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GREEN SYNTHESIS OF LIGNIN NANOPARTICLES FROM AGRICULTURAL WASTE OF COCONUT COIR

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ABSTRACT
Bio-materials in the nano size are promising high-value products with diverse applications. The green synthesis of lignin nanoparticles has opened a novel method to utilize lignin in advanced uses. In the present study lignin nanoparticles with dimensions of about 35nm were prepared from alkaline lignin extract directly in the moist condition. By rapid acid precipitation using methane sulphonic acid, accompanied by mild ultrasonication. The size, surface morphology, and thermal properties of the lignin nanoparticles were studied using different techniques such as; DLS, FTIR, XRD, UV, SEM, TGA, and DTA.
Keywords: Agro-Industrial Waste, Lignin Nanoparticles (LNPs), Green Synthesis, Methane Sulphonic Acid, Acid Precipitation, Ultrasonication.
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INTRODUCTION

Renewable natural materials such as; cellulose, lignin, and other biopolymers can be suitably used to produce nanoparticles for various uses. Among these natural materials, lignin has emerged as a potential biopolymer with pronounced attention. Lignin nanoparticles (LNPs) owing to their biocompatibility, environment benignity, non-toxicity, and cost-attractiveness overcome the drawbacks of synthetic nanomaterials. The development of nanostructured lignin with improved morphology allows it to form a colloidal dispersion of lignin in an aqueous medium which is otherwise water insoluble and thus makes these LNPs a potential candidate in the field of industry.[1] The present investigation involves a rapid straightforward and energy-efficient highly scalable synthesis of LNPs by blending the two preparation methods, acid precipitation and ultrasonication.[2] Lignin nanoparticles were directly formulated from alkaline lignin extracted from coconut coir by rapid acid precipitation using methane sulphonic acid (MsOH) and a surfactant, coco glucoside, accompanied by mild ultrasonication. MsOH has been adopted in the preparation of lignin nanoparticles because of its salient features such as; being environment-friendly, odorless, colorless, less corrosive, and readily biodegradable acid.[3] To the best of ourknowledge, the environment-safe, green route for LNP preparation by applying acid precipitation and sonication method using MsOH is novel.

EXPERIMENTAL

Materials

The coconut coir utilized in the present work was procured from one of the local Agro Industries. Sodium hydroxide, anhydrous methane sulphonic acid, and Coca glucoside are procured from spectrochem. All these chemicals were of AR grade and were used as it is. All the solutions used in the experiment were prepared using deionized water.

Method for the Synthesis of Lignin Nanoparticles

The green synthesis of LNPs comprises a two-step process, first is the extraction of lignin from the preconditioned coir fiber using sodium hydroxide followed by the synthesis of LNPs by acid precipitation of the alkaline extract using green reagent MsOH followed by ultrasonication.

Isolation of Lignin from Coconut Coir Using Alkaline Solution

The alkaline extract of lignin was prepared from the preconditioned coir fiber using NaOH under optimized

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conditions as mentioned in our prior work.[4]

Synthesis of LNPs using MsOH and Ultrasonication
To synthesize LNPs, 50 ml of alkaline extract obtained previously was taken in a 250 ml beaker and mixed rapidly with MsOH till the pH reached ~2 followed by a subsequent addition of 2 ml of the emulsifying agent, coca glucoside. The solution was then immediately kept in an ice bath to prevent the damage induced by heat and was subjected to sonication for a specific time. The sonicated emulsion was centrifuged at 300 rpm. These obtained LNPs were stored in a sealed container. The optimization of the lignin nanoparticle synthesis, based on the size of the obtained nanoparticles, was accomplished by carrying out different trials with two varying parameters, viz., (i) variation in the strength of MsOH (2%, 4%, 8% and 12%) and (ii) variation in the time of sonication (10 and 15 min).

