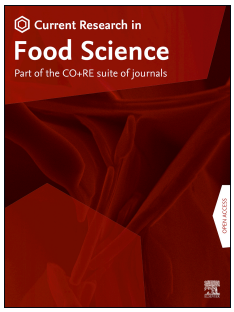

A review on biomass-derived materials and their applications as corrosion inhibitors, catalysts, food and drug delivery agents

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Green and sustainable materials with advanced applications

A review on biomass-derived materials and their applications as corrosion inhibitors, catalysts, food and drug delivery agents

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Abstract

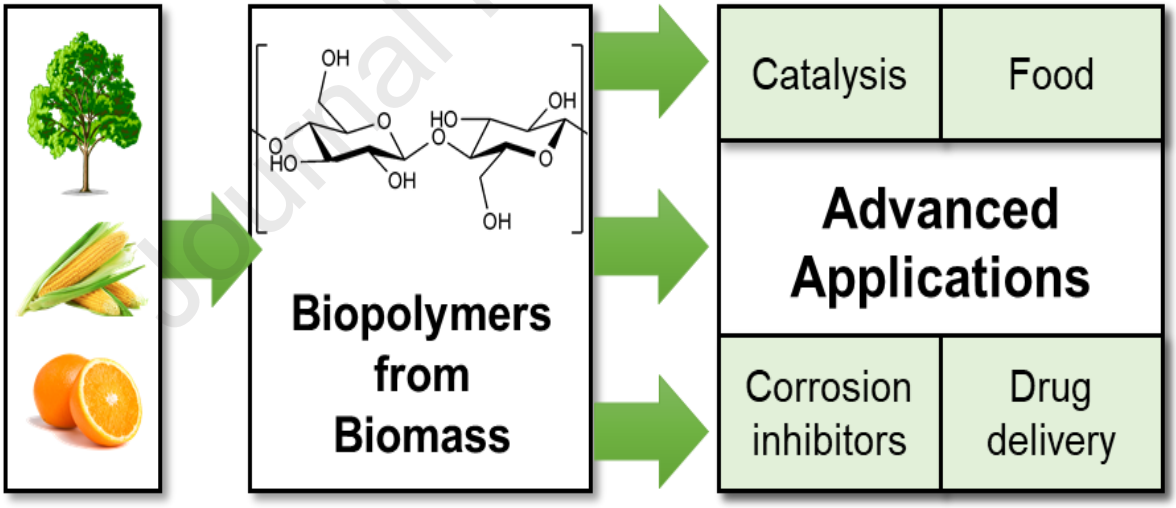
Owing to the overconsumption of petroleum-based resources and growing demand for fossil-based fuels and chemicals, it has become imperative to adopt alternative resources that are renewable. With the availability of biomass, it is believed that this technology has the capability to valorize waste into wealth. Recently, efficient utilization of plant biomass, a chief renewable resource, has gained tremendous attention in research as it offers distinct

social, economic, and sustainable benefits. The present review focuses on the various biomass from waste resources. Subsequently, the applications of these polymeric biomass composites are reviewed in catalysis, drug delivery, and food applications. Finally, corrosion studies along with DFT calculations and theoretical aspects have also been reviewed.

Naturally occurring carbohydrate polymers found in lignocellulosic biomass are biopolymers have been used for various physical and chemical applications; as catalyst, coatings, drug delivery, corrosion inhibitors etc. This review reports these material applications of carbohydrate polymers.

In this review we focus on new and emerging applications of polymers from lignocellulosic biomass.

Graphical Abstract



Keywords: Waste biomass; Carbohydrate Polymers; Catalytic applications; Green inhibitors; Food applications; Drug delivery applications

1. Introduction

The world has been facing unprecedented challenges due to increasing pollution which can be primarily attributed to consumption of fossil fuel. This has not only cause

global warming but also been aggravated by the problem of the recent pandemic (COVID-19) [1].

We are also moving towards depletion of these fossil fuels as they are finite, from a non-renewable source. These challenges have forced us to look for raw materials from benign sources in the form of renewable resources which are, or could be, available in abundance. The processing of these renewable resources, specifically here we focus on lignocellulosic biomass, must be economically competitive in comparison to non-renewable sources for their gainful utilization [2].

