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Biosynthesis of silver nanoparticles using aqueous *Balanite aegyptiaca* extract-characterization and study of water purification.

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Abstract

Vegetable mediated synthesis of nanoparticles is a green chemistry approach that connects nanotechnology and biotechnology, in the present investigation, we have used a fast convenient environmental friendly method for the synthesis of silver nanoparticles by biologically reducing silver nanoparticles with aqueous extract of *balanite aegyptiaca* under optimum conditions (pH 10). The formation of silver nanoparticles was indicated by the colour change from colourless to brown. Biosynthesized nanoparticles were characterized by UV-VIS, FT-IR analysis. The AgNPs was characterized by UV – visible spectrophotometer showing peak between 350 – 450 nm (maximum peak at 430nm). A peak characterized by all nanoparticles. FT-IR analysis was carried out to identify the possible biomolecule responsible for the bio-reduction which was likely to be phenolic group. The synthesized AgNPs was further used to purify water which shows significant changes in the boiling point, turbidity and temperature, conductivity and colour of the water when AgNPs were added.

Keywords: *Balanite aegyptiaca*; FT-IR; UV-VIS

1. Introduction

Nanoscience (science at 1- 100 nanoscale) is the most promising technology that can be applied almost in all spheres of life, ranging from electronics, pharmaceutical, defense, transformations, heat transfer to sports and aesthetics. Metallic nanoparticles are of great interest due to their excellent physical and chemical properties, such as high surface-to volume ratio and heat transfer [1]. Nanoparticles can be synthesized through different methods; chemical, physical and biological methods. Conventionally, chemical synthesis has been the method of choice because it offers faster synthetic route. However, chemical synthesis has raised environmental concerns because of the nature of chemicals used, such as reducing agents (sodium borohydride), organic solvents and non – biodegradable stabilizing agents (sodium citrate dehydrates). These chemicals are potentially hazardous to the environment and biological systems [2]. The biosynthesis of nanoparticles is also considered to be a bottom up technique, where the oxidation or reduction is the main reaction that occurs during the production of nanoparticles. Metal compounds usually reduce into their respective nanoparticles because of microbial enzymes or the plant phytochemicals with antioxidant or reducing properties.

A silver nanoparticle, in the form of colloidal silver, have been used for more than 150 years and has been registered as a biocidal material in the United States since 1954. There is anecdotal evidence of its use as far back as ancient Egypt

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and Rome. Silver can form many different inorganic and organic complexes, and its most stable oxidation states are +0 and +1, although others (+2, +3) exist as well due to its partially filled 3d – orbital (properties characterized by transition metals). Silver nitrate is often used as a precursor in the synthesis of the different forms of silver nanoparticles. Silver nanoparticles exist in a huge variety of different forms. Silver nanoparticles can be of different shape such as; spheres, rods, wires, triangles and coatings as in citrate, polymer, peptide, sugars and of different sizes from few up to 100nm [3].

Noble metal nanoparticles exhibit unique electronic and optical properties that are critically related to their size and shape. These effects are the result of changes in the surface plasmon resonance, the frequency at which conduction electrons oscillate in response to the alternating electric field of incident electromagnetic radiation. However, only metals with free electrons (essentially Au, Ag, Cu, and the alkali metals) possess plasmon resonances in the visible spectrum, which give rise to such intense colours. Elongated nanoparticles (ellipsoids and nanorods) display two distinct plasmon bands related to transverse and longitudinal electron oscillations. The longitudinal oscillation is very sensitive to the aspect ratio of the particles, so that slight deviations from spherical geometry can lead to impressive colour changes. Apart from single particle properties, the environment in which the metal particles are dispersed is also of relevance to the optical properties. The refractive index of the surrounding medium, as well as the average distance between neighboring metal nanoparticles, has been shown to influence the spectral [4].

