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Valorization of Lignin Based Nanoparticle from Grass Biomass: An Overview on Synthesis, Characterization and Application

Sandesh Behera ^a , Bikash Chandra Behera ^b and Hrudayanath Thatoi a*

^a Department of Biotechnology, Maharaja Sriram Chandra Bhanja Deo University, Baripada, 757003, Odisha, India. b School of Biological Sciences, National Institute of Science Education and Research, Bhubaneswar, 752050, Odisha, India.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The Lignin-related nanomaterials have received a lot of attention from the academic and industry communities in the present nanotechnology research area. Advanced performance can be provided by converting lignin into micro and nanostructures, which may be formed using practical standard apparatus. To improve the functionality of the applications, tunable lignin nanoparticles may also be produced. Because lignin contains a variety of chemical moieties and has a unique network structure, it has useful qualities such UV absorbance, biodegradability, stabilizing and reinforcing effects, as well as anti-fungal and antibiotic action. Thus, the nanoscale transformation of lignin and

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^{}Corresponding author: E-mail: hnthatoi@gmail.com;*

its translation into nanomaterials might definitely open up new possibilities for the development of novel materials with intriguing features.

Keywords: Grass biomass; lignin nanoparticle; synthetic pathway; valorization.

1. INTRODUCTION

Lignin serves a significant role in plants by carrying water and nutrients, offering mechanical support, and shielding plants or wood from chemical or microbial attack. Lignin is plentiful and also the greatest reservoir of aromatic polymer in the world [1]. The location of the biomass, the species, and, most crucially, the extraction procedures all have a significant impact on the lignin's molecular structure [2]. The functional groups and molecular weights of various types of lignin, as well as their elemental compositions differ [3]. However, it is generally known that lignin is a biomacromolecule made up of three fundamental phenylpropane monomers: guaiacyl, syringyl, and p-hydrophenyl. The lignin structure contains a variety of functional groups and it has properties that set it apart from other products, including antioxidant activity, good chemical reactivity, biodegradability, affinity to inorganic oxides, and the potential to adsorb harmful compounds from the environment [4]. Lignin can perform a wide range of useful actions because of its many functional groups. Due to these qualities, lignin is being used to make nanocarrier, antioxidant UV-absorbing and antimicrobial, drug delivery products.

Biomass made of lignocellulose is essential for building sustainable societies. The primary sources of biomass made of lignocellulose are trees and large grasses. Moreover in case of production of lignocellulose biomass, large-sized grasses overcome tree biomasses. In general, grass lignin is simpler to isolate than wood lignin [5]. In grass, cellulose, hemicelluloses, lignin, phenolic chemicals, and small quantities of pectin make up the majority of the cell walls. Although lignin-carbohydrate interactions are often stronger, the lignin concentration of grasses is substantially lower than that of wood. Particular covalent cross-linking occurs between arabinoxylans and lignin polymers (through phenolic acids). The cuticle is made up of waxes and waxy polymers that can crosslink with phenolics that resemble lignin. Different genotypes and growing environments can have a considerable impact on the relative proportion of the lignin interunit connections, relative quantities of S, G, and H units, and total lignin content.

Compared to hardwood and softwood, grass lignin has a similar amount of S and G units and a considerably larger fraction of H units. The γhydroxyl groups of the lignin side chains are frequently esterified by acetate and p-coumarate (pCA) in the lignin from grass sources, aside from the variation in the relative quantities of monolignols. The hemicellulose (mainly arabinoxylan) and lignin are joined by ferulate (FA) bridges in the lignin carbohydrate complex (LCC) linkage found in grass [6]. The use of grass biomass will become increasingly to promote the future bioeconomic activities.

Increasing the effectiveness of lignin consumption may also be accomplished by structurally altering lignin. It is possible to chemically alter lignin to change its characteristics. Additionally, the shape and structure of lignin may be controlled by turning raw lignin into lignin nanoparticles (LNPs). The production of LNPs may open the way for the development of other lignin-based materials, even for high-value applications like tissue engineering and drug delivery. Due to their increased surface area and significantly different properties from a larger-dimensional material of the same composition, particularly in the 1-100 nm range, might provide distinctive features. For uses including improving mechanical characteristics, antibacterial and antioxidant capabilities, and impregnations to drug carriers for hydrophobic and hydrophilic chemicals, the synthesis of LNPs has received a lot of interest in recent years. The methods for converting lignin into nano-size materials, their characterization, and their applicability in cutting-edge applications are condensed in this review paper with an emphasis on current studies.