1.1 Waste lignocellulose biomass from different sources

Globally 190 billion tonnes of lignocellulose biomass is generated every year [3]. Out of this, a little amount is used for extracting wood, edible crops and fruits, for non-edible purposes (e.g. paper production) and medicinal plants etc. Our activities are responsible for generation of approximately 5.5 billion tonnes (Table 1) of waste lignocellulosic biomass every year, most of which is handled in an unscientific manner and ends up in unmanaged waste sites thus contributing to global warming potential. In some cases agricultural residue is burnt onsite thus causing great difficulties for the people not only in surrounding but faraway places giving rise to air pollution [4]. The waste mentioned in Table 1 does not account for food waste due to consumption activities. It has been estimated that approximately one-third of all food produced today goes to landfill [5]. Nevertheless, the amount of waste presented in Table 1 from different focused sources presents an opportunity to make use of it in a socially and environmentally responsible manner. It can be utilised for producing natural polymers which are biodegradable and eco-friendly.

Table 1. Generation of lignocellulosic waste from different sources

Source	Major Examples	Global production (million tonnes)	Reference
Forestry plantations and residues	Stems, wood from forests or trees outside forests, residues of wood industry (bark, sawdust, recycled wood)	800	[6]
Agricultural residues	Straw from cereals, rice, wheat, corn, bagasse, olive and oil palm plantations, Processing residues such as kernels, sunflower shells, rice husks	4600	[7]
Industrial wastes	Pulp and paper mill industry	2	[8]
Food processing wastes	Dairy, sugar, beer, wine, fruit juice industry	139	[9]

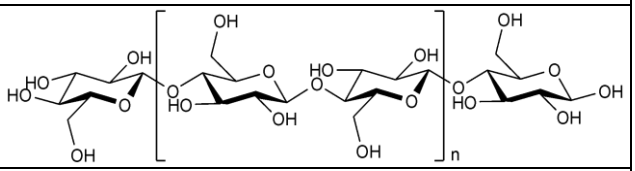
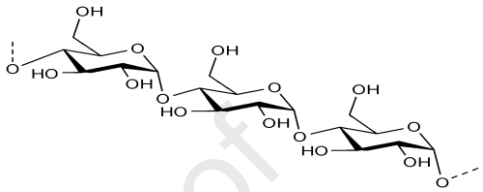
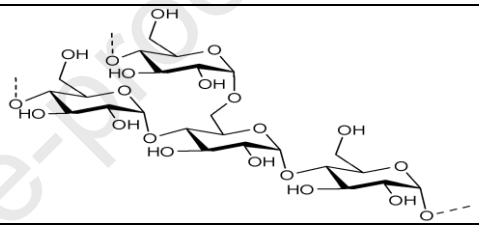
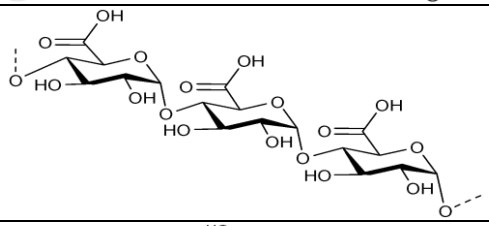
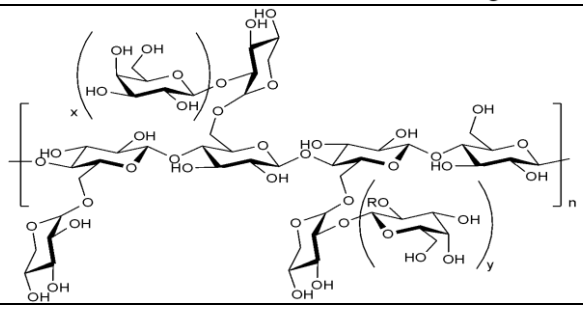
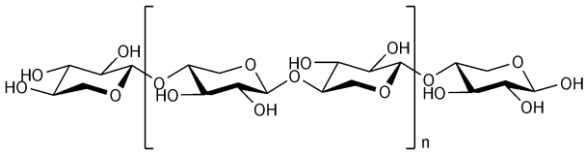
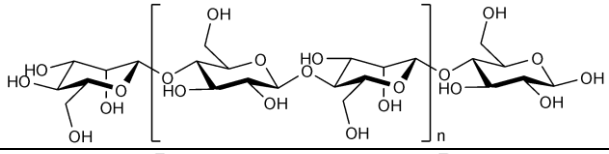
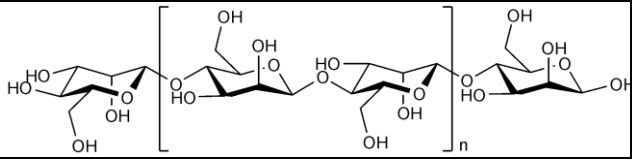
1.2 Natural polymers from lignocellulosic biomass

Lignocellulosic biomass, comprise of carbohydrate polymers and lignin, is a major component of dry plant mass, with contents usually in the region of 50-90% depending on the source [10], [11]. Lignocellulose structure also varies between different plant species which impacts degradation; higher lignin content reduces the degradability of the biomass. It can be described as a structure comprising cellulose fibers and amorphous hemicelluloses within a lignin matrix.

