

MICROWAVE-ASSISTED *In-situ* GENERATED COTTON/SILVER NANOPARTICLES COMPOSITE BY USING AN AQUEOUS EXTRACT OF *Acacia Lignin* BARK

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ABSTRACT

In general, silver has been recognized as an antimicrobial agent and helpful for the treatment of burns, wounds, and various infections. Now a day silver nanoparticles production in eco friend method is required. Here in, we report a novel method of silver nanoparticles in situ to generate a cotton matrix using *Acacia lignin* bark aqueous extract as a reducing agent and stabilizer. The silver nanoparticles were *in situ* generated by combining an *Acacia lignin* bark extract, cotton fabric, and aq.AgNO₃ in one pot, irradiated under microwave for five minutes. The silver nanoparticles (AgNP's) formed as film inside and outside of the cotton as a matrix was characterized by TEM, FTIR, UV, and EDX spectroscopic techniques. These bio-renewable films show good antibacterial activity and can be used for the bandage, and packing material for medical purposes.

Keywords: Aq. *Acacia Lignin* Bark Extract, Microwave, In situ Generation, Cotton, Antibacterial Activity.

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INTRODUCTION

Despite their unique physical and chemical characteristics, silver nanoparticles (Ag NPs) are used increasingly in a wide range of fields, including medicine, food, health care, consumer products, and industry. Among these include optical, electrical, and thermal characteristics, as well as electrical solid conductivity and biological qualities. As antibacterial agents, in consumer goods, medical device coatings, optical sensors, and cosmetics, as well as in the pharmaceutical and food industries, as well as in diagnostics, orthopedics, drug delivery, and as anticancer agents, they have ultimately improved the tumor-killing effects of anticancer medications. Recently, Ag NPs are present in a variety of textiles, keyboards, bandages, and biomedical devices. Metallic nanoparticles have been used for a variety of purposes because they are special and may significantly alter physical, chemical, and biological characteristics due to their surface-to-volume ratio. To meet the need, a variety of Ag NPs are needed. As nanomaterials become increasingly popular in a variety of technical applications, they are gaining popularity due to their unique qualities, such as small volume, large surface area, cheap cost, catalytic activity, as well as antibacterial properties.¹ However, polymers and polymer composites have several uses in our daily lives, including aircraft, electronics, automobiles, medical, packaging, and soon.² Significant Polymers are both natural and manmade; most synthetic polymers are non-green and generate environmental difficulties, as well as reasonable pollution. Following green chemistry, several researchers are focusing on developing biocompatible polymers to create noble composites from bio-renewable sources.³ Several physical and chemical approaches of nano metal composite polymer formulations have significant drawbacks such as insufficient energy, excessive cost, and toxicity. To address these issues, plant extracts such as Fig fruit extract⁴, Aloe vera⁵, Coriandrum sativum⁶, Neem leaf⁷, Ocimum sanctum leaf⁸, orange peel⁹, and eucalyptus wood¹⁰ were used as reducing agents in the biologically motivated synthesis of composite silver nanoparticles and pure silver nanoparticles. Furthermore, researchers concentrated solely on producing nanoparticles that may subsequently be employed as fillers in suitable polymer matrices. Even though there are two forms of formulations in polymer matrices, in situ production and dispersion of nanoparticles in

polymer matrices are the most common. Because of agglomeration in the dispersion technique of polymer matrix formation, in situ polymer matrix synthesis provides uniform distribution of nanoparticles. So far, in situ generated cotton/silver/graphene¹¹, poly(vinyl alcohol)/silver/graphene¹², cotton/polypyrrole/silver composite¹³, cotton/silver¹⁴, cotton/silver/carboxymethylchitosin¹⁵, cotton/silver¹⁶⁻¹⁷ have been prepared, and some researchers have prepared in situ generated silver composites using plant extracts Ocimum leaf extract¹⁸, etc. In contrast, whereas the creation of silver nanoparticles via plant extract takes time, the irradiation-assisted technique shortens the reaction duration. The authors used a variety of medicinal values comprising Acacia lignin bark as well as a reducing and stabilizing medium. At the moment, the authors are creating microwave-assisted Silver nanoparticles in Acacia bark extract placed on a cotton matrix in situ. TEM, FTIR, UV, EDX, and antibacterial screening were performed on the produced cotton/AgNp composite matrix.