Due to their distinct form and extensive multifunctional group, LNPs have a tremendous potential for downstream valorization. The most promising technique from the standpoint of lignin valorization and sustainable development is the manufacturing of valueadded products made from lignin-based biopolymers. The possibility for producing biopolymers such polyhydroxyalkonates,
polyhydroxybutyrates, and polyurethane polyhydroxybutyrates, and increases with lignin's valorization. Due to lignin's recalcitrant nature, which limits its ability to yield value products, lignin valorization technologies still need to be developed. To simplify the recovery of important products and break up the lignin structure, several creative extraction techniques have been developed.

2. LOCATION, VOLUMES, AND PRICING

Prices for low-purity lignin [7], lignin produced using lignosulphonates and the kraft process, range from 180-500 USD/MT and 50-280 USD/ MT, 260-500 USD/MT respectively [8]. Most businesses are conducting research and manufacturing at the same time to turn lignin into a profitable, desirable raw material [9]. Different kinds of lignin-derived goods, such as various kinds of glue, chemicals, and binders, are produced by businesses in the Europe, Canada, and USA. Some of these businesses create products using lignin that is both sulfurcontaining and sulfur-free. India, Japan, and China are the major producers of goods made from lignin in Asia. In expanding economies like India, Japan, China, and Indonesia, there is an increasing need for lignin. China now holds the global top spot for the manufacturing of ligninbased chemicals. The lignin market in China is growing at a 10% compound annual growth rate (CAGR).

3. BIOSYNTHESIS OF LIGNIN AND PATHWAY INVOLVED

In the model plant Arabidopsis and other dicot species, lignin production has been thoroughly investigated, and these investigations have resulted in the discovery of genes encoding the enzymes catalyzing many of the stages in the system (Fig. 1) [10]. The PAL and CAD enzymes, which catalyze the first step in the overall phenylpropanoid pathway and the last step in the production of monolignols, are thought to play crucial roles in controlling the accumulation of lignin in plants. Since the majority of the lignin biosynthetic enzymes have isoforms, it appears that gene families are responsible for encoding them. While repression of F5H or COMT, which are involved in the synthesis of the S unit of lignin, results in an alteration of the S/G ratio of lignin with only a minimal impact on total lignin content, it suppresses genes early in the pathway, such as PAL, C4H, HCT, C3H, and CCoAOMT in alfalfa and tobacco. Reduced S/G ratio and little impact on overall lignin concentration are both results of

genetic suppression of CAD, which codes for the last enzyme in the production of monolignols. Similar to the F5H1 and COMT mutants, the C4H, 4CL1, CCoAOMT1, and CCR1 mutants have lower levels of total lignin than the wildtype. In contrast, the F5H1 and COMT mutants of plant have decreased quantities of S unit containing oligolignols without affecting the content of total lignin [11].

4. EXTRACTION OF LIGNIN

It is a difficult effort to extract lignin derivatives from diverse lignocellulosic biomass sources. Lignin is frequently both a byproduct at a laboratory scale and a co-product of the pilotscale lignin extraction method. Extracted lignin offers a potential source for the creation of valueadded products in a variety of industries, including food, cosmetics, pharmaceuticals, chemicals, and textiles. Several pulp and paper industries treated a large quantity of lignocellulosic biomass in the past in order to recover high-quality lignin as a target. Due to the increased need for the manufacturing of valueadded products, the lignin recovery has recently attracted the attention of academics and policy makers. Here, we described about significant lab and pilot-scale lignin extraction processes that are practical for producing biopolymers.

4.1 Lab Scale Lignin Extraction

Pretreatment method is another name for the lab scale lignin extraction procedure. To extract lignin from diverse types of lignocellulosic biomass, several researchers have effectively used a variety of pretreatment techniques. Five kinds of pretreatment techniques for lignin extraction include physical, chemical, biological, and combination physiochemical [12-14]. The structure and chemical content of native lignin yield are substantially influenced by the pretreatment technique choice [15].

4.2 Pilot Scale (Industrial) Lignin Extraction

The extraction of lignin at the pilot size involves a technically difficult process that may be divided into five main categories: soda, sulfite, kraft, steam explosion, and Organosolv process. The structure and chemical makeup of technological lignin varies from native lignin depending on the extraction procedure or heating method [16].