1.2.1 Carbohydrate Polymers

Carbohydrate polymers commonly found in lignocellulosic biomass are shown in Table 2, including cellulose, starch, pectin and hemicelluloses.

Table 2**.** Chemical structures of carbohydrate polymers found in lignocellulosic biomass.

Carbohydrate Polymer found in Lignocellulosic Biomass		Repeat units	Chemical Structure
Cellulose		Glucose β(1→4)	
Starch	Amylose	Glucose α(1→4)	
	Amylopectin	Glucose α(1→4)	
Pectin		Galacturonic acid α(1→4)	
Hemicelluloses	Xyloglucan	Glucan backbone β(1→4) with side chains comprising xylose and galactose	
	Xylan	β(1→4) Repeat unit = xylopyranose	
	Glucomannan	β(1→4) Repeat unit = glucose + mannose	
	Mannan	β(1→4) Repeat unit = mannose	

Cellulose consists of repeat glucose units with β-(1-4) glycosidic bonds rendering it degradable by acid treatment and cellulase-catalyzed hydrolysis [12]. Cellulose fibers have been utilised in various composite applications due to their relative high strength and stiffness and low density [13]. Cellulose fibers can be isolated from biomass using ball milling, and/or aqueous hydrolysis, often including a bleaching or delignification step. In recent years, the investigation of the use of nanocelluloses; cellulose nanocrystals (CNC), cellulose nanofibrils (CNF) and bacterial cellulose (BNC), in nanocomposite applications has increased sharply due to their abundance and reinforcing behaviour [14]. While CNC and CNF can be extracted from biomass, BNC is biosynthesised by bacteria. CNC can be isolated by hydrolysis of the amorphous regions of a purified cellulose source, most commonly using sulfuric acid hydrolysis, often followed by ultrasonic treatment resulting in the crystalline CNC to be obtained [15]. Cellulose nanofibrils (CNF) are often isolated by first pre-treatment of cellulose fiber, for example using TEMPO oxidation, then subsequent mechanical treatment (e.g. high-pressure homogenisation) to liberate the nanofibrils [16].

Starch (amylose and amylopectin) also comprises repeat glucose units, the α-(1-4) glycosidic bond configuration renders the physical properties of starch drastically different from cellulose. This is primarily due to the difference in hydrogen bonding between chains resulting in a much lower crystallinity for starch compared with cellulose, which is even lower for branched amylopectin compared with linear amylose. Pectin consists of repeat galacturonic acid units bonded *via* α-(1-4) glycosidic bonds (Table 2) and is well-known as a gelling agent in food. Hemicelluloses are carbohydrate polymers commonly found in plant cell walls with cellulose, they comprise a β-(1-4)-linked backbones in an equatorial configuration [17]. Hemicelluloses that are found in all terrestrial plants include xyloglucans, xylans, mannans and glucomannans (Table 2). It is worth noting that while all of these carbohydrate polymers are typically extracted using some type of aqueous treatment,

depending on the precise source of the lignocellulose biomass, different conditions may be preferred [18].

1.2.2 Lignin

Lignin is an aromatic branched natural polymer, see Figure 1, which is an essential component of plant cell walls, providing structural support [19]. Lignin can be utilised either intact or it can be depolymerised into monomer units, such as monolignols *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol which can be isolated by have been investigated as renewable building blocks. Kraft lignin is a by-product of the pulp and paper industry where the Kraft process is used (sodium hydrosulfide, sodium hydroxide, high temperature). However, currently the majority of this Kraft lignin is used as boiler fuel. Other methods of extraction include dilute acid or hydrothermal treatments and alkali extraction of lignin and organosolv lignin [20].

