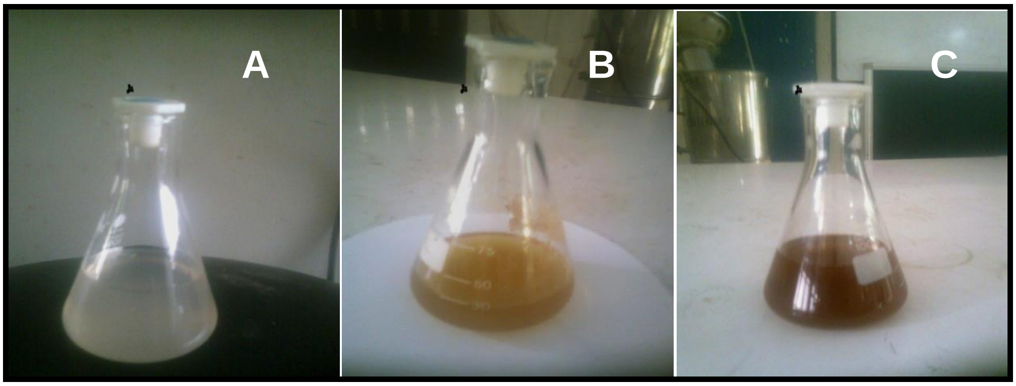

Figure 1: Leaf extracts of *Allium cepa* (A), *Azadirachta indica* (B) and *Moringa oleifera* (C)

Preparation of copper nanoparticles

0.9 g copper nitrate was weighed and dissolved in 50 mL distilled water and placed in a 100 mL Erlenmeyer flask to prepare a 0.1 M copper nitrate solution; a light blue colour was observed as shown in Figure 2A. This was stirred using magnetic stirrer for 2 hours with drop wise addition of 1 mL of the extract until colour changed to light green as indicated in Figure 2B. This colour change was observed for all the extracts. The product was then centrifuged at 3000 rpm for 10 minutes, washed with distilled water and ethanol and allowed to dry at room temperature.

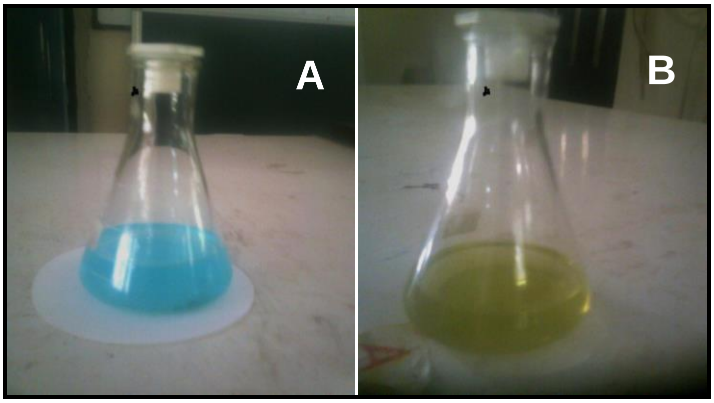

Figure 2: Aqueous solutions of copper nitrate (A) and copper nanoparticles (B).

UV – visible spectral analysis

The synthesized copper, nanoparticles were confirmed by sampling the aqueous component using UV – visible spectrophotometer. Distilled water was used as blank and the various measurements of absorbance were carried out at the wavelength of 300–700 nm. The measurements were taken for both the metal nanoparticles synthesized with all the three extracts and also that of the plant extracts used for the synthesis. The entire spectrums are presented in Figures 4 – 7.