Nanoparticles have been intensively studied over the last decade due to its characteristic physical, chemical, electronic, electrical, mechanical, magnetic, thermal, dielectric, optical and biological properties [5]. The oxides of transition metals are of important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics, gas sensors, and catalysis [6]. Micro emulsion method [7] arc submerged nanoparticles synthesis system [8], flame based aerosol methods [9] sonochemical [10] hydrothermal [11] and solid state techniques [12]. Eco-friendly synthesis of silver nanoparticles was carried out by using plant extract, a report of a simple biological and low-cost approach for preparation of stable silver nanoparticles by reduction of silver nitrate solution with a bio reduction method using a manner of *hydesarum* aqueous extract as the reducing agent. The characteristics of the obtained silver nanoparticles were studied using UV-vis, XRD, EDX, and SEM techniques. The results confirmed the reduction of silver nitrate to silver nanoparticles with high stability and without any impurity. Comparison of experimental results showed that the average size of synthesized silver nanoparticles was about 40 nm [13].

Due to the increasing interest in nanoparticles synthesis and applications; there is a need for eco-friendly approaches based on green chemistry principles [14].

2. Material and methods

Balanite aegyptiaca leaves, silver nitrate, Hanna instrument 2211 P^H meter, Jenway 6400 UV-visible spectrophotometer, Perkin Elmer Frontier Fourier Transform Infrared Spectroscopy, Ultrasonic bath, measuring cylinder, analytical balance, beakers, conical flasks, magnetic stirrer, heating mantle, spatula, funnel, reagent bottles, burette, retort stand, test tubes, test tube rack, Whatman filter paper, centrifuged silver nitrate solution, ethanol and distilled water were used for the analysis.

2.1. Preparation of the sample extract

Fresh leaves of *Balanite aegyptiaca* plant was collected from the plant, washed thoroughly with distilled water to remove dust and cut into pieces. 10g of the fresh leaf were placed in a 250 mL Erlenmeyer flask and boiled with distilled water for 20 minute, then the mixture was allowed to cool under room temperature. The solution was then filtered with Whatmann filter paper No. 1 to obtain the *balanite aegyptiaca* leaf extract. This was later used as reducing agent for the bio-reduction.

2.2. Synthesis of silver nanoparticles

0.042 g of silver nitrate was weighed with a top load balance and dissolve in 100 mL distilled water to prepare a 0.001M silver nitrate solution. 60 mL aqueous solution of 1mM of silver nitrate was reduced using 5 mL of leaf extract at room temperature for 10 minutes; change in colour of the solution indicates the formation of silver nanoparticles. The product was then being centrifuged at 3000 rpm for 10 minutes, after that it was washed with ethanol and distilled water, the solution was allowed to dry at room temperature. The formation of silver nanoparticles is inferred by visual observation followed by UV-Visible spectrum and FT-IR studies [15].

3. Results

The fourier transform infrared spectroscopy analysis was performed to identify the possible biomolecule responsible for the bioreduction of silver ion (Ag^+) and capping of the reduced silver nanoparticles synthesised using *balanite aegyptiaca* leave extract.

The FT-IR analysis of AgNPs shows a shift in the bands at 3203.93cm^{-1} , 2114.87cm^{-1} , 1550.01cm^{-1} , 1380.37cm^{-1} , and 1029.56cm^{-1} . The band which appeared at 3203.93cm^{-1} corresponds to trans O-H stretch of H – bond, the bands at 2114.87cm^{-1} is due to $-\text{C}\equiv\text{C}-$ stretching, the IR band observed at 1380.37cm^{-1} is due to $-\text{C}-\text{H}$ bending and the band at 1029.56cm^{-1} corresponds to $-\text{C}-\text{O}$ stretching vibration.

Therefore, the bands at 1074.61 (see table 1) arises most probably from C – O group of polyol such as hydroxyflavones and catechines. The total disappearance of this band after the bio-reduction may be due to the fact that the polyols are mainly responsible for the reduction of Ag^+ ions.

