CONVERSION OF NATURAL FIBERS ADAVI BENDA INTO NANOCOMPOSITE FIBERS WITH *IN SITU* GENERATED SILVER NANOPARTICLES BY A SIMPLE METHOD – A NEW APPROACH

R. Pushpalatha and M. Madhusmitha
Department of Chemistry, S. S. B. N. Degree College, Ananthapuramu
Email: pushpakanth8@gmail.com

***Abstract*- Plastic pollution is a burning problem and there are many environmental issues associated with the polymers as they are non-biodegradable. In this direction, many completely biodegradable polymer composites were developed with biodegradable matrix materials and natural fibers reinforcement. Though these are completely biodegradable, they do not possess any antibacterial activity. A new approach in imparting antibacterial activity to the completely biodegradable polymer composites is to convert the natural fiber reinforcement into antibacterial nanocomposite natural fibers with *in situ* generated metal nanoparticles such as silver and copper. In the present work, the newly identified natural fibers from the plant Adavi Benda (Adavibenda lampas) were converted into nanocomposite fibers with *in situ* generated silver nanoparticles (AgNPs) by simple and low cost hydrothermal method. The prepared nanocomposite fibers were characterized by FTIR spectroscopy, Scanning electron microscopy and antibacterial tests. The nanocomposite Adavibenda fibers showed good antibacterial properties against both Gram negative and Gram positive bacteria. These nanocomposite natural fibers possessing antibacterial activity can be used as reinforcement to make completely biodegradable antibacterial nanocomposite films for packaging and medical applications.**

Index terms: Natural fibers; Adavibenda; nanocomposites; *in situ* generation; Silver nanoparticles; antibacterial activity

I.INTRODUCTION

Due to their unique properties such as chemical, magnetic, mechanical, optical, antibacterial activity, noble metal nanoparticles are finding innumerable applications in medicine, electronics, cosmetics, coatings etc. [1-4]. Recently, Sadanand et al al.[5,6] successfully prepared antibacterial cotton fabrics with *in situ* generated silver and copper nanoparticles by simple one step hydrothermal method. They reported excellent antibacterial properties against both Gram negative and Gram positive bacteria. As polymers in general and polymer composites in particular are causing environmental pollution due to their non-biodegradable nature, the trend is now is now shifting towards developing completely biodegradable polymers and their composites. In this direction, recently, Reddy et al.[7] extracted and studied the properties of natural fibers from the newly identified plant Adavibenda (Adavibenda lampas) and reported their properties. They recommended these newly identified fibers as reinforcement in the preparation of composites in general and completely biodegradable polymer composites in particular. Ashok et al.[8] prepared completely biodegradable composite films using cellulose as matrix and the Adavibenda fibers as reinforcement and reported improved properties for packaging applications. In order to impart antibacterial property to the composites, in this work, the author *in situ* generated silver nanoparticles (AgNPs) by one step simple hydrothermal method and converted the fibers into nanocomposite fibers. The nanocomposite Adavibenda fibers with *in situ* generated AgNPs were characterized by FTIR spectroscopy, Scanning electron microscopy (SEM) and Antibacterial tests.

II. MATERIALS AND METHODS

Materials

Extracted Adavibenda fibers, sodium hydroxide pellets (Merck Ltd., Mumbai, India), acetic acid(S.D. Fine Chemicals, Mumbai, India), analytical grade Silver nitrate (Merck Ltd.) and deionized water were used for the experiments.

Methods

Fiber extraction

The Adavibenda lampsshrub were collected from Mahabubabad forest in the Warangal district in Telangana state of India. Adavibendafibers were extracted from the stems by combined water and mechanical retting process. The separated fibers were washed thoroughly using water and then sun dried for 1 week and then kept in a hot air oven for 24 h to ensure maximum moisture removal. The extracted

fibers were treated with 2% (w/v) sodium hydroxide solution for 2 h at room temperature, to remove the surface impurities. Finally, the fibers were neutralized using 1% (w/v) acetic acid solution followed by water and then the fibers were dried at 105^{o}C`

Conversion of Adavibenda natural fibers into nanocomposite Adavibenda fibers:

The pre-treated Adavibenda fibers were added to 5 mM aq. AgNO3 source solution 10% by weight in a beaker and kept in an oven maintained at 80 ^{o}C for 24 h. The color change in the modified fibers at the end of 24 h was noticed. The modified fibers were thoroughly washed with deionized water several times to remove un-reacted silver salts if any. The color of the modified fibers remained unchanged in spite of repeated washes in water indicating the capping of *in situ* generated AgNPs in them.