Results and Discussion

Copper nanoparticles synthesized from Allium cepa

Many metals can be treated as free-electron systems. Such metal called plasma contains equal numbers of positive ions which are fixed in position and conduction electrons which are free and
highly mobile. Under the irradiation of an electromagnetic wave, the free electrons are driven by the electric field to oscillate coherently. These collective oscillations of the free electrons are called plasmons. These plasmons can interact, under certain conditions, with visible light in a phenomenon called surface plasmon resonance (SPR). An example of this interaction between light and electrons of a metal particle is illustrated in Figure 3

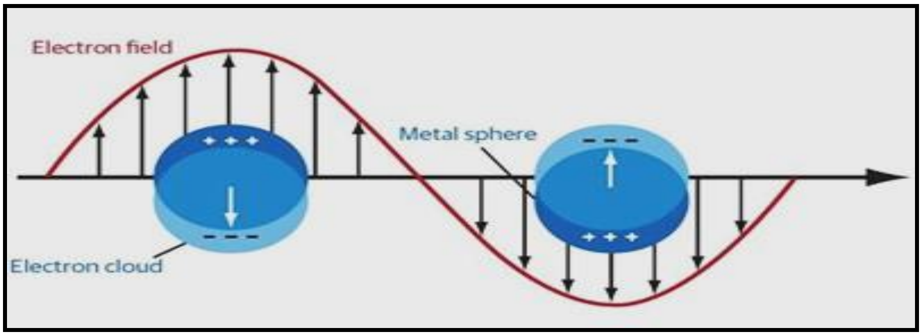

Figure 3: Surface Plasmon's are wavelike oscillations in charge distribution triggered by interaction with light and they boast powerful electromagnetic fields

During the course of adding 1 mL of extract to the flask containing 0.1 M copper nitrate there was no immediate change in the colour, however a colour change was observed after 50 minutes. At the end of two hours, the colour of the solution became light green indicating the formation of nanoparticles (Figures. 2A and B). The colour is similar to that reported by Ramanathan, Bhargava & Bansal (2011), where copper nanoparticles were synthesized using *Morganella sp.* a dark green solution was obtained. The difference in shade of colour is most likely due to excitation of surface Plasmon vibration in copper nanoparticles (Lukman, Gong, Marjo, Roessner & Harris, 2011). It is known that metal surfaces' plasma oscillations, and their optical properties, depend upon size and shape. Kumar *et al*, (2011) work on gold nanoparticle showed that the usual appearance of gold gives way to a blue colour when light is shone through a thin film of it. Gold particles can also be blue but acquire several tones of purple, through to red and orange as particle size reduces to 3 nm.

More information on copper nanoparticles by reduction of aqueous metal ions during exposure with *Allium cepa* extract was followed by UV-visible spectroscopy. The UV-visible absorption spectrum of copper nanoparticles is shown in Figure 4B. The spectrum shows the characteristic surface plasmon resonance (SPR) spectrum with absorbance at approximately 307 – 315 nm and peak maxima at 310 nm, which can be attributed to the formation of copper nanoparticles. The shape of the plasmon bands was almost symmetrical, suggesting that the nanoparticle sizes are well-dispersed and uniform.When 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 (Smitha, Nissamudeen, Philip & Chopchandran, 2008; Baia, Muresan, Baia, Popp & Simon, 2007). Ramanathan *et al*, (2011) observed a peak maximum at 610 nm. The exact position of the SPR band may shift depending on the individual particle properties including size, shape, and capping agents. It is also well known that the optical absorption spectrum shifts to lower wavelength with decreasing particle size. This shows that the size of the copper nanoparticle synthesized using *Allium cepa* is smaller than those reported by Ramanathan *et al.* (2011) and are monodispersed in solution.

Furthermore, the peaks of nanoparticles at 310 nm which corresponds to one of the peaks in that of the *Allium cepa* extract (Figure.4A) might have come from one of the phytochemicals present in the *Allium cepa*, and bound to the nanoparticle which suggests the possibility of this phytochemical acting as the reducing and capping agent as the peak indicates the various absorption bands of the phytochemicals present (Ugwoke & Ezugwe, 2010). Similar absorbance spectra were observed for *Azadirachta indica* (Figure 5A) and *Moringa oleifera* (Figure 6A).