Table 1 FT-IR analysis of *balanite aegyptiaca* sample extract

| S/N | Wavelength (cm-1) | Transmittance | Functional group | Type of vibration | Characteristic Absorption | Intensity |
|-----|-------------------|---------------|------------------|----------------------|---------------------------|-----------------------------|
| 1. | 3227.75 | 90.99 | O – H | Stretch (H – bonded) | 3200 – 3600 | Strong, broad |
| 2. | 1566.48 | 69.84 | N – H | Bending | 1550 – 1640 | Medium-weak, multiple bands |
| 3. | 1395.38 | 65.79 | - C – H | Bending | 1350 – 1480 | Variable |
| 4. | 1074.61 | 81.64 | = C – O | Stretch | 1000 – 1300 | Strong |
| 5. | 863.60 | 82.49 | - C – O | Bending | 675 – 1000 | Strong |

Table 2 FT-IR analysis of AgNPs synthesized from *balanite aegyptiaca* sample extract

| S/N | Wavelength (cm-1) | Transmittance | Functional group | Type of vibration | Characteristic Absorption | Intensity |
|-----|-------------------|---------------|------------------|----------------------|---------------------------|------------------|
| 1. | 3203.93 | 82.83 | O – H | Stretch (H – bonded) | 3200 – 3600 | Strong, broad |
| 2. | 2114.87 | 86.51 | - C \equiv C - | Stretch | 2100 – 2260 | Medium, weak |
| 3. | 1550.01 | 77.28 | N – O | Stretch | 1515 – 1560 | Strong two bands |
| 4. | 1380.37 | 78.19 | - C – H | Bending | 1350 – 1480 | Variable |
| 5. | 1029.56 | 71.46 | - C – O | Stretch | | strong |

The data (table 3) shows the physical parameters of water samples before and after the addition of AgNPs solutions. It was observed from the (table 3) that the temperature drops significantly with the addition of AgNPs. High temperature leads to the growth of undesirable water plants and water fungus in water, these indicates that AgNPs reduces the rate of growth of undesirable water plants and water fungus. The pH of the water before and after the addition of AgNPs does not show significant changes but with an infinitesimal change of 0.05. Turbidity is said to be the measure of the light transmitting properties of the water due to presence of suspended materials. The turbidity of the water was 10 TU

before addition of AgNPs which was clearly and easily seen in the beaker because the colour seems to be milky but after addition of the AgNPs solutions with filtration, the turbidity drops drastically to 1 TU. This indicates that the AgNPs was able to form precipitates with the particles in the water and coagulate them which were separated by filtering (decantation can be used). Conductivity is a quantitative measure of the ability of water to pass through electric current. This ability depends largely on the quantity of dissolved salts present in any water sample. The conductivity result of the water before the addition of AgNPs was found to be 424 μ s which shows that there is high level of dissolved salts in the water but upon addition of the AgNPs the value drops drastically to 286 μ s. this indicates that the AgNPs has acted on the dissolved salts in the water.

Table 3 Application of AgNPs in water purification

| S/N | SAMPLE | Sample before | Sample after |
|-----|-------------------------------|---------------|--------------|
| 1. | Temperature ($^{\circ}$ C) | 29.3 | 26.0 |
| 2. | pH | 7.55 | 7.5 |
| 3. | Turbidity (TU) | 10 | 1 |
| 4. | Boiling point ($^{\circ}$ C) | 96 – 98 | 100 |
| 5. | Conductivity (μ s) | 424 | 286 |
| 6. | Colour | Milky | Colourless |

Figure 1 shows the brown colour AgNPs labelled as “A”, the colourless aqueous solution of AgNO₃ (0.001M) labelled as “B” and the orange colour leave extract of *balanite aegyptiaca* labelled as “C”.

Upon the addition of 5mL of the leave extract of *balanite aegyptiaca* to the aqueous solution of 0.001M of AgNO₃ with a constant stirring using a magnetic stirrer, a light brown colour was observed within 10 minutes and later the solution changed completely to brown colour, this indicates the formation and presence of the AgNPs in the solution. AgNPs is known to exhibit characteristic brown colour [16].