Microscopic analysis

In order to examine the presence of AgNPs and their particle size distribution in the modified Adavibenda fibers, the SEM images were recorded using Zeiss EVO 18 scanning electron microscope. The specimens were gold coated prior to the observation and recording of the images. Using the same instrument, the EDX spectrum was also recorded for the modified fibers.

FTIR spectral analysis

The FTIR spectra of unmodified and the modified Adavibenda fibers with *in situ* generated AgNPs were recorded on a Smart iTR ATR Nicolet is 10 FTIR spectrophotometer in the 4000–500 cm^{-1} range with 32 scans in each case at a resolution of 4 cm^{-1}.

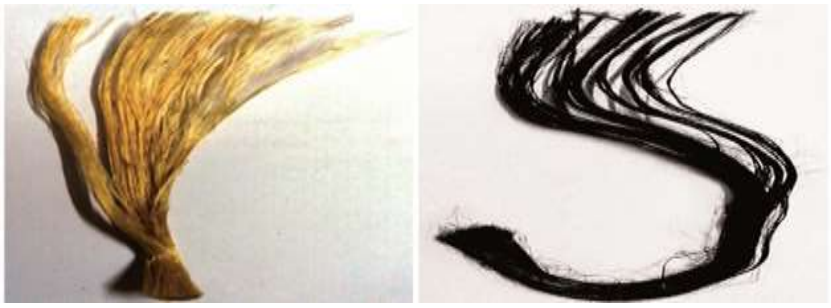
Antibacterial test

The antibacterial activity of the modified Antibacterial test

The antibacterial activity of the modified Adavibenda fibers was tested against Gram negative (E.coli and Pseudomonas) and Gram positive (Bascillus and Staphylococcus) bacteria by disc method adopting the procedure described elsewhere [9]. The observed inhibition zones were photographed and the zone diameter in each case was measured using the Image J software..

II. RESULTS AND DISCUSSION

In this study, natural Adavibenda fibers were used as a reducing agent system for AgNPs synthesis. Silver nanoparticles were formed by the reduction of Ag^{+} into Ag^{0} with the addition of Adavibenda fibers to the solution of 5 mM $AgNO_3$. The results revealed the synthesis was a slow process at 80^{o}C for 24 h. It can be visually observed that the unmodified Adavibenda fibers (Figure 1(a)) were light yellow in color and the modified Adavibendafibers (Figure 1(b)) with *in situ* generated AgNPs appeared dark brown. The color change from yellow to dark brown indicated the formation of AgNPs[10]. This phenomenon was in accord with the reported work in which the polyphenols of lignin and polysaccharide (cellulose) hydroxyl groups reduce Ag^{+} to Ag^{0} [11].



(a) (b)

Figure 1: Digital images (a) unmodified and (b) modified Adavibenda fibers with *in situ* generated AgNPs by hydrothermal method

SEM provided further approach to probe the morphology and size details of the silver nanoparticles. In order to observe the presence of the AgNPs in the modified Adavibenda fibers, their SEM image of the surface was recorded and is presented in Figure 2. The SEM image (Figure 2(a)) illustrates the presence of AgNPs which were predominantly in spherical shape and a few particles are seen aggregated into lager irregularly shaped structures on the fiber surface. This is due to the presence of secondary metabolites in the Adavibenda fibers.

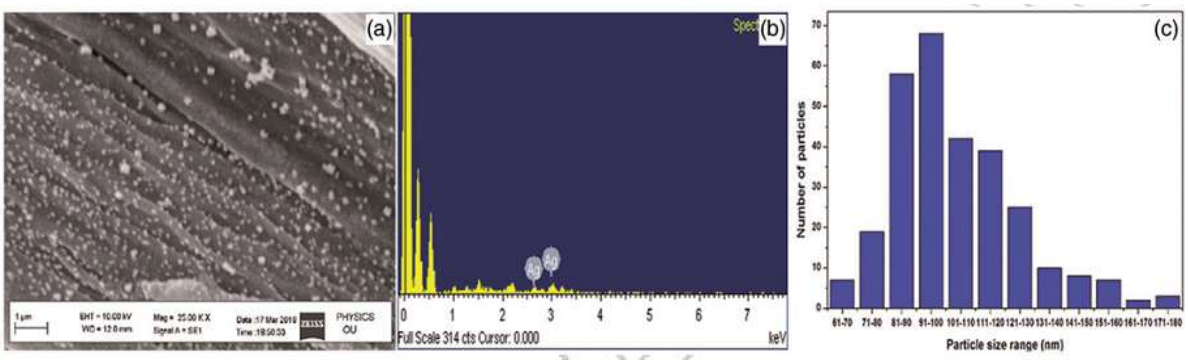


Figure 2: SEM images of the surface of modified Adavibenda fibers with *in situ* generated AgNPs using 5 mM aq. $AgNO_3$ source solution by hydrothermal process (a), EDX spectrum (b), and histogram representing the particle size distribution (c)