Characterization of Lignin Nanoparticles
The characterization study of the LNPs was accomplished to get a detailed study of shape, size, size distribution, and surface morphology by various physio-chemical and spectral techniques.

Dynamic Light Scattering (DLS) Studies
DLS method with HORIBA, SZ-100.nsz was adopted for the determination of hydrodynamic diameter, particle size, and particle size distribution of LNPs.

FTIR Spectroscopy
The FTIR spectra of the LNPs were recorded for investigating the functional groups using an Infrared Spectrophotometer Bruker Alpha II Germany ATR module with a scan rate of 32 scans/min.

SEM and EDX Studies
SEM and EDAX studies were performed using Hitachi SU 3500 run at an accelerating voltage of 10kV to understand the morphology of LNPs.

XRD Studies
XRD studies were performed to study the crystallographic structure present in a material. XRD of the LNPs obtained at the optimized condition was investigated using XRD -Rigaku smart lab 3kW (Japan). The Cu Kα (1.5418 Å radiation) was used as the source of X-rays. The sample was scanned from a 2θ value of 10 - 80 ° at the rate of 5°/min. The angles and intensities of the diffracted X-rays are measured. The crystallite size, lattice parameter, d spacing values, dislocation density, the volume of the unit cell, and hoping length were calculated.[5]

Differential Thermal Analysis and Thermogravimetric Analysis
The thermal properties of the synthesized LNPs were found by TGA and DTA measurements. The studies were performed with a Rigaku 8150 thermal analyzer.

UV-Visible Spectroscopy
The UV-Vis spectra of LNPs were noted on a Metrohm ASM80063 spectrophotometer, within the span of 200-800 nm using deionized water as a blank sample.

RESULTS AND DISCUSSION

DLS Studies
DLS studies of LNPs are depicted in Fig.-1, which shows the size distribution of the nanoparticles prepared with different percentages of MsOH (2%, 4%, 8%, and 12%) at different sonication times (10, 15 min). The obtained data shows that the size of the LNPs fabricated in the current investigation was 35.5nm to 262.4 nm. The minimum particle size of 35.5 nm and a narrow particle size distribution was achieved by using 4% MsOH along with 10 min of ultrasonication. It was also noted that the particle size of the fabricated LNPs augmented as the concentration of MsOH was increased. It was observed that the sonication time had a profound effect on the size of the LNPs. The enhancement of sonication time increased the size of the synthesized LNPs from 35.5 to 824.7 nm. This study shows a distinct negative impact of the increment of sonication time from 10 min to 15 min on the dimension of the LNPs. The phenolic hydroxyl groups present

in LNPs may be the cause of such a contrary phenomenon. During the extended sonication process, the phenolic hydroxyl groups of LNPs may form phenoxy radicals, which in turn, due to extensive oxidation, initiates radical-induced cross-linking polymerization reactions and results in the generation of LNPs with bigger particle sizes.[6] Further, the addition of the surfactant, coca glucoside during the preparation of LNPs demonstrated a remarkable effect on their particle size Fig.-1(b). Coca glucoside used in this method assumes to achieve maximal surface coverage over the particles and also supports the steric resistance effect by developing a layer on the surface of the particles.[7]