Fig. 1. Lignin biosynthesis pathway in plants. Coniferyl, sinapyl, and p-coumaryl alcohols are monolignols that are produced from phenylalanine through the general phenylpropanoid pathway (A) and monolignol-specific pathway (B) are oxidized and incorporated into the G (guaiacyl), S (syringyl) and H (hydroxyphenyl) units, respectively, in the lignin complex (C) [10,11]

Table 1. An overview of laboratory-scale lignin extraction techniques and their operational parameters

Table 2. An overview of the operating parameters for several pilot size lignin extraction techniques

5. LIGNIN CHARACTERIZATION

Lignin's capacity for future uses may be inferred and issues with its use can be found by properly characterizing their structure, content, and characteristics. Lignin can be produced using many sources and extraction methods. Therefore each one has its own features and has to be assessed separately [17]. The biological source, extraction methods, and purifying procedures can all affect the molecular weight of lignin. This is a crucial quality since it affects the lignocellulosic biomass' recalcitrance as well as the commercial viability and application of technical lignin. It is not suggested to analyze lignin's structure and composition using only one methodology since doing so might lead to inconsistent results from using several analytical techniques on the same lignin samples. Fluorescence spectroscopy, Fourier transform infrared (FTIR), and FT-Raman spectroscopy may all be used to determine the functional groups and overall composition. Nuclear magnetic resonance (NMR) spectroscopy techniques can be used to determine a
structure's robustness in one- and structure's robustness in onemultidimensional space [18]. Transmission electron microscopy (TEM), optical microscopy (OM), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) are the most often employed assays to infer lignin macromolecular structure, while thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC)are

frequently employed to explore the thermal activities in lignin, The MW distribution may be analyzed using high-performance liquid chromatography (HPLC) and gel permeation chromatography (GPC) [17].

5.1 Lignin Quantification

The Klason method [19] is a gravimetric assay used for the direct quantification of lignin from plant materials. It is also employed to evaluate the extracted lignin's degree of purity. The National Renewable Energy Laboratory's (NREL) Laboratory Analytical Procedure (LAP) has developed modified Klason-related procedures in recent years, which have lowered the quantity of sample needed and the hydrolysis time [20]. Lignin can be filtered, dried, and weighed since it is present in the solid fraction after the polysaccharides are removed. It is known as Klason lignin, sulfuric acid lignin, or insoluble lignin when it is isolated. It is crucial to keep in mind that the hydrolysis processes have the potential to change its structural makeup [21]. By measuring the UV absorbance of the filtrate, it is also able to calculate the total quantity of lignin (both insoluble and soluble), which includes the soluble lignin component.

5.1.1 UV spectrophotometric method

Because of the aromatic nature of lignin, it significantly absorbs in the UV area, with peaks often showing at wavelengths of around 200, 240, 280, and 320 nm [18]. The superposition of the absorption of five different chromophore systems accounts for the three spectral bands that have been seen in the UV spectrum of lignin [22]. The degree of lignin purity is also significantly associated with the UV absorbance intensity. Less absorbance indicates the coprecipitation of non-lignin materials, such as polysaccharide breakdown products, wax, and lipid breakdown products [23]. The type and structure of the lignin, the solvent, and the pH of the solution are all factors that might affect the UV/Vis spectrum's form [24,25].

5.2 Molecular Weight Characterization

To determine the MW, size exclusion chromatography, or GPC, is frequently utilized [26]. This method offers details on polydispersity, weight-average MW, and number-average MW [27]. Depending on the type of detector, the number of columns, a precise molecular mass determination can be obtained. A precise molecular mass determination depends on the type of detector, the number of columns, and the columns themselves [28]. Aqueous or nonaqueous solvents can be used in relation to the mobile phases depending on the type of lignin. Tetrahydrofuran (THF) is the most used nonaqueous solvent and is more suited for hydrophilic lignins (such as lignosulfonate) than hydrophobic lignins (such as kraft lignin) [29].