Usually silver nanoparticles are found to easily agglomerate during synthesis. EDX spectrum was recorded in the spot-profile method from one of the regions on the fiber surface which was densely populated with AgNPs. The presence of the Ag element in the modified fibers was confirmed by the presence of the peaks corresponding to Ag as indicated in the EDX spectrum (Figure 2(b)). The particle size histogram of AgNPs (Figure 2(c)) shows the distribution of particle sizes. The sizes of particles are ranged from 61 to 120 nm and the average particle size comes out to be 95 nm. The difference in size is possibly due to the fact that the nanoparticles are being formed at different times.

FTIR Spectroscopy

FTIR spectroscopic study was carried out to identify the possible functional groups of theAdavibenda fibers for the reduction of the Ag^+ in the formation of AgNPs and the spectra are presented in Fig.3.

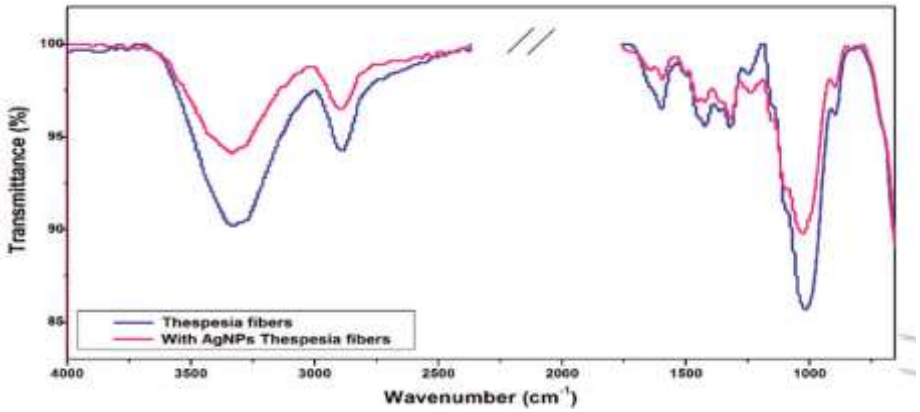


Figure 3: FTIR spectra of unmodified and the modified Adavibenda fibers with *in situ* generated AgNPs by hydrothermal method

In the Adavibenda fibers spectrum, the strong and broad band in the region 3490–3500 cm^{-1} corresponds to O–H stretching H-bonded alcohols and phenols[12]. The peak at 2894 cm^{-1} represents the C–H stretching of methyl and methylene units of polysaccharides and lignin constituents. In the region 1600–1100 cm^{-1}, many absorption peaks are noticed whose intensities differ from low, moderate to high. Among them, notable are 1610: aromatic ring stretching of lignin, 1428: OH bending of cellulose, 1328: CH2 bending of lignin and 1231: acetyl (–COO) groups vibrations of hemicelluloses [12,13]. The band at 1030 corresponds to the C–O–C stretching vibration of polysaccharides. FTIR spectrum revealed the presence of different functional groups present in the material such as alkaline methylene, alkene and carboxylic acid functional groups etc. According to earlier studies, [14] these chemical groups were proved as reducing agents, which help in the synthesis of AgNPs. The similarity in the band positions of the modified Adavibenda fibers indicates that the generated AgNPs did not change their structure. However, the peaks intensities are lowered in the modified fibers due to the reduction of silver ions into AgNPs. While the intensity of the peak at 1240 cm^{-1} corresponding to the–COO groups was higher than that of the unmodified. This is understandable as some of the aldehyde groups can be oxidized to C–O and C–O–O groups due to the oxidizing nature of AgNPs [15]. The Adavibenda plant fibers refereed synthesis process is green since it requires no extra capping or stabilizing agents for the synthesized AgNPs minimizing the use of chemicals in accordance with the principles of green chemistry.