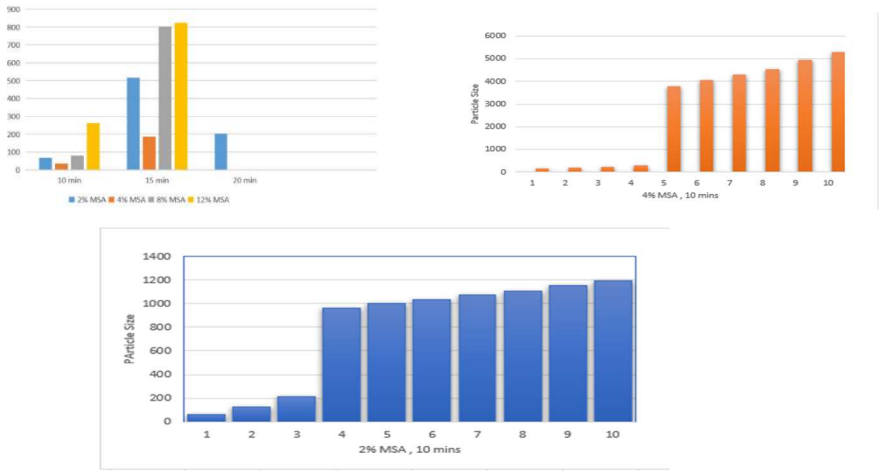

Fig.-1: (a) Particle Size and Particle Size Distribution of LNPs by DLS Method; In the Presence of Emulsifiers, (b.) in the Absence of the Emulsifier. (Coco glucoside)

Fourier Transform Infrared Spectroscopy

Figure-2 displays the FTIR spectra of the LNPs. The IR spectrum of the produced LNPs showed some distinctive peaks. At 3356 cm^{-1} a broad peak appears which is due to O–H group stretching vibration, this also indicates that phenolic and alcoholic OH groups are involved in hydrogen bonds. [8] The 2954 cm^{-1} peak is due to the C-H stretching of the aromatic group, the peak at 2853 cm^{-1} is due to C–H stretching of the aliphatic group, the peak at 1608 cm^{-1} is due to C=C aromatic stretching, the peak at 1209cm^{-1} is due to C–O stretching of the C–OH bond, 1044 cm^{-1} peak is due to symmetric C-O-C stretching. The peak at 1712 cm^{-1} is due to the C=O stretching of carbonyl moieties of hemicellulose impurities that could be present in lignin. The peaks at 1608, 1513, and 1427 cm^{-1} indicate the presence of a benzene ring in the lignin structure. The peaks at 1365 and 1326 cm^{-1} indicate the ether stretching of syringyl and guaiacyl groups in lignin.[9]

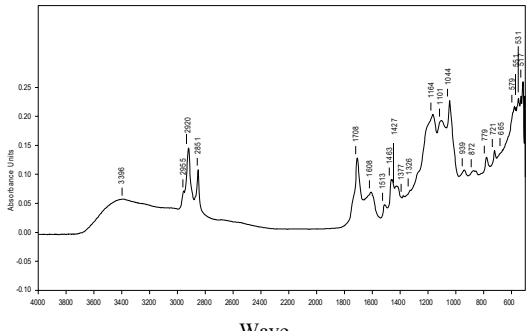

Fig.-2: FTIR of Lignin Nanoparticles

EM and EDX Analysis

SEM micrographs of the LNPs are depicted in Fig.-3. While synthesizing the LNPs in the absence of ultrasonication, irregular and agglomerated lignin particles in the size range of 2–5µm were observed (Fig. 3a) owing to strong intermolecular hydrogen bonding between macromolecular lignin.[10] LNPs obtained via

ultrasonication showed non-uniform morphology with particle sizes nanometer range (Fig.-3(b)). The ultrasonication process plays an important role in the effective disintegration of lignin particles from the micro to the nanometer range. The EDX spectra of the LNPs show the existence of major elements in the form of carbon, oxygen, and traces of silicon.