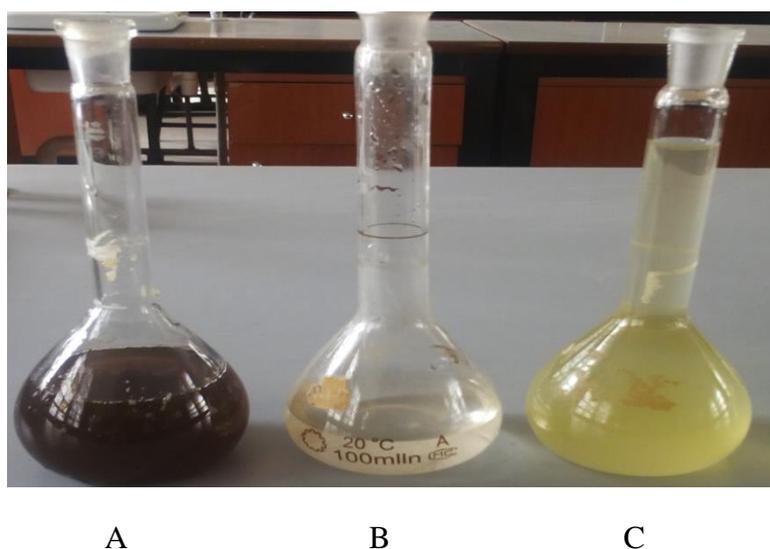


Figure 1 Optical behavior of silver nanoparticles A, silver nitrate solution B and leave extract C

Figure 2 shows UV-Vis spectra recorded at different time intervals from aqueous solution of silver nitrate with *balanite aegyptiaca* leave extract. The samples display an optical absorption band peak at about 430 nm, typical of absorption for metallic Ag nanoclusters, due to the Surface Plasmon Resonance (SPR). The observation indicated that the reduction of the Ag⁺ ions took place extracellularly. The non-uniformity of the AgNPs leads to the absorption peak at higher wavelength. Effect of the reaction time on AgNPs synthesis was also evaluated with UV-Visible spectra and it is noted that with an increase in time the peak becomes sharper. The increase in intensity could be due to increasing number of nanoparticles formed as a result of reduction of silver ions presented in the aqueous solution. The weak absorption

peak below 365 nm (not shown here) indicates the presence of several organic compounds which are known to interact with silver ions into solution and suggests a possible mechanism for the reduction of the metal ions presented in the solution. UV-Visible absorbance spectroscopy has proved to be a very useful technique for studying metal nanoparticles because the peak positions and shapes are sensitive to particle size.

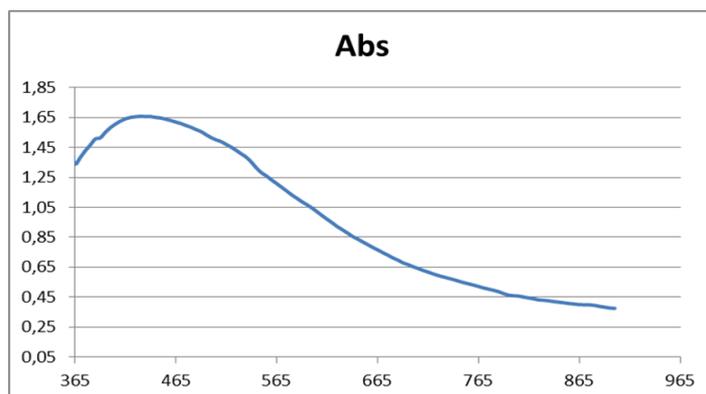


Figure 2 UV/Visible spectrum of AgNPs synthesized from *balanite aegyptiaca* leave extract

FT-IR spectroscopy was used to investigate the interaction between different species and changes in chemical compositions of the mixtures. FT-IR measurements of both the aqueous *balanite aegyptiaca* extract and the synthesized dried silver nanoparticles were carried out to identify the possible bio-molecules responsible for the reduction, capping of and efficient stabilization of the bio-reduced AgNp.