5.3 Structural Properties Assessment

5.3.1 Infrared spectroscopy

Methoxyl groups, hydroxyl groups, and carbonyl groups are present in the structure of lignin. FTIR spectroscopy is a flexible and quick approach for detecting these functional groups and figuring out their relative amounts [30]. By using attenuated total reflectance (ATR), photoacoustic (PAS), and diffuse reflectance (DRIFT) techniques, the FTIR spectra may be directly acquired on solid materials including pulp, paper, and wood [21,31]. The spectrum of lignin typically shows two key regions: (1) the $3700-2750$ cm⁻¹ region, assigned to the -OH groups of the physically absorbed water or bonded in aliphatic and aromatic groups and to the methyl groups; and (2) the 1800–900 cm⁻¹ region, also known as the "fingerprint region-", which is primarily assigned to guaiacyl and syringyl structural units but also contains other functional groups [32]. The carbonyl groups and ether linked to the aromatic units are known to produce an intensive

adsorption band in the 1710-1600 cm^{-1} range. At 1710 cm⁻¹, the valence vibrations of the carboxyl and carbonyl groups may be seen [33]. The three sections assigned to the syringyl plus condensed guaiancyl ring $(1330-1325 \text{ cm}^{-1})$, the guaiancyl $ring$ (1270–1266 cm⁻¹), and the syringyl ring (1128–1125 cm-1), respectively, were where the greatest differences were observed [34,35].

5.3.2 Raman spectroscopy

Raman spectroscopy, a useful technique for learning about structural information, is often carried out with visible lasers. However, the study of lignin's structure has benefited greatly from near-IR laser-based Raman spectroscopy [17]. Kihara et al. [36] examined the carbonyl groups contained in cedar and pine milled wood lignin and gave an example of its applicability. The C-O groups were reduced or enhanced chemically, and vibrational modes at 1620 and 1660 cm⁻¹ were found as a result. The band at 1620 cm⁻¹ is a marker for carbonyl content, whereas the peak at 1660 cm-1 was identified as an α,β-unsaturated bond indicator. The effectiveness of lignin extraction from maize stover following an ammonia fibre expansion pretreatment has also been evaluated using FT-Raman spectroscopy [37]. In comparison to the pretreatment sample, the control sample had around a three-fold greater intensity of the vibrational modes at 1600 and 1635 cm⁻¹. The c innamoyl ester (1170 cm^{-1}) analysis also revealed that the residual lignin had reduced functions for ferulate and p-coumarate [38]. In a different investigation, the FT-Raman spectra of milled wood lignin from black spruce and aspen were obtained [17].

5.3.3 Nuclear magnetic resonance (NMR) spectroscopy

Utilizing modern analytical techniques based on NMR spectroscopy, such as 2D-NMR, C-NMR, H-NMR, and P-NMR, many structural features pertaining to the chemical reactivity, composition, and molecular properties have been accessible [39]. Due to the polymeric structure of lignin, the basic proton NMR (H-NMR) method for lignin investigation frequently yields overlapping and poorly resolved spectra. On the other hand, aryl ethers, together with aromatic and aliphatic carbons, may be detected using C-NMR [40]. Lignin structures may be characterized in astonishing detail using two-dimensional (2D) NMR. In two-dimensional heteronuclear single quantum coherence (2D-HSQC-NMR), the difference between C enriched lignin samples and an unenriched control is striking; signals are only detected in the C enriched lignin side-chain carbons, meaning that all signals can be ambiguously attributed to those carbons [41]. Quantification of several functional groups may be possible with P-NMR [17]. In order to quantify the amount of each hydroxyl functional group present in kraft, soda, and ethanol Organosolv lignins, Hussin et al. used cyclohexanol as an internal standard [42].

5.4 Thermal Properties

Technical lignins' thermal characteristics are rigorously governed by their structural variations, which are brought on by variations in source as well as in the length and temperature of the
extraction operations [43]. DSC is a extraction operations [43]. DSC is a thermoanalytical technique that enables inferences about the thermal stability of the lignin structure by gradually raising the temperature of a sample and a reference material. Another thermoanalytical method is thermogravimetric analysis (TGA), which reports changes in a sample's mass as a function of an increase in temperature that occurs dynamically or as a function of time (isothermally) [17]. TGA is mostly dynamically carried out in the lignin scenario and offers details on degradation temperatures as well as other thermally-induced phase changes [17].