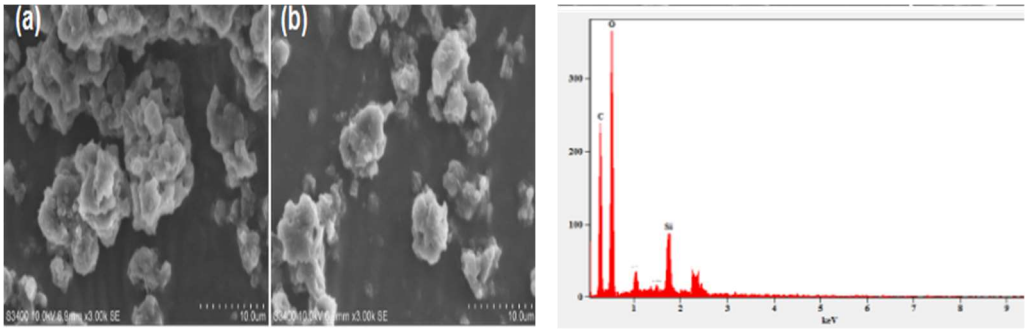

Fig.-3: SEM images of (a) Virgin Lignin Nanoparticles without Ultrasonication and (b) Virgin LNPs with Ultrasonication (c) EDX of virgin LNPs

XRD Analysis

The XRD pattern of the LNPs is represented in Fig.-4. A broad peak at 21° represents the partially crystalline nature of the sample. The crystallinity nature of the sample can be improved depending on the fabrication conditions.[11] The sharp peaks in the XRD pattern indicate the crystallinity nature of the sample, which may be the result of smaller particle size and liberation of substances such as extractives, cellulose, hemicellulose, tannin, and cellulose. The strong diffraction peak located at 21° was adopted for the calculation of crystallite size, lattice parameter, d spacing values, dislocation density, the volume of the unit cell, and hoping length and the results are shown in Table-1.[12]

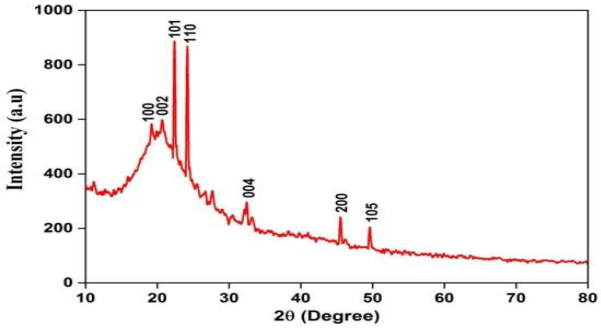

Fig.-4: XRD Pattern of Lignin Nanoparticles

Table-1: X-ray Powder Diffraction Values of Synthesized Lignin Nanoparticles

D(nm)	d (Å)	α (Å)	δ (10^{15}) (lines/m^2)	V(Å)^3	L_A(Å)	L_B(Å)
37.89	3.971	5.615	0.696	177.030	2.431	1.985

TGA and DTA Studies

DTA and TGA curves are shown in (Fig.-5b and 5a). A weight loss in the region 150 °C - 250 °C might be due to the exclusion of HCOOH, HCHO, CO_2, and H_2O resulting from the degradation of phenylpropane side chains.[13] Major weight loss according to Fig.-5b has been observed in the region from 275°C to 500°C and weight loss was around 30%. This weight loss occurs due to the deprivation of the lignin structure. During the process of LNP degradation, multiples of responsive volatile components were generated. In the range between 250°C -500°C the monomeric phenols would be changed into the vapor form due to the fragmentation of inter-unit linkages of phenolic -OH, C=O, and benzylic groups.[14] The ultrasonication process carried out for LNP synthesis, has effectually detached hemicellulose components from lignin by the cleavage of lignin-carbohydrate linkage, which can be confirmed by the absence of a peak in the 340 °C region. From 400–600 °C, methoxy group decomposition was observed, whereas beyond 600 °C there

was the occurrence of the fragmentation of the carbonyl and C–O–C bonds. From 4005-750 °C the weight loss was about 21% for LNPs. The weight was found to be the same at 800 °C due to the presence of solids which are non-volatile and related to condensed aromatic structures and the ash in LNPs.[15] Commonly the deprivation of ester and aliphatic hydroxyl bonds are detected at lower temperatures in contrast to the aromatic bonds. Figure-5 b and a provide clear evidence for the stability of LNPs up to 250 °C. Tg is a straightforward sign for the flexibility of the macromolecular chain.[12] The results mentioned in our case indicate that LNP thermal stability has improved upon ultrasonication through size reduction.

