

BIOGENIC SYNTHESIS OF SILVER NANOPARTICLES USING PLANT WASTE MATERIAL

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ABSTRACT

Synthesis of silver nanoparticles with suitable attributes is important for its successful application. Green methods of synthesis have many advantages as compared to commonly used chemical and physical methods. Biopolymers provide a suitable condition for the synthesis, growth, and stability of nanoparticles. A biopolymer which does not put pressure on resources, biocompatible obtained as waste and easily available has the potential for application in the synthesis of AgNP. Biopolymer which is a waste from paper manufacturing process has been employed to synthesize AgNP, and the synthesis has been confirmed by UV-Vis spectroscopy. The role of the biopolymer in the synthesis of stable AgNP has been confirmed by FTIR and TEM.

Keywords: Green synthesis, Silver nanoparticles, Lignosulphonic acid, Biopolymers.

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INTRODUCTION

Nano silver is one of the most commercialized materials with an estimated yearly consumption of five hundred ton.¹ Its applications include catalysis, high sensitivity biomolecular detection, biosensors, and medicines. It shows anti-fungal, anti-inflammatory and anti-angiogenesis activity² and this property has made it a suitable candidate for biomedical applications. Properties of AgNP are known to be affected by the shape, size, and size distribution.³

With growing application field, there is a pressure to develop synthetic methods of AgNP with a suitable shape, size, and functionality. There are two approaches for synthesis - the top down and bottom up; achieved either through physical or chemical methods. Physical methods like evaporation-condensation, laser ablation are commonly used for AgNP synthesis. These methods can synthesize stable and pure AgNP of suitable size and shape but are associated with issues like elaborate setup, consume more energy and toxicity.^{4,5}

Chemical methods involve reduction of the silver ion into metallic silver using reducing agents in the aqueous or non-aqueous medium. Commonly used reducing agents are sodium borohydride, tollen's reagent, sodium citrate, and ascorbate. Silver atoms then agglomerate into oligomeric clusters of nanometer size.⁶⁻⁸

These particles are unstable and tend to agglomerate, surfactants with functionality like thiol, amines, acids, and alcohol are used to control particle growth and prevent them from agglomeration. These chemicals used for synthesis are often associated with health and environmental issues.⁹⁻¹² Recently many researchers have adopted green synthetic methods of synthesis of AgNP which is a chemical method based on the use of natural materials like plant products, polymers and microorganisms (bacteria, fungi, and virus) and plants.³

Biopolymers have the ability to reduce metal ion, enable the synthesis of nanoparticle of controlled shape and size and stabilize them by coordinating.¹³

Lignin is a complex biopolymer present in the support tissue of plants and provides rigidity. Its composition depends on the species and its approximate formula can be written as $(C_{31}H_{34}O_{11})_n$. Lignosulphonate (LS), a water soluble form of lignin is a waste in sulphite pulping process during paper manufacturing and finds application as a dispersant in high-performance cement, water treatment formulations, textile dyes,

additives in specialty oil field and starting material for synthesis of chemicals like humic acid, DMSO etc. It has also been explored as renewable cathode material¹⁴, as a green material for synthesis of phenol¹⁵, catalyst¹⁶ etc.

In this present study, we have used sodium salt of lignosulphonic acid (LS) for the synthesis of AgNP in an aqueous medium and in absence of any additional reducing or stabilizing agent. This method involves mainly on the Principle of Green Chemistry.

EXPERIMENTAL

Chemicals

Lignosulphonic acid (LS) of average molecular weight 52000 and silver nitrate (AgNO₃) were purchased from Sigma-Aldrich and Ranbaxy Chemicals, India respectively and used as received. Solutions of required concentration were prepared by using double distilled water.

Preparation of AgNP

In this experiment, 25 ml of LS solution (0.2%) was mixed with 25 ml of AgNO₃ solution (1%) in a 100mL beaker to obtain the AgNP. The temperature was maintained at 60°C during the entire experiment.

Ultraviolet-visible (UV-Vis) Spectrometer

The AgNP synthesized are examined using UV-Vis spectroscopy. UV-Vis spectra were recorded over the range of 300-500 nm with Shimadzu 2600 UV-Vis spectrophotometer.

Fourier Transform Infra-Red Spectrometer (FT-IR)

This FT-IR instrument was used in the spectral range of 4000-400cm⁻¹ in order to detect the absorption bands of AgNP synthesis in AgNO₃ solution on addition of LS. The AgNP synthesized are dried and powdered and mixed with KBR salt and further grounded to get in the form of pellets.

Transmission Electron Microscope (TEM)

TEM images were taken using a JEOL Model JSM - 6390LV microscope.