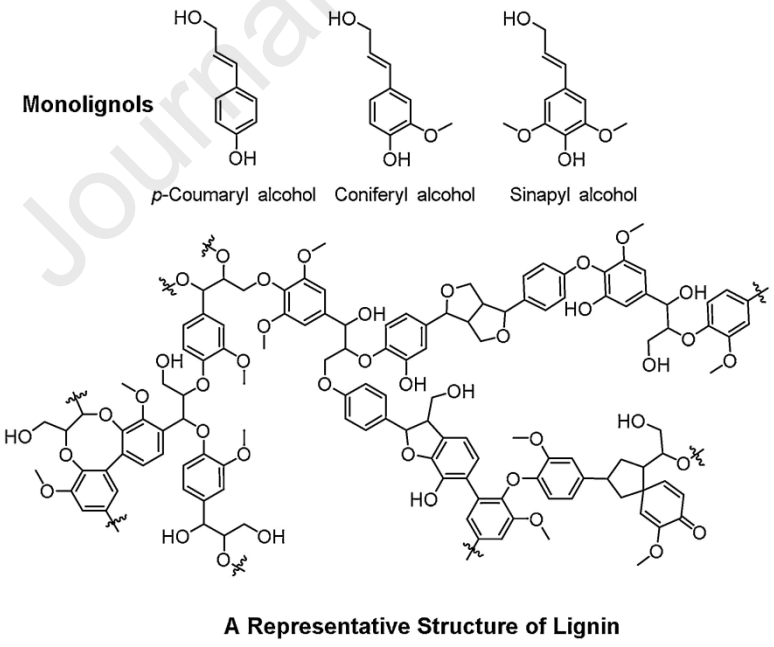


Figure 1. Monomeric units and a representative structure of lignin. Reproduced with permission from Elsevier [19].

2. Applications of natural polymers

The naturally occurring polymers found in lignocellulosic biomass, lignin and carbohydrate polymers, have been used for various physical and chemical applications. Here, the recent use of natural polymers in important applications including catalysis, corrosion inhibition, within the food industry and for drug delivery, will be discussed in detail.

2.1 Catalytic applications

Catalysis, being a core area of contemporary science, is not only crucial to aid economic success but is also important to develop materials that sustain society [21]. Catalytic technologies have shown outstanding ability in different domains such as bulk and fine chemicals production, beverage and food manufacturing, oil refining, pollutant abatement, and many more [22]. Notably, heterogeneous catalytic systems have gained tremendous attention due to their various advantages over homogeneous catalysts including simple storage and handling, easy separation from the reaction media, regeneration, and reusability [23, 24].

With the aim of greener and sustainable chemistry, recent developments are being driven from petrochemical-based feedstocks to bio-based feedstocks. Recently, researchers are attracted to eco-friendly support materials in catalytic systems due to their environmental and economic attributes [25, 26]. Thus, besides having high thermal and chemical stability, long durability, air and moisture inertness, easy modification, and simple handling, the catalytic system needs to have environmental friendliness. In this regard, natural polymers, in particular polysaccharides, have gained tremendous attention as excellent support material due to their high abundance, biocompatibility, and renewable nature [27]. Moreover, their chemical inertness, high-performance, low cost, and larger loading capacity have made them excellent alternatives in contrast to petrochemical-based polymers and other catalytic support

materials [28]. Polysaccharides provide multiple functionalities that can be employed for grafting organometallic moieties, enabling them to have superior properties than other catalytic supports. Also, due to the electrostatic interaction between their functional groups and nanoparticles (NPs), they have the ability to stabilize NPs through [29]. Even though the exploitation of naturally derived polysaccharides is soaring up to produce numerous industrially significant products, their use as catalytic supports is still in its infancy. Recently, efforts have been made towards the usage of various biopolymers including cellulose, starch, chitosan, lignin, pectin, hemicellulose, and chitin as environmentally benign catalytic support [30-36].

In this section, we describe the catalytic applications of metal and metal nanoparticles supported on natural polymers including lignocellulose, hemicellulose, and nanocellulose.

2.1.1 Lignocellulose

Recently, one of the biggest lignocellulosic biomass, oil palm frond (OPF) from oil palm industry has been reported as a sustainable support material for metal NPs. This support material not only prevents the aggregation tendency of NPs and stabilizes them, but also enhances their properties. In this regard, Sohni *et* al. developed an easy, economic and environmentally friendly route to synthesize highly dispersed copper and cobalt mixed NPs on OPF support [37]. The catalyst was produced via wet co-impregnation technique under room temperature and the inherent porosity along with hydrophilic characteristic of OPF assisted immobilization of copper and cobalt ions. The synthesized OPF-derived nanocatalyst (Cu+Co@OPF) was characterized using various physico-chemical techniques such as scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and to study morphology, composition, thermal stability, crystal structure, and functional groups, respectively. The porous and 3D- framework of biomass provided a huge

surface area for mixed metal NPs to form maximum possible catalytic sites to allow greater interaction between NPs and pollutant molecules in reduction reactions. This nanocatalyst was thus found to display high catalytic activity for the reduction of toxic dyes and nitroarenes including congo red (CR), methyl orange (MO), rhodamine B (RB), methylene blue (MB), ortho, meta and para-nitrophenol (ONP, MNP, PNP) and 2, 4-dinitrophenol (DNP) using sodium borohydride ($NaBH_4$) as a reducing agent (Figure 2). In case of dyes, the order for the rate of catalytic reduction was found to be MO>RB>MB>CR and for nitrophenols the order was reported to be PNP>MNP>ONP>DNP. The salient features of this work include the use of greener, cheaper and sustainable OPF support, simple preparation of nanocatalyst at room temperature, use of comparatively cheaper Cu NPs, effortless recovery of the catalyst, and rapid reduction of toxic organic pollutants in wastewater treatment.