EXPERIMENTAL

Preparation of Cotton/Silver Nanoparticle Composite Films

The silver nanoparticles containing cotton films were created by collecting Acacia Lignin bark from the surrounding region, washing it with distilled water, and drying it. 10gms of Acacia bark were coarsely chopped and cooked in 50 cc of distilled water for 45 minutes at 70 degrees Celsius. The dark brown extract was filtered using Whatman filter paper No.5, and the filtrate was saved for future studies. Sigma Aldrich chemicals provided AR-grade silver nitrate, and the pure white cotton fabric was acquired locally. Aq. AgNO₃ solution was made at various concentrations ranging from 1mM to 5mM. Each test tube containing varied concentrations of concentrated silver nitrate received 1cc of Acacia lignin bark aqueous extract. A little cotton piece was submerged in each solution and microwaved for 10 minutes. The cotton fabric became dark, suggesting the development of silver nanocomposite coatings in situ. The silver nanocomposite cotton fabric was fully washed with distilled water, and the color of the material did not change even after multiple items of washing. It was then dried at room temperature.

Characterization

The synthesized cotton fabric silver nanoparticles matrix films were confirmed with the help of XRD (Bruker E D8) analysis, FTIR (Smart iTR ATR Nicolet) spectrophotometer, UV-Vis (Perkin-Elmer Lambda 25) spectrometer, transmission electron microscopy TEM (Philips, TECHNI FE12) images and EDX spectral analysis. The antibacterial efficacy of cotton nanosilver composite films against gram-positive and gram-negative bacteria was investigated using the disc technique. UV-vis spectroscopy is a highly helpful and dependable approach for the primary characterization of produced nanoparticles, as well as for monitoring the production and stability of AgNPs. AgNPs have distinct optical characteristics that cause them to interact strongly with certain wavelengths of light. Furthermore, UV-vis spectroscopy is quick, straightforward, simple, sensitive, selective for different types of NPs, requires just a brief measurement time, and no calibration is necessary for particle characterization of colloidal suspensions.

X-ray Diffraction (XRD)

A well-known analytical technique for analyzing both molecular and crystal structures is X-ray diffraction (XRD). Evaluation of crystallinity, isomorphism, substitutions, particle sizes, and other properties as well as qualitative identification of various substances and quantitative resolution of chemical species. The diffraction patterns that emerge when X-ray light reflects on a crystal represent the physicochemical characteristics of the crystal formations.

The physicochemical characteristics of a powder specimen are reflected in diffracted beams. The structural characteristics of a variety of materials, such as inorganic catalysts, superconductors, biomolecules, glasses, and polymers, can thus be examined using XRD. It is imperative to develop diffraction patterns in order to analyze these materials. In the Joint Committee on Powder Diffraction Standards (JCPDS) library, each substance has a distinct diffraction beam that can be defined and identified by comparing it to the reference database. The diffracted patterns reveal whether the sample materials are pure or contaminated. As a result, XRD has long been used to characterize and classify bulk and nanomaterials, as well as forensic specimens, and industrial, and geochemical sample materials. XRD is a basic tool for determining crystalline nature at the atomic scale. X-ray powder diffraction is a nondestructive method that may be used to characterize both organic and inorganic crystalline materials.