FTIR analysis was used for the characterization of the *balanite aegyptiaca* leave extract and the resulting nanoparticles. Absorbance bands are observed in the region of 500-3500 cm^{-1} [17].

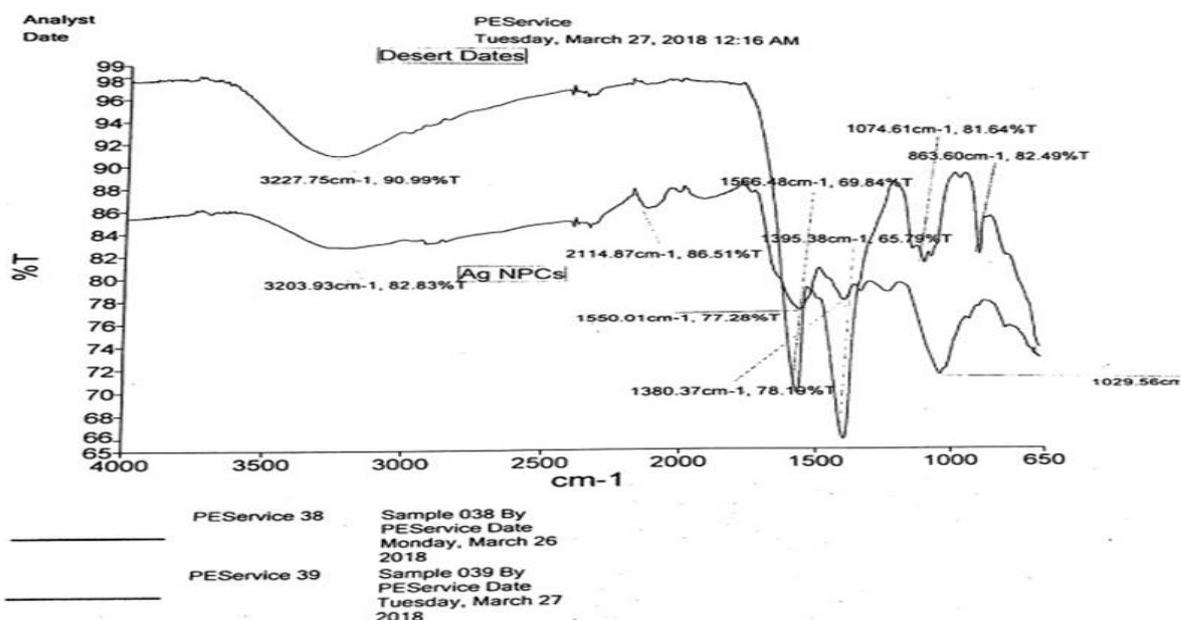


Figure 3 FT-IR absorption spectra of silver nanoparticle synthesized from *balanite aegyptiaca* leave extract.

4. Conclusion

The biosynthesis of silver nanoparticles using aqueous *balanite aegyptiaca* extract and its study for water purification is of paramount importance environmentally, which is an economical, efficient and eco-friendly process. The use of natural antioxidants for the synthesis of AgNPs showed that it is a good alternative for silver nanoparticles synthesis. UV-Visible spectrophotometric techniques have confirmed the reduction of silver nitrate to silver nanoparticles. The FT-IR techniques have also confirmed or identified the possible biomolecules responsible for the reduction and stabilization of AgNPs to be phenols. The phenolic in *balanite aegyptiaca* exhibit an excellent antioxidant activity which can react with a free radical to form the phenoxyl radicals. The experimental parameters such as temperature, turbidity, boiling point, conductivity and colour were examined and proved to be important parameters in water purification process.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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