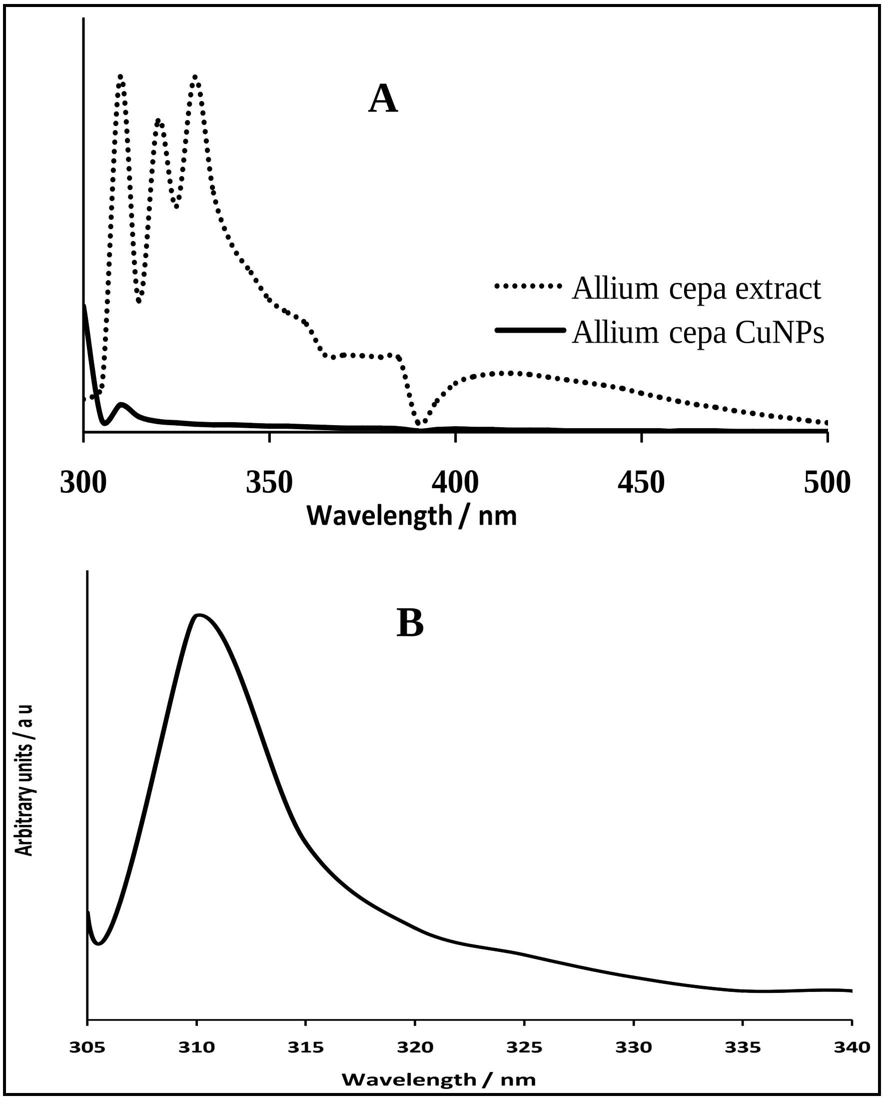

Figure 4: UV-visible absorption spectra of *Allium cepa* and copper nanoparticles (A), copper nanoparticles synthesized from *Allium cepa* broth with 0.1M copper nitrate

Copper nanoparticles synthesized from Azadirachta indica extracts

Copper nanoparticles were synthesized from copper nitrate solution containing Cu^{2+} ions by treating with the leaf extract of *Azadirachta indica*. Addition of 1 mL of *Azadirachta indica* results to change in colour of the copper nitrate solution from light blue to a pale green colour after 30-40 minutes of reaction with the Cu^{2+} ions. UV-visible absorption spectrum of copper nanoparticles in the presence of *Azadirachta indica* extract is shown in (Figure 5B). The surface Plasmon band shows absorbance at approximately 301 – 310 nm with a peak maximum at 305 nm and almost spherical in shape, suggesting that the nanoparticles are smaller in size than those synthesized from *Allium cepa* and are monodispersed in the aqueous solution with no evidence for aggregation.