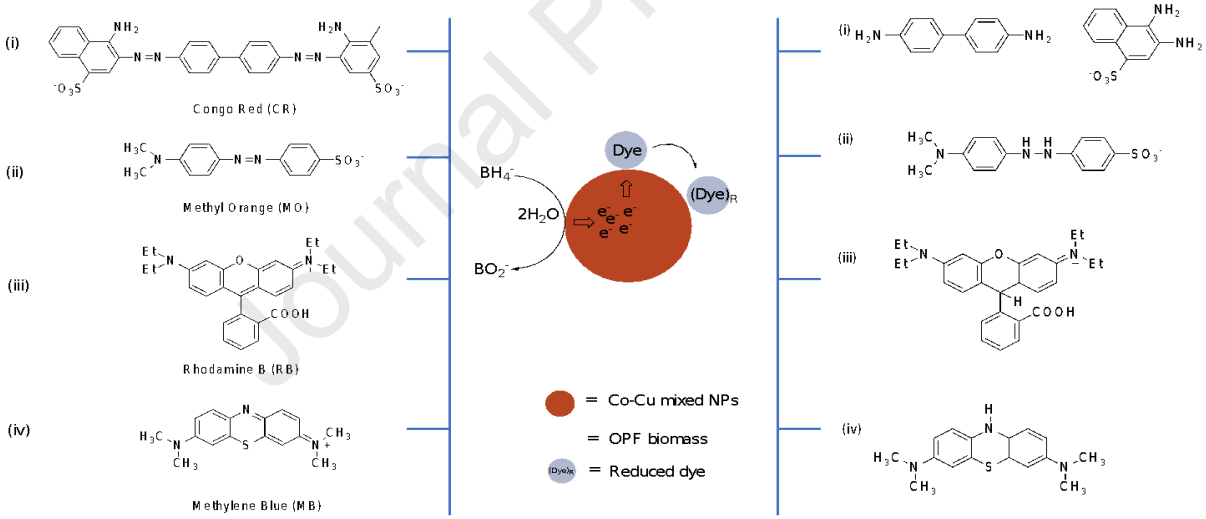


Figure 2. Possible mechanism for reduction of organic dyes using Co+Cu@OPF nanocatalyst and $NaBH_4$ as reducing agent along with their reduced forms.

2.1.2 Hemicellulose

Another most common and abundant polymer is hemicellulose which has been very little explored as catalytic support. Xylan-type hemicellulose (XH) is the major constituent of cell walls of herbaceous plants and hardwood [10]. It mainly constitutes a β(1→4)-D-

xylopyranose backbone (see Table 2) with substituents on the 2- or 3-position and the presence of hydroxyl and ether groups on the XH chain make it suitable polymeric support for metal NPs [38]. Besides, XH is available in huge amounts as a waste product from biorefineries and paper and pulp industries. Owing to the large abundance of XH, Chen et al. reported a simple method where palladium nanoparticles (PdNPs) were anchored on XH to obtain PdNPs@XH which was analyzed by XRD, transmission electron microscopy (TEM), FT-IR, X-ray photoelectron spectroscopy (XPS), and TGA and applied in the C–C bond-forming reactions under aerobic conditions [39]. The final catalyst was reported to exhibit excellent catalytic performance for Suzuki, Heck, and Sonogashira cross-coupling reactions (Figure 3) in comparison to other biopolymer-based catalysts and carbon supported catalysts. Moreover, this catalytic system possessed several noticeable features including low palladium loading, ligand-free conditions, high activity, good chemical, and thermal stability, easy recovery, and reusability up to six times without any appreciable loss in its catalytic performance.