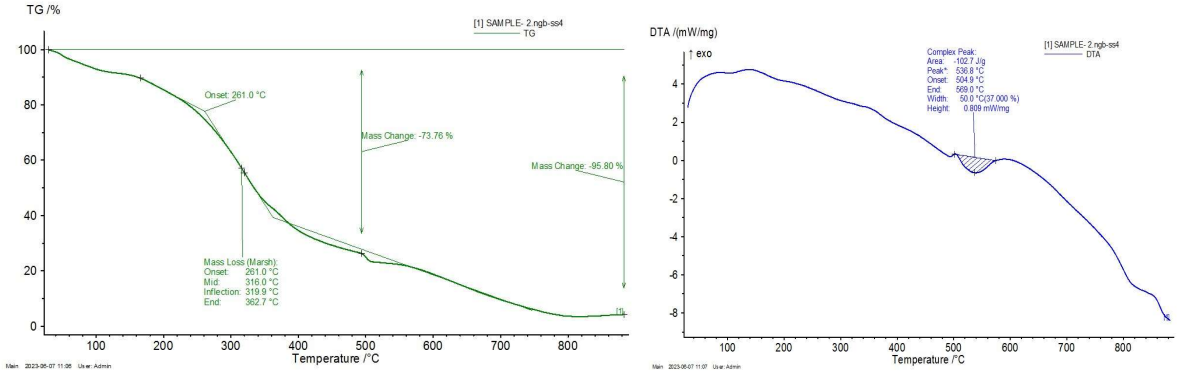

Fig.-5: (a)Thermogravimetric Curves and (b) Differential Thermal Analysis of Lignin Nanoparticles

UV-Visible Spectral Studies

The UV-visible spectrum related to the LNPs has been presented in Fig.-6(a). The conjugated moieties (carbonyl groups) of the LNPs show characteristic absorption bands as shoulder in the range of 300-350 nm. A distinct absorbance peak at 253 nm, corresponds to the non-conjugated phenolic groups in LNPs. The band at 253 nm is owing to the π-π* electronic transition in guaiacyl (G) units or the aromatic ring. This higher absorbance peak indicates the presence of a greater phenolic hydroxyl amount, which further supports the Fourier transform infrared spectral data. Another sharp absorbance peak was observed at 210 nm, which can be assigned to the carboxylic acid present in the sample. The optical band gap energy (Eg) obtained from Tauc's plot was calculated to be 4.02 eV[16] (Fig.-6b)

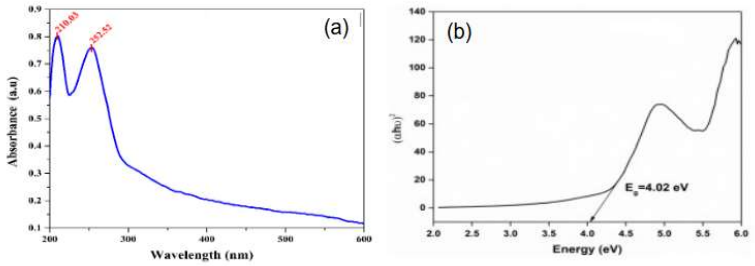

Fig.-6: (a) UV-VIS Spectra and (b) Tauc's Plot of Lignin Nanoparticles

CONCLUSION

In the present study, a simple energy efficient, rapid, green synthesis of lignin nanoparticles from coconut coir fiber, an agro-waste is reported. LNPs with dimensions in the nano range (~35 nm) are obtained by acid precipitation using methane sulphonic acid (4%) followed by mild ultrasonication for a short period (10 min). The physical and chemical characterization of the synthesized LNPs is performed with different analytical techniques, such as DLS (particle size), FTIR, SEM, EDX, UV, TGA, and DTA.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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