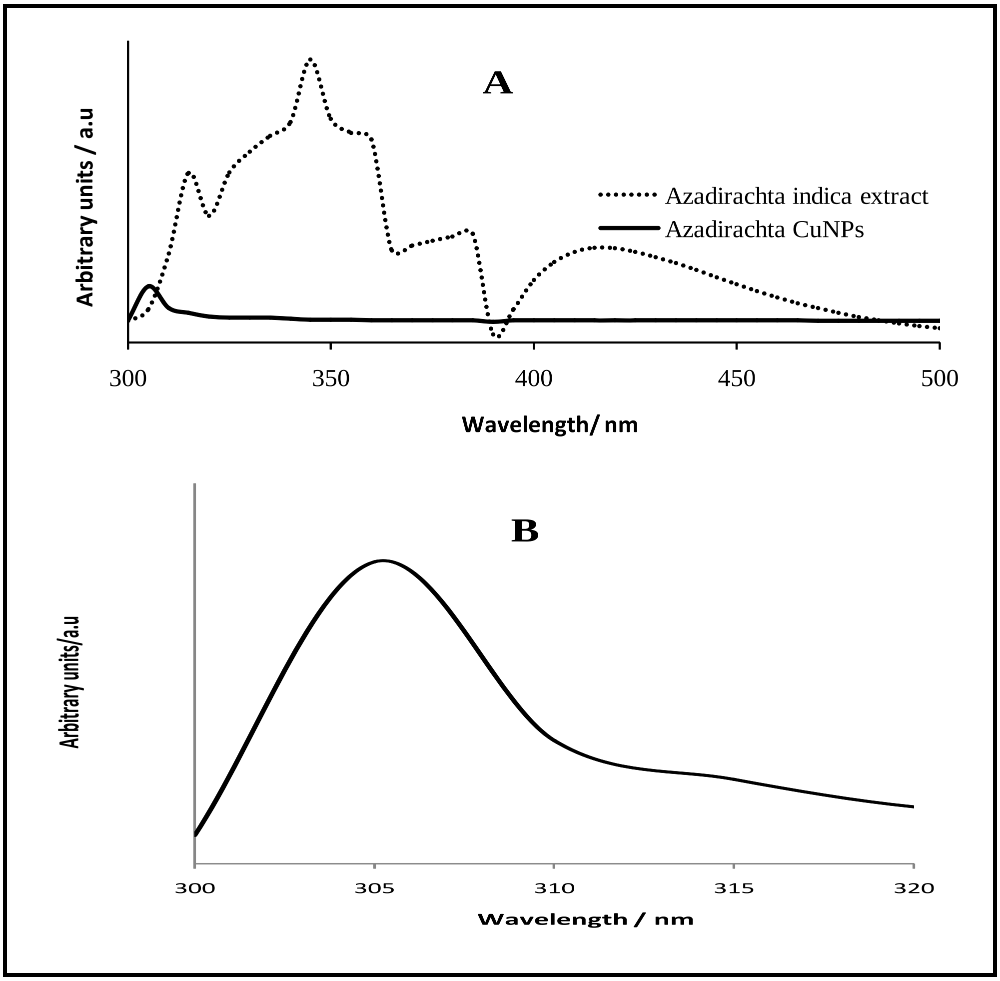

Figure 5: UV-visible absorption spectra of copper nanoparticles synthesized from *Azadirachta indica* broth with 0.1M copper nitrate

Copper nanoparticles synthesized from Moringa oleifera extract.

Addition of 1 mL *Moringa oleifera* extract to the flask containing 0.1 M copper nitrate, led to the appearance of a dark green coloured solution within 15-20 minutes, indicating the formation of nanoparticles. The UV-visible spectroscopy (Figure 6B) recorded from this solution shows the characteristic surface Plasmon resonance spectrum with absorbance at approximately 301 – 310 nm and a peak maximum at 305 nm, which can be attributed to the formation of copper nanoparticles.