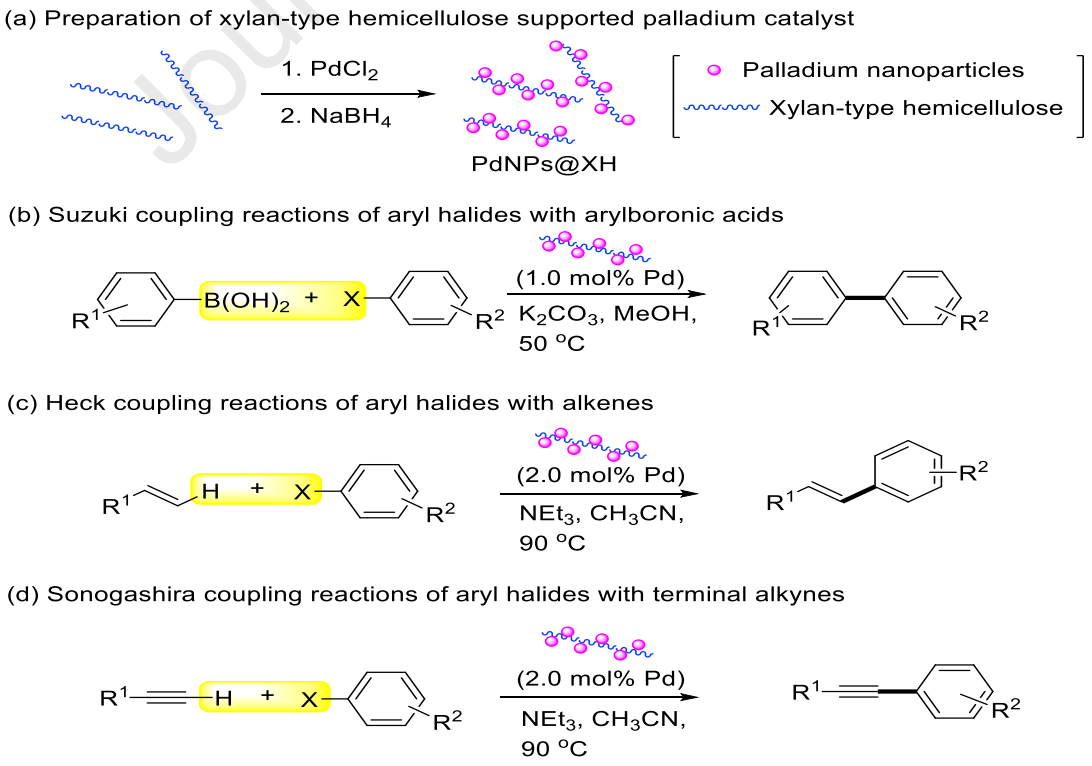
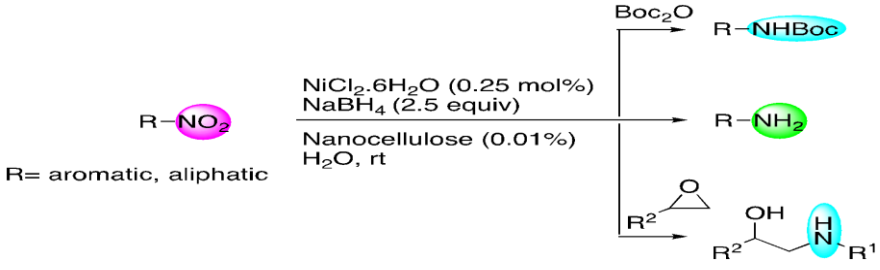


Figure 3. Synthesis of xylan-type hemicellulose supported Pd nanocatalyst and its applications in C-C cross-coupling reactions.

2.1.3 Nanocellulose

Within the family of cellulose derivatives, nanocellulose (NC) has gained particular interest as it combines the fascinating properties of both nano-scale materials and cellulose. It is usually obtained when cellulose (vegetal or bacterial) is hydrolyzed with a strong acid like sulphuric acid. Among many other applications, nanocelluloses have proved to serve as versatile catalytic supports in the design of sustainable catalysts. This can be attributed to their large surface area, thermal stability, functionalizable motif, chiral properties, enhanced stability, non-toxicity, and inexpensiveness. Besides this, organometallic species can be easily grafted onto the surface of NCs [40].

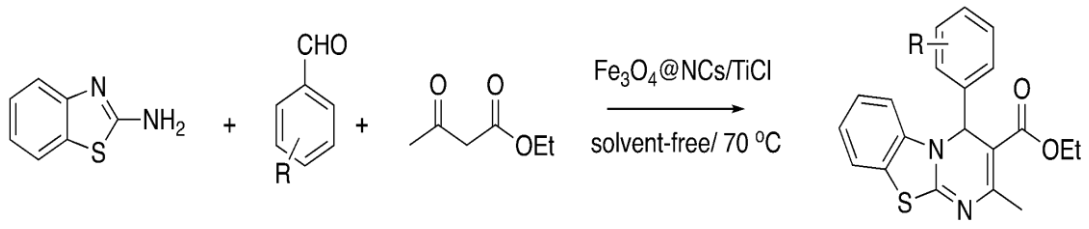
In recent times, Prathap et al. developed a simple and effective protocol for the in-situ reduction of a broad range of aliphatic nitrocompounds and nitroarenes to amines in excellent yields by employing nickel chloride and sodium borohydride in a solution of TEMPO-oxidized CNF in water (0.01 wt %) [41]. This work was reported to use low loading of nickel catalyst which is ascribed to the stabilizing effect of nanocellulosic support on the catalyst which was also responsible for the increase in the turnover number. Moreover, tandem reactions were observed which yielded amines, *N*-protected amines and amino alcohols in high yields (Scheme 1).