RESULTS AND DISCUSSION

LS is a lignin-based biopolymer rich in an oxygen containing hydroxyl and ether groups. The sulfonated derivative of LS is soluble in water at a pH of 7.4 and retains a negative charge. Because of this negative charge, the polymer attracts positively charged silver ion. A sample of LS used in the present experiment contains 4% of reducing sugar which is expected to reduce the silver ion to metallic silver atom¹⁷ and the polymer matrix supports and controls the growth of AgNP.¹⁸

Visual Observations and UV-Vis Spectroscopy

AgNP show the unique optical property as the conductive electrons on the surface of NP undergo collective oscillation when excited by light of a specific wavelength in the visible range, known as surface plasmon resonance (SPR), these phenomena help in easy detection of AgNP by the naked eye. Henglein and co-workers observed the stepwise development of AgNP by spectroscopic methods¹⁹ and suggested that UV-Vis spectroscopy can be used for the characterization of metal and semiconductor nanoparticles with plasmon resonance lines in the visible range. UV-Vis spectroscopy has been widely used to detect the presence of AgNP during green synthesis.²⁰⁻²²

Visual indication of synthesis of AgNP was observed immediately after mixing the solutions at 60°C as the color started changing from yellowish to reddish brown (Fig.-2). Dark brown color appeared after 50 minutes indicating completion of synthesis. Formation of AgNP was also confirmed by UV-Vis spectroscopy which showed the appearance of high intensity (3.5) band at 409 nm (Fig.-3). Similar bands confirming AgNP synthesis has also been reported in earlier studies.^{1, 23}

The role of biomolecules in the reduction, capping, and stabilization of synthesized AgNP has been confirmed by FTIR spectroscopy. The FTIR spectra confirmed the presence of bio-molecule around the syn-

thesized AgNP. The IR spectra (Fig.-4), shows the characteristic bands at 1370 cm^{-1} is due to CH bonding. The absorption bands at 1045 cm^{-1} are observed due to C-C stretching in aromatic rings and 785 cm^{-1} is attributed to =C-H bending. Whereas the bands of LS appeared at 3450 cm^{-1} show the vibration stretching of O-H groups.²⁴ These functional groups have role in stability/capping of AgNP as reported in many studies.²⁵⁻²⁶

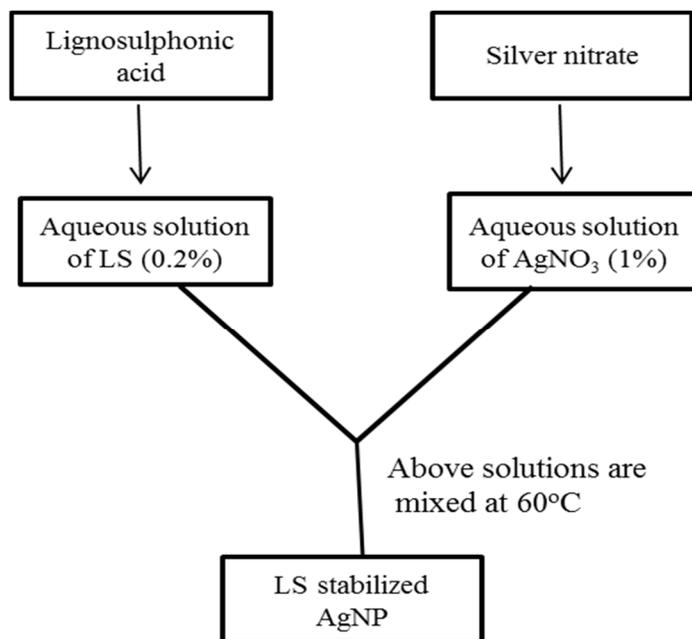


Fig.-1: Steps showing the synthesis of AgNP.

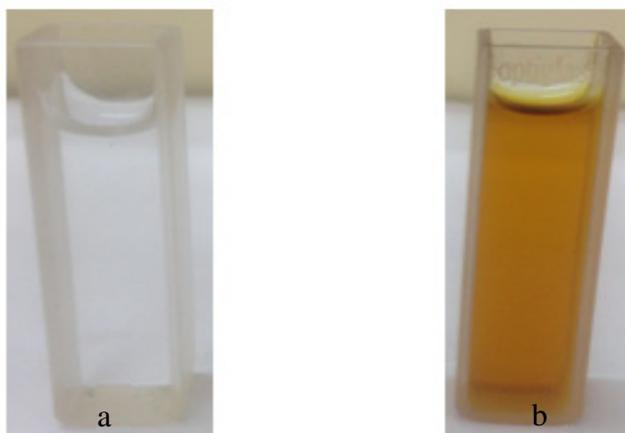


Fig.-2: Synthesis of AgNP (a) Pure lignosulphonic acid (b) AgNP

The role of LS in the synthesis of AgNP is also investigated using TEM. TEM image clearly indicates the entrapping of synthesized AgNP by LS polymer which is an indication of the role of LS in the reduction of Ag^+ ion and also in the stabilization of synthesized nanoparticles as the nanoparticle appears to be embedded in the LS structure (Fig.-5).