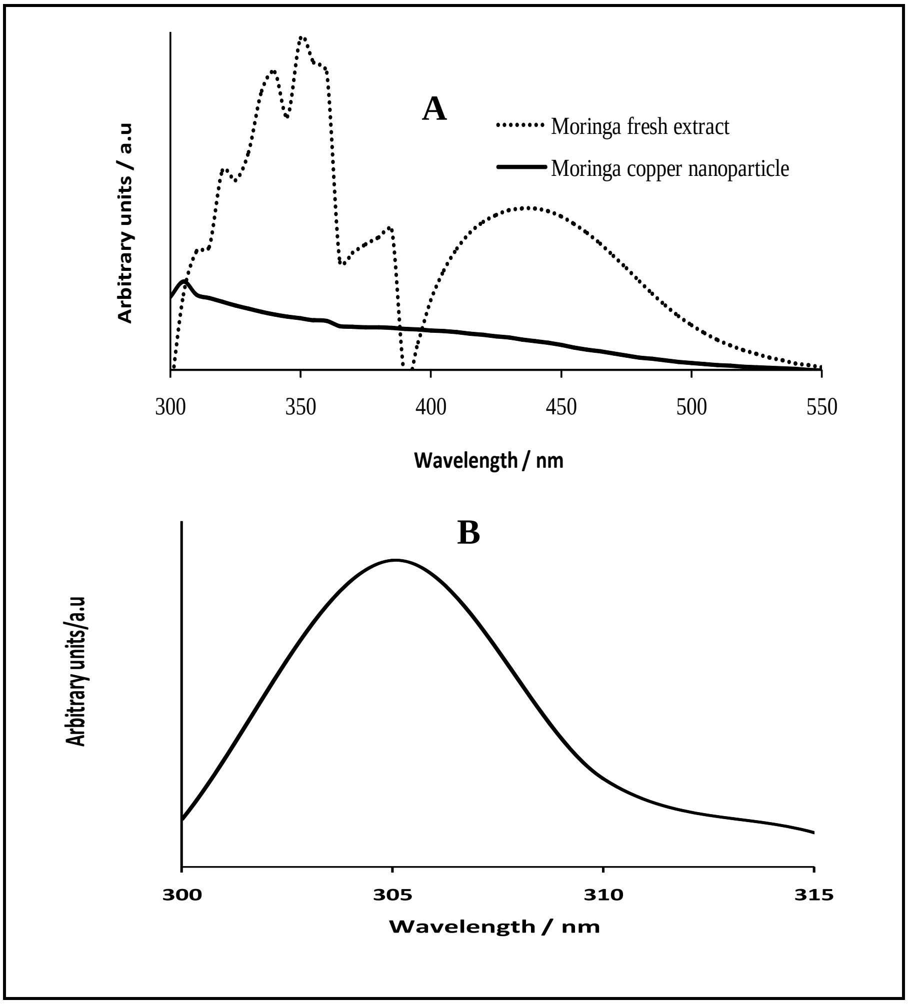

Figure 6: UV-visible absorption spectra of copper nanoparticles synthesize from *Moringa oleifera* broth with 0.1M copper nitrate

Comparison of copper nanoparticles synthesized from Allium cepa, Azadirachta indica and Moringa oleifera.

The colour changed faster on using *Moringa oleifera* extract within 15-20 minutes as against 40 and 50 minutes for *Azadirachta indica* and *Allium cepa*, respectively, suggesting that the reaction proceed faster in *Moringa oleifera* than the others, also more greenish when compared to *Allium cepa* and *Azadirachta indica* which were light green and pale green respectively. However, UV-visible spectra (Figures 5B and 6B) revealed that the size of nanoparticles synthesized from *Azadirachta indica* and *Moringa oleifera* are smaller than those synthesized using *Allium cepa*.