Scheme 1. Nitro group reduction with nanocellulose under mild conditions.

Recently, Jabasingh and co-workers coupled TiO_2 with NC to produce NC-TiO_2 which was used as a catalyst to yield cellulosic ethanol (a renewable fuel) from bagasse *via* hydrolysis [42]. In this work, the NC-TiO_2 composite was developed to integrate with bagasse to produce glucose, which was further used to produce ethanol. The group thoroughly investigated the interaction of NC-TiO_2, bagasse, and cellulase. It was reported that NC-TiO_2 yielded more glucose in comparison to enzymatic hydrolysis of bagasse which is attributed to the increased surface area of the catalytic structure. This process was reported to be both cost and energy efficient.

Another work with nanocellulose as catalytic support was reported by Azad and Mirajalili, where they first prepared the magnetic core-shell nanoparticles, Fe_3O_4 @nano-cellulose by co-precipitation technique in the aqueous solution of NC which was further treated with titanium tetrachloride to form the final catalyst, Fe_3O_4@NCs/TiCl [43]. The as-synthesized catalyst was analyzed using several techniques including field emission scanning electron microscopy (FESEM), FT-IR, X-ray fluorescence (XRF), XRD, TGA, and vibrating sample magnetometry (VSM). The catalyst was highly efficient for synthesizing 4H-pyrimido[2,1-b] benzothiazoles derivatives *via* a multi-component one-pot reaction of 2-aminobenzothiazole, aldehydes, and ethyl acetoacetate at 70 °C under bulk conditions, see Scheme 2. This is another good example of greener protocol wherein outstanding properties of magnetic nanoparticles were coupled with that of nanocellulose and catalytic properties of titanium to form bio-based reusable magnetic nanocatalyst. The multifaceted positive aspects of this work include mild experimental conditions, excellent yields, simple work-up, short reaction time, effortless separation of catalyst through magnetic forces, and recyclability up to seven times without significant loss in its activity.



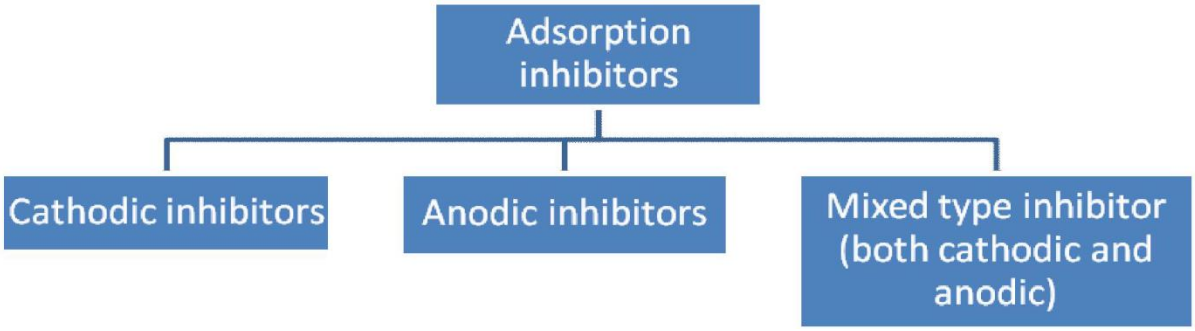
Scheme 2. Synthesis of benzothiazoles derivatives *via* multi-component reaction using Fe_3O_4@NCs/TiCl as catalyst.