Fourier Transform Infrared (FTIR) Spectroscopy

To ascertain whether biomolecules are involved in the formation of nanoparticles, FTIR spectroscopy is widely used in academic and industrial research. Additionally, FTIR has been used in the investigation of nano-scaled materials to confirm functional molecules covalently grafted onto silver, carbon nanotubes, graphene, and gold nanoparticles, as well as interactions between enzyme and substrate during the catalytic reaction. It is a non-invasive procedure, too. FTIR spectrometers also have a lower sample heat-up, a stronger signal, a higher signal-to-noise ratio, and a faster data collection rate. Attenuated total reflection (ATR)-FTIR spectroscopy is a recent advancement in FTIR methodology. Using ATR-FTIR, we can analyze the chemical properties of the polymer surface, and sample preparation is easier than with conventional FTIR. As a result, FTIR is a suitable, useful, non-intrusive, affordable, and simple tool for figuring out how biological molecules function in the conversion of silver nitrate to silver.

Transmission Electron Microscopy

Quantitative measurements of particle and/or grain size, size distribution, and shape can be made using the useful, widely used, and essential technology known as TEM for the characterization of nanomaterials. When TEM is used, magnification is determined by the distance between the objective lens and the specimen compared to the distance between the objective lens and the specimen's image plane. Higher spatial resolution and the capacity to conduct more analytical experiments are two advantages TEM has over SEM. The drawbacks consist of the requirement for a strong vacuum and a small sample slice. The time required for sample preparation is the most crucial aspect of TEM. Therefore, sample preparation is essential for producing the best possible images.

RESULTS AND DISCUSSION

As depicted in the experiment, the synthesis of cotton fabrics with in situ generated AgNPs using 1mM to 5mM aqueous AgNO_3 solutions under MW radiation noted that the cotton color changed brown color and we conform from Fig.-1a, indicates color deepened with increasing AgNO_3 concentration. In situ generation of AgNPs was evaluated by observing the uniform color of cotton fabric and the absorbance of the UV-Visible spectrometer at progressive time intervals (Fig.-2). The uniform color of the cotton fabric silver nanoparticles matrix after three to four washings confirms that lignin acted as a stabilizer.

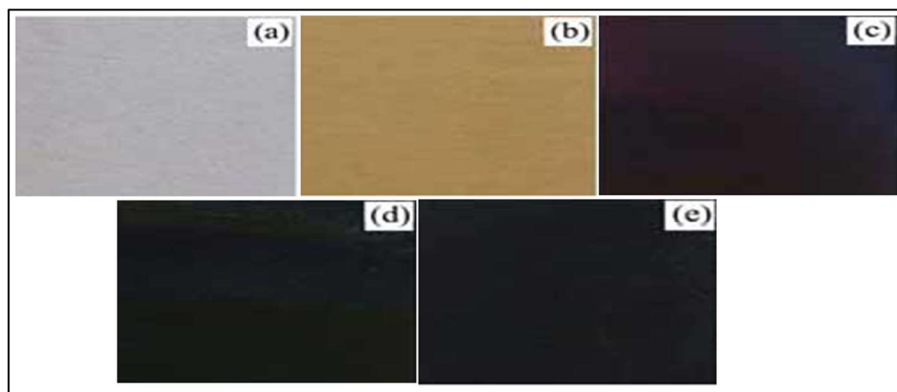


Fig.-1: AgNPs Embedded in Cotton

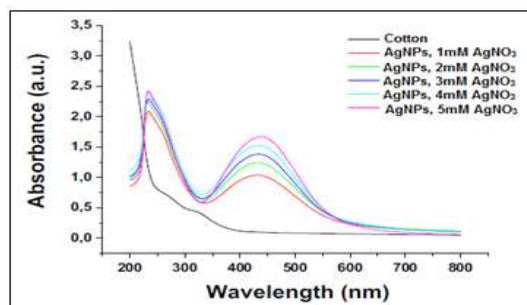


Fig.-2: UV Visible Spectrum

Further, the SEM image Fig.-3a explains the uniform size distribution and diameter of silver nanoparticles and is evident in the spherical nature of particles. The TEM images of silver nanoparticles presented in Fig.-3b, show particle size 15-70 nm. The EDX spectra, Fig.-4 reveal that silver nanoparticles are present in cotton fabric composite films. The FTIR spectra Fig.-5 of cotton/silver nanocomposites bands appearing at 3389 cm^{-1} (OH-str.), 3168 cm^{-1} carboxylic acid –OH str., 3066 cm^{-1} (aromatic CH-str.), 1698 cm^{-1} carbonyl, $1431, 1340\text{ cm}^{-1}$ (CH_2), 1098 cm^{-1} (C-O-C) indicates cellulose structure and evident that the missing band at 1805 cm^{-1} confirms the formation of nanocomposite as per previous reports.¹⁹⁻²⁰