CONCLUSION

The LS has the ability to reduce silver ions which are also supported by the presence of reducing sugar in the sample. The synthesized nanoparticles are spherical and in the nanometer range, which is confirmed by the UV-Vis spectroscopy. The FT-IR clearly indicates the presence of polymer on the surface of AgNP

which helps in the stability of nanoparticles. TEM image also supports this fact. This method is based on the principles of green chemistry that are renewable LS is used which is also a waste material. All experiment is carried out in an aqueous medium, at moderate temperature, and in a very simple laboratory set-up. The process is relatively fast as synthesis completed in 50 minutes.

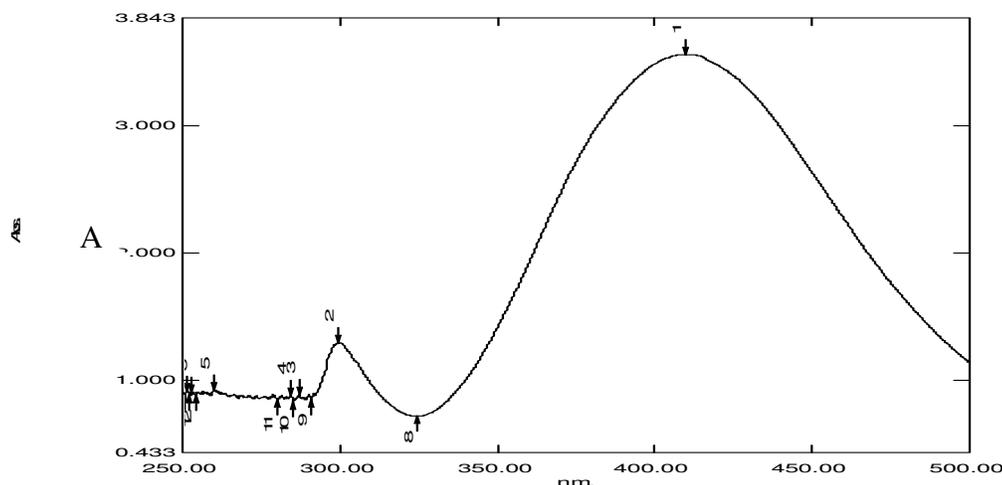


Fig.-3: UV-visible spectra of AgNP

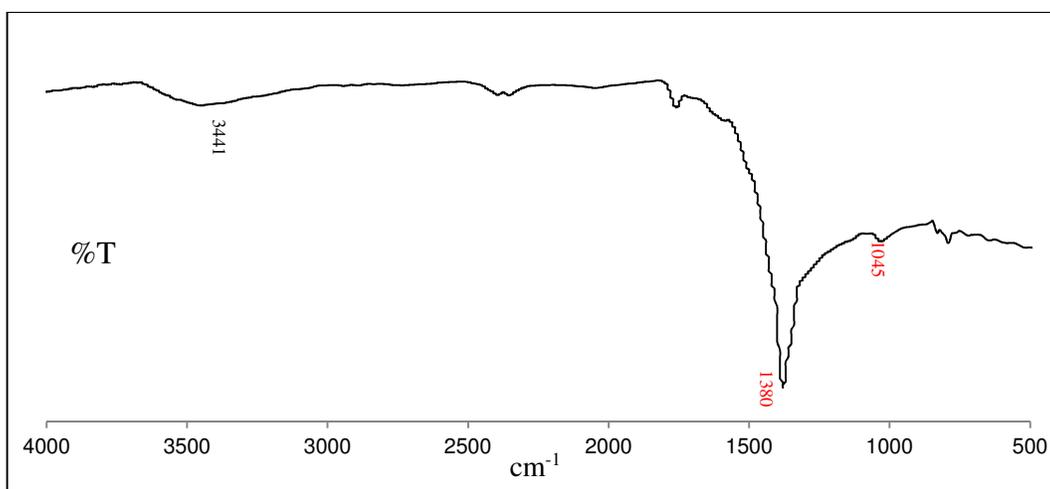


Fig- 4: FTIR of silver nanoparticles (AgNP)

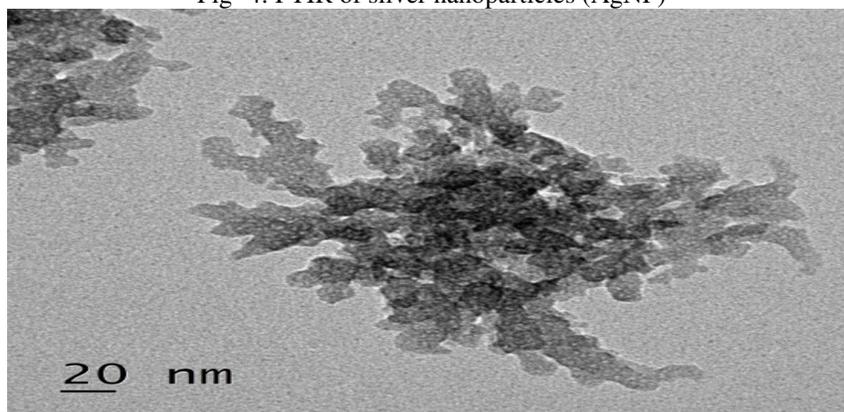


Fig.-5: TEM image of synthesized silver nanoparticles (AgNP)

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