Antibacterial activity:

It is a well-established fact that silver nanoparticles possess excellent antibacterial activity. In order to examine whether the modified Adavibenda fibers with *in situ* generated AgNPs also exhibit the antibacterial properties or not, the antibacterial test of the unmodified (AB1) and the modified Adavibenda fibers (AB2) was conducted by the well method against both Gram negative bacteria (Escherichia coli and Pseudomonas aeoginosa) and Gram positive bacteria (Bacillus lichenformis and Staphylococcus aureus). The clear zones indicating the annihilation of bacteria by the AgNPs present in the modified Adavibenda fibers after 24 and 48 h incubation were photographed and the corresponding images are presented in Figure 4.

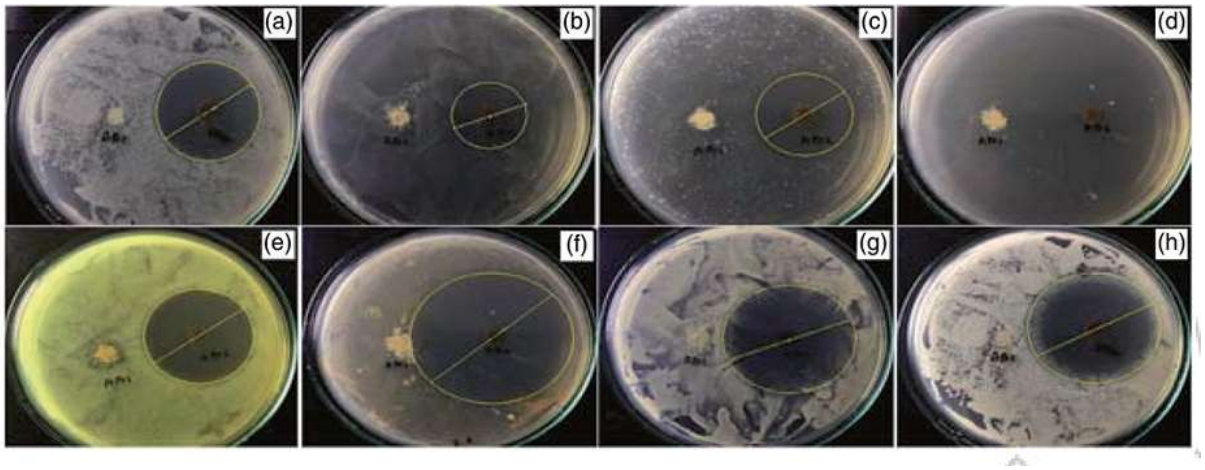


Figure 4: Images of the clear zones formed for the modified Adavibenda fibers (AB2) against Gram negative (E. coli and Pseudomonas) and Gram positive (BacillusandStaphylococcus) bacteria after 24 h incubation (a–d) and after 48 h incubation (e–f), respectively

For comparison, the images for the unmodified (AB1) are also included in the sub figures. From Figure 4, it is evident that the unmodified fibers did not result any clear zone indicating their inability to inhibit the growth of the bacteria. However, the modified Adavibenda fibers exhibited effective antibacterial activity against Gram negative bacteria and one Gram positive bacteria (Bacillus) after 24 h of incubation. But after 48 h of incubation, the modified Adavibenda fibers showed excellent antibacterial activity against all the bacteria tested as evidenced by the appearance of clear zones in all the cases (Figure 4). In order to quantify the antibacterial activity of the modified Adavibenda fibers, their clear zone diameters against both Gram negative and Gram positive bacteria were measured using ImageJ program and the values are presented in Table 1. From Table 1, it is evident that the antibacterial activity of the modified Adavibenda fibers was enhanced after 48 h of incubation. These observations indicate the significant antibacterial activity of the modified Adavibenda fibers. Hence, when these modified Adavibenda fibers are embedded as fillers in polymer matrices, the resulting composites are expected to exhibit antibacterial activity.

Table 1. Clear zone diameters of the modified Thespesia fibers against Gram negative (E. coli and Pseudomonas aeoginosa) and Gram positive (Bacillus lichenformis and Staphylococcus aureus) bacteria after 24 h and 48 h incubation.

	Escherichia coli MTCC 1652		Pseudomonas aeoginosa MTCC 2453		Bacillus lichenformis MTCC 73537		Staphylococcus aureus	
Time (h)	Area (mm^2)	Length (mm)	Area (mm^2)	Length (mm)	Area (mm^2)	Length (mm)	Area (mm^2)	Length (mm)
After 24 h	602.1	28.1	299.1	19.8	457.9	Na	Na	
After 48 h	773.9	30.9	715.8	30.1	1056	6.82	1400.5	Na