5.5 Macromolecular Structure

To detect and track lignin dissolution in various solvents, optical microscopy is highly helpful. Additionally, morphological characteristics and particle size may be inferred using it [44,45]. To analyze the lignin structural properties with improved resolution, scanning electron microscopy (SEM) is also highly beneficial [46]. Due to its ability to clearly distinguish between the core and shell of lignin nanoparticles, transmission electron microscopy (TEM) is particularly useful for this purpose [47].

6. VARIOUS PROCESSES FOR LIGNIN NANOPARTICLES SYNTHESIS

Several techniques have been developed for making LNPs utilizing various physical, chemical, and biological approaches as a result of the expanding study into green nanobiotechnologies. One of these techniques is antisolvent precipitation. solvent exchange [48], biological methods [49], ultrasonication [50], interfacial crosslinking [51], polymerization [52], and others. Following the self-assembling principle, the lignin must first be dissolved in an organic solvent before the formation of the nanoparticles, which typically take place during the dialysis process or with the addition of an antisolvent (typically water) [53]. Other procedures that were adapted from Frangville et al., (2012) utilised a variety of solvents and antisolvents [54]. Aqueous sodium hydroxide and dimethylformamide (DMF) are also utilized as solvents in addition to acetone [55], dimethyl sulfoxide (DMSO) [53]. The process of precipitating nanoparticles involves a change in pH is known as pH shifting. In their field techniques for creating LNPs, Frangville et al., (2012) suggested this [54].

7. LIGNIN VALORISATION

Engineering lignin structures to minimise biomass resistance and permit lignin valorization, such as conversion to higher value chemicals, is one of the most difficult biorefining tasks. The desired application has a significant impact on the lignin type selection. The primary use of lignin from the pulp and paper industries is in the production of electricity. This is a major assault on the environment and a waste of resources. There are several new uses that might raise its value. However, the majority of these applications still face several difficulties. For instance, lignin has a poor reactivity and brittle character, making it incompatible with other polymeric systems. This is mostly because of its complicated structure. Therefore, some studies use lignin modification targeting new derivatives as a strategy to promote the creation of ligninbased products with improved performance. The information obtained from the characterisation techniques previously covered has helped to clarify the natural recalcitrance of lignin, aiding in the development of more efficient methods to create products with added value based on lignin.

Method	Advantages	Disadvantages
Precipitation	Good lignin dissolution Synthesized LPNs with desired size and	Use of costly and toxicity solvent Solvent recovery difficulty
	shape Low cost antisolvent use	
Ultrasonication	High yield LNPs Green synthesis of LNPs LNPs synthesis with Low cost Fast LNPs synthesis	Irregular shape and morphology of LNPs Low yield of LNPs
Solvent exchange/ Solvent shifting	High yield LNPS Good dissolution of lignin Desired sizes and morphologies of LNPs Low-cost antisolvents use	Use of costly and toxicity solvent Solvent recovery difficulty Use of high cost dialysis membranes
Aerosol flow	High yields of LNPs Absence of liquid antisolvent	Use of costly and toxicity solvent
Biological pathway	Simple and low-cost synthesis Green synthesis of LNPs	Irregular shape and morphology of LNP Low yield of LNPs
Interfacial crosslinking/ Polymerization	Good dissolution of lignin Desired sizes and morphologies of LNPs	Use of high cost and toxicity crosslinking agents

Table 3. Overview of the advantages and disadvantages of the primary LNP synthesis methods

Fig. 2. Various potential applications of lignin nanoparticle

7.1 Composites and Blends

It has thus been logical to employ lignin as a reinforcing ingredient in polymer formulations and various composites because it is recognized as a "natural glue" that is due to the plant's mechanical support. Lignin has been used in composites and blends as an additive, matrix material, filler, or formulation strengthening agent, according to a number of studies. In the present day, lignin is recognized as the most well-liked and interesting reinforcing compounds for the creation of composites with outstanding activity due to the low cost and sustainability of these lignin-based composites [56].

7.2 Food Packaging

The major reason why lignin has attracted attention is due to its antioxidant properties, which are caused by the large number of aromatic rings containing methoxy and hydroxyl functional groups. Alkali lignin has anti-oxidation characteristics that are equivalent to those of commercial antioxidants, according to research by Azadfar et al. (e.g., butylated hydroxytoluene) [57].