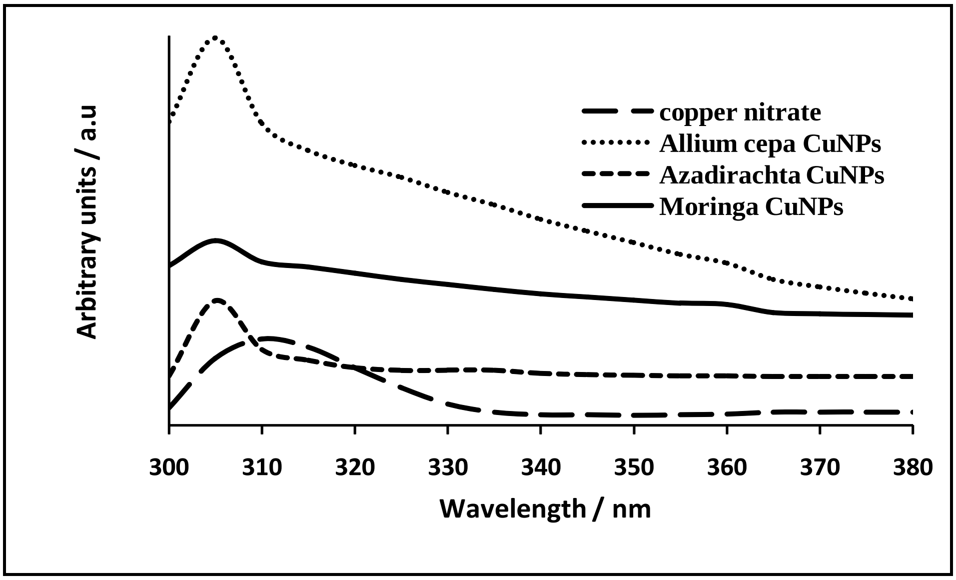

Figure 7**:** UV-visible absorption spectrum of copper nanoparticles synthesized from *Allium cepa, Azadirachta indica, Moringa oleifera* and copper nitrate

Conclusion

Copper nanoparticles were synthesized using plant leaf extracts of *Allium cepa*, *Azadirachta indica and Moringa oleifera*. Initial synthesis was confirmed by colour changes from light blue to different shades of green. The nanoparticle was characterized using UV-visible spectroscopy. Optical properties of the nanoparticles show that nanoparticles synthesized using *Moringa oleifera* gives a darker shade of colour than the others. In addition, the shift to a lower wavelength of the SPR reveals that the size of the nanoparticles synthesized from *Moringa oleifera* is smaller than even that reported in literature. Therefore, nanoparticles produced from *Moringa oleifera* can be considered a potentially efficient material in catalysis.

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.

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

Kumar, V.G, Gokavarapub, S.D, Rajeswarib, A, Dhasa, T.S, Karthicka, V, Kapadiab, Z, Shresthab, T, Barathyb, I.A, Royb, A, Sinhab, S, (2011), Facile green synthesis of gold nanoparticles using leaf extract of antidiabetic potent Cassia auriculata, *Colloids and Surfaces B: Biointerfaces* 87, 159– 163

Lukman I. Audra, Gong Bin, Marjo E. Christopher, Roessner Ute and Harris T. Andrew (2011), Facile synthesis, stabilization and anti-bacterial performance of discrete silver nanoparticles using *Medicago sativa* seed exudates, *Journal of Colloid and Surface Science* 353, 433-444.

Narayanan K. B, and Sakthivel N, (2011) Green synthesis of biogenic metal nanoparticle by terrestrial and aquatic phototropic and heterotrophic eukaryotes and biocompatible agents, A*dvances in Colloids and Interface Science*, 169 59-79

Ramanathan, R., Bhargava, S.K., Bansal, V., (2011) Biological synthesis of copper/copper oxide

nanoparticles Chemeca 2011- engineering a better world, RMIT, Australia http://www.conference.net.au

Saxena A, Tripathi P. R and Singh P. R, (2010) Biological synthesis of silver nanoparticles by using onion (*Allium cepa*) extract and their antibacterial activity, *Digest Journal of Nanomaterials and Biostructures* 5(2) 427–432

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.

Ugwoke C.E.C, and Ezugwe C.O., (2010) Phytochemical screening and proximate composition of onion bulb (*Allium cepa* L) *Journal of Pharmaceutical and Allied Sciences*, 7(2) 1596-1599

Zaheer K, Javed I.H, Athar A.H, (2012), Shape-directing role of cetyltrimethylammonium bromide in the green synthesis of Ag-nanoparticles using Neem (*Azadirachta indica*) leaf extract, *Colloids and Surfaces B: Biointerfaces*, 95, 229-234.