VI CONCLUSION

The Adavibenda lampas plant natural fibers were modified by the *in situ* generation of silver nanoparticles (AgNPs) in them by the simple hydrothermal method. The modified Adavibenda lampas fibers were characterized by FTIR, SEM and antibacterial activity tests. The SEM coupled EDX spectrum indicated the formation of spherical AgNPs on the surface of the modified fibers with the size in the range 61–120 nm and the average size of the AgNPs on the surface was 95 nm. FTIR spectrum of the modified fibers indicated the role of OH groups of the fibers in reducing the silver salts into AgNPs. The modified Adavibenda fibers exhibited excellent antibacterial activity against both Gram negative and Gram positive bacteria. These modified Adavibenda fibers can be used as antibacterial fillers in polymer matrices in the preparation of polymer nanocomposites

REFERENCES

[1] Moores, A., and F. Goettmann. 2006. The plasmon band in noble metal nanoparticles: an introduction to theory and applications. New J. Chem. 30:1121–1132.

[2] Mohanty, A., N. Garg, and R. Jin. 2010. A universal approach to the synthesis of noble metal nanodendrites and their catalytic properties.Angew. Chem. Int. Ed. 49:4962–4966.

[3] Doria, G., J. Conde, B. Veigas, L. Giestas, C. Almeida, M. Assunc ¸~ao, J. Rosa, and P. V. Baptista. 2012. Noble metal nanoparticles for biosensing applications. Sensors. 12:1657–1687.

[4] Arvizo, R. R., S. Bhattacharyya, R. A. Kudgus, K. Giri, R. Bhattacharya, and P. Mukherjee. 2012. Intrinsic therapeutic applications of noble metal nanoparticles: past, present and future. Chem. Soc. Rev. 41:2943–2970.

[5] Vajja Sadanand · Tia Hua Feng · A. Varada Rajulu · Battu Satyanarayana. 2017. Preparation and Properties of Low Cost Cotton Nanocomposite Fabrics with in situ Generated Copper Nanoparticles by Simple Hydrothermal Method. Int. J. Polym. Anal. Charact. 22: 587-594.

[6] Vajja Sadanand, Huafeng Tian, A. Varada Rajulu & Battu Satyanarayana. 2017. Antibacterial cotton fabric with *in situ* generated silver nanoparticles by one-step hydrothermal method. Int. J. Polym. Anal. Charact. 22: 275-279.

[7] Reddy, K. O., B. Ashok, K. R. N. Reddy, Y. E. Feng, J. Zhang, and A. V. Rajulu. 2014. Extraction and characterization of novel lignocellulosic fibers from Thespesia lampasplant. Int. J. Polym. Anal. Charact. 19:48–61.

[8] B.Ashok[a]K. ObiReddy[b]K.Madhukar[a]J.Cai[c]L.Zhang[c]A. Varada Rajulu. 2015. Properties of cellulose/*Thespesia lampas* short fibers bio-composite films. Carbohydrate Polym. 127:110-115.

[9] Sadanand, V., N. Rajini, A. V. Rajulu, and B. Satyanarayana. 2016. Preparation of cellulose composites with *in situ* generated copper nanoparticles using leaf extract and their properties. *Carbohyd. Polym.* 150:32-39.

[10] Wu, J., N. Zhao, X. Zhang, and J. Xu. 2012. Cellulose/silver nanoparticles composite microspheres: Ecofriendly synthesis and catalytic application. Cellulose. 19:1239–1249.

[11] Raveendran, P., J. Fu, and S. L. Wallen. 2003. Completely“green”synthesis and stabilization of metal nanoparticles.J. Amer. Chem. Soc. 125:13940–13941.

[12] Reddy, K. O., B. R. Guduri, and A. V. Rajulu. 2009. Structural characterization and tensile properties of borassus fruit fibers.J. Appl. Polym. Sci. 114:603–611.

[13] Maheswari, C. U., K. O. Reddy, E. Muzenda, B. R. Guduri, and A. V. Rajulu. 2012. Extraction and characterization of cellulose microfibrils from agricultural residue–Cocos nucifera L. Biomass Bioenergy. 46:555–563.

[14] Suresh, G., P. H. Gunasekar, D. Kokila, D. Prabhu, D. Dinesh, N. Ravichandran, B. Ramesh, A. Koodalingam, and G. V. Siva. 2014. Green synthesis of silver nanoparticles using delphinium denudatum root extract exhibits antibacterial and mosquito larvicidal activities. Spectrochim. Acta A Mol. Biomol.Spectrosc. 127:I61–I66.

[15] Li, R., M. He, T. Li, and L. Zhang. 2015. Preparation and properties of cellulose/silver nanocomposite fibers. Carbohydr. Polym. 115:269–275