7.3 Resins

Phenol-formaldehyde (PF) resins are formed when polycondensation reaction of phenol and formaldehyde. These systems, which were the first truly synthetic polymers to be manufactured, continue to be among the most crucial products. With impressive mechanical strength, respectable moisture and heat resistance, and cutting-edge ablative properties, these synthetic polymers are extensively employed in a variety of applications, including electronics, plywood adhesives, paints and coatings, wood bonding, lamination, and insulating foams [58].

7.4 Hydrogels

A significant class of lignin based materials with applications in tissue engineering and drug delivery is lignin-based hydrogels, especially given that their porous structure resembles the biological extracellular matrix. Their stimulidependent swellability in aqueous conditions may also be crucial for applications involving drug application [59].

7.5 Sensors

Lignin-based sensors are made to identify and measure biologically important species even in complicated matrices with competing species. These lignin-based biosensors are also reasonably priced and exhibit decent compatibility with different polymeric matrixes. Since they have shown high biocompatibility and high resolution in fluorescence imaging, among other beneficial properties, lignin-based carbon quantum dots have emerged as a novel class of materials in bioimaging and biosensor applications [60].

7.6 Particles

It has taken a lot of work to create lignin-based nanoparticles (LNPs) for therapeutic and biomedical uses, but once the right solvent is found, LNPs may be created without the use of chemical modification. Lignin nanoparticles are typically seen as non-toxic or having a low toxicity, although this perception may change if

they are chemically altered or used in formulations with other substances [61].

7.7 Heavy Metal Absorption

The capacity of lignin to adsorb heavy metal ions has been acknowledged and recognized among its other characteristics. Typical adsorbent materials interact with ions in wastewater systems through a charge neutralization process since they are typically charged. The adsorbents and the ions that result from this electrostatic interaction are complexed. Since there are presently no affordable treatment options, it is difficult to effectively treat wastewater that
contains beavy metals. Although contains heavy metals. Although
employed techniques such as adsorption. employed techniques such membrane filtering, electrolytic extraction, ion exchange, and chemical precipitation have drawbacks like high production costs, significant chemical inputs, and insufficient removal. Lignin has been investigated as a potential low-cost and renewable adsorbent for wastewater purification in this context [62].

7.8 Fibers

In many fields where high conductivity, high stiffness, and low weight are required, carbon fibres (CFs) are amazing materials with excellent utility. Their uses are many and spread throughout a variety of industries, including electronics, the building sector, aircraft, and transportation. The majority of CFs are currently made from polyacrylonitrile, a costly petroleumbased feedstock that is neither renewable nor sustainable. LCFs (lignin-based carbon fibres) have gained popularity during the past few decades. Lignin-based carbon nanofibers (LCNFs), are of special interest because they have prospective uses in electrical devices including batteries and supercapacitors [63].

7.9 Batteries

It is vital to look into innovative strategies for substituting expensive, limited, fossil-based components with renewable substitute, and lignin can in fact act a significant role in helping to transform the energy industry. New methods for creating green batteries have been described in recent research. Lima et al. studied the use of lignin biomass for power generation utilizing direct carbon fuel cells. After combining them with commercial activated carbon, two types of technical lignins—namely, lignosulfonate and kraft lignin—were used to assess the efficacy of the cells. Both of the tested lignins were found to be feasible for the direct lignin fuel cell.
Additionally, it was shown that lignin Additionally, it was shown that lignin hydrophilicity, which is pH-tunable, is crucial for cell function [64].

7.10 Biocide

Lignin is a source of naturally occurring antibacterial chemicals and comprises a variety of phenolic monomer fragments (whose structures have the most inhibitory effects). Using LNPs enhances the surface area and, consequently, the contact area, which in turn boosts the antimicrobial impact [65].

7.11 Nano and Micro-carrier

The LNPs may be utilized in the structure of drug carrier seems in the medical industry by carrying the material encapsulated when they are hollow particles or infused with the conveyed substance if they are solid and porous particles [66].

8. CONCLUSION

Due to its availability, renewability, and affordability, lignin is a particularly alluring sustainable bioresource. We have reviewed and discussed several significant features of this research, including its complex structure, characterization techniques, extraction methods, and some of its applications. Due to its complexity and wide range of uses, lignin is still now undervalued and underutilized. Its use in value-added applications has been hindered by these qualities. Here, several recent developments in lignin usage technology were covered, the majority of which show great promise as long-term "greener" substitutes for traditional goods.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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