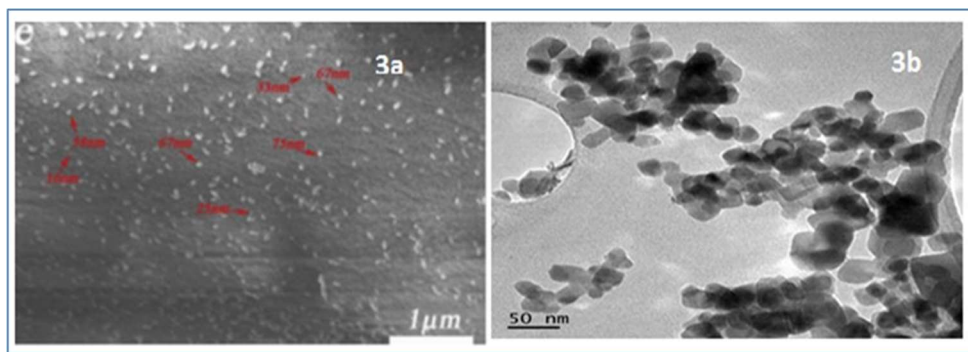


Fig.-3a: SEM Image Silver Nanoparticles Fig.-3b. TEM of Silver Nanoparticles

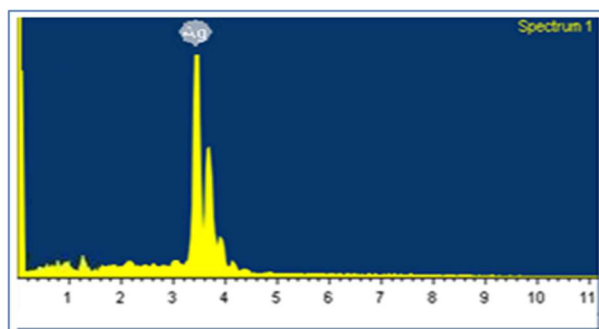


Fig.-4: EDX of Ag Nanoparticles

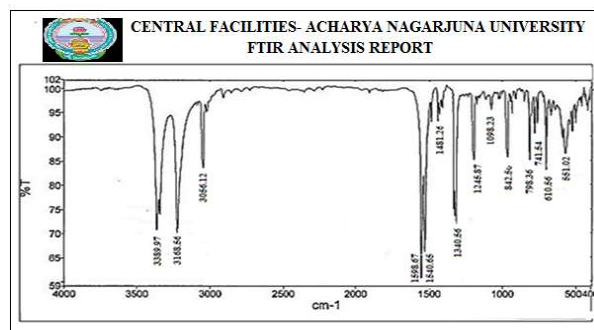


Fig.-5: IR Analysis of Cotton and Lignin

Further, the most evident XRD of lignin capped silver nanoparticles formation was presented in Fig.-6 revealing characteristic peaks at 26° , 64° , and 77° in the 2θ region which corresponds to 111, 220, and 311 planes confirming AgNPs. Another small peak was observed in the XRD spectrum at a 78° peak indicating reducing and capping lignin on the surface of AgNPs. Differently concentrated silver nitrate solutions were treated with equal-volume bark extract solution and obtained almost the same diffraction values (A, B, C, D, E) shown in Fig.-6.

As silver nanoparticles show antibacterial activity, the authors examined the cotton fabric silver nanoparticles composite films against gram-positive and gram-negative bacteria. The clear zones (zone inhibition) formed to represent the killing of bacteria as shown in Fig.-7. However, All the cotton/silver nanoparticles films formed using 1mM to 5 mM aq. AgNO_3 solutions showed good antibacterial activity.

But the zone diameter decreased when compared to composite films of higher concentrated aq.AgNO₃ solution to lower concentrations.

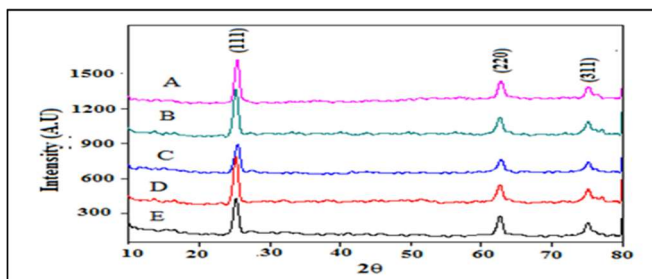


Fig.-6: XRD of AgNps

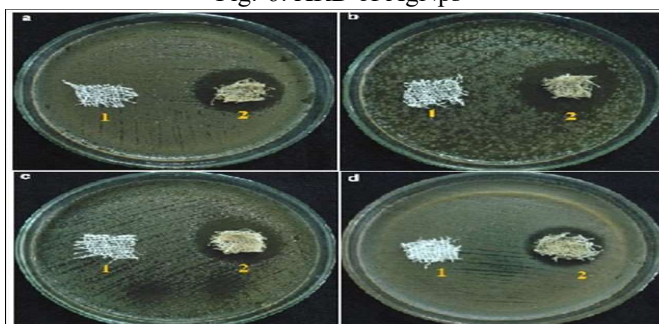


Fig.-7: Zone Inhibition

Information on the antimicrobial activity of lignin-stabilized silver nanoparticles is presented in Table-1. Disc plates were evaluated after the incubation period based on the zone of inhibition using silver nanoparticles and antibiotics as control. Silver nanoparticles have successfully inhibited the growth against a variety of selected bacteria i.e. against gram-positive and gram-negative bacteria. It was suggested that silver nanoparticles generally reduce the development of bacteria by incorporating the cell surface and interrupting the function of the cell.²¹⁻²³ Erythromycin was used as a control to inhibit the growth of various bacteria reported higher zone of inhibition.²⁴ However, in the present study lignin, stabilized AgNPs observed a higher zone of inhibition compared to erythromycin. Moreover, lignin was confirmed as an antimicrobial in previous reports.

Table-1: Average Zone Diameter of Silver Nanoparticles

AgNPs	Zone of inhibition (cm)			
	E.coli (mm)	P.aeruginosa (mm)	B. subtilis (mm)	S. aureus (mm)
20μl of – A	1.0 ± 0.20	1.0 ± 0.06	1.0 ± 0.05	0.6 ± 0.08
20 μl of – B	1.0 ± 0.10	1.1 ± 0.12	1.0 ± 0.06	0.9 ± 0.07
20 μl of – C	1.1 ± 0.06	1.1 ± 0.13	1.1 ± 0.08	1.0 ± 0.12
20 μl of – D	1.1 ± 0.05	1.2 ± 0.08	1.1 ± 0.10	1.1 ± 0.06
20 μl of – E	1.2 ± 0.12	1.3 ± 0.10	1.2 ± 0.20	1.1 ± 0.06
Erythromycin	-	-	0.7 ± 0.24	0.9 ± 0.08

CONCLUSION

The simple and eco-friendly green method for the synthesis of nanocomposite silver films on cotton with in situ generations using various concentrated aq.AgNO₃ and Acacia lignin bark extract as reducing agents and stabilizing agents in presence of microwave radiation. The formation of AgNPs was monitored and confirmed by UV-Visible spectra, EDX, TEM, SEM analysis, and FTIR spectra showing the presence of bioactive particles involved in the reduction and stabilization process. Exclusively, the cotton silver nanocomposite films displayed an efficient anti-bacterial activity against tested microorganisms, and hence these composite films are potentially used as surgical, dressing, and cleaning nanomaterials.

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