2.2 Application as corrosion inhibitor

2.2.1 Green inhibitors

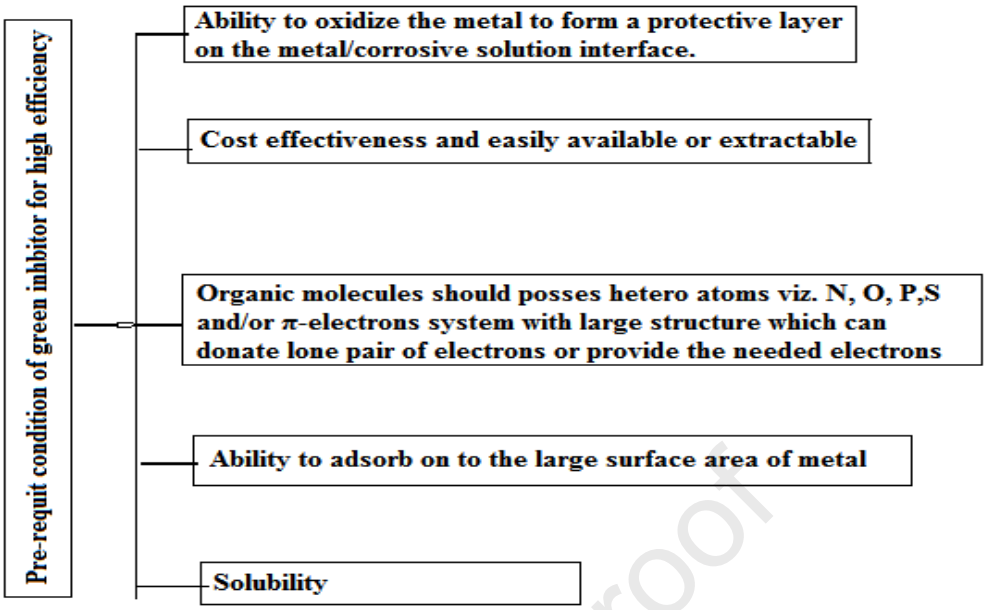
The corrosion is a process of deterioration or destruction or 'eating away' of metals or alloys due to their electrochemical reaction with a corrosive environment containing air (O_2), moisture (H_2O) or both. It is a serious problem in industry, infrastructure sector and technological advancement for sustainable development. Thus results in premature failure of structural materials, increase in maintenance costs and demolishment of resources [44]. HCl and H_2SO_4 are widely used mineral acids in many industries for various metallurgical purposes like acid pickling, chemical cleaning and descaling [45].

The inhibitive action of a corrosion inhibitor takes place in two ways; (i) by using environment modifiers to alter the corrosive media into noncorrosive or less corrosive environment, and (ii) by adsorbing green corrosion inhibitors on to the surface of metals to develop a protection layer of adsorbed inhibitors. The assessment of carbohydrate biopolymers and their derivatives as green inhibitors against metal corrosion *via* adsorption features are presented in Scheme 3.



Scheme 3. Classification of adsorbed inhibitor molecules on the basis of their inhibition effect.

The corrosion inhibition efficiency of a large number of synthesized organic compounds in different acidic environments have been investigated from time to time, but hazardous impacts of these inhibitors on marine and probably on animal lives has hardly been considered earlier [46]. Therefore, alternative routes for corrosion inhibition and corrosion inhibitors, which could be biodegradable, non-toxic, environmentally acceptable and economically feasible have been searched for a few decades [47]. Literature survey on green corrosion inhibitor suggest that the essential requirements for the selection of natural products include those containing phytochemicals, or isolated organic compound containing hetero atoms viz. N, O, P and S, having π-electrons system [48]. The inhibition efficiency of these compounds can be measured in terms of number of mobile electrons present, character of the orbital containing free electrons and the density of electron at hetero atoms [49]. The suitability of an organic compound for corrosion inhibition can be understood by Scheme 4.



Scheme 4. Condition for selection of inhibitor for high efficiency.

The corrosion inhibition efficiency of organic molecules can be investigated by using gravimetric analysis methods and different electrochemical techniques like potentiodynamic polarization and impedance spectroscopy. However, the correlation between structures of inhibitors with its efficiency can be established by using Density Function Theory (DFT) method at the suitable basis set level [50]. In such studies, quantum chemical optimized structure and its structural parameters like Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies of the selected biopolymers are obtained. The frontier molecular orbital energies provide its energy gap, ionisation potential, dipole moment, absolute electro-negativity, electrophilicity index, fraction of electron transfer, back donation, charge distribution, electron affinity, and hardness and softness of the inhibitors can be obtained by using algebraic relations discussed in Ref. [50-52]. These theoretical and computational studies help in establishing the mechanics of inhibiting phenomena as well as the correlation between HOMO and inhibiting properties of the investigated carbohydrate.

2.2.2 *Experimental and Computational Analysis*

Recently, several carbohydrate polymers either in their pure state or modified form have been reviewed or investigated as green inhibitors for the metallic corrosion in different corroding environments [51–54, 57]. The corrosion inhibitive action of extracted biopolymers can be understood by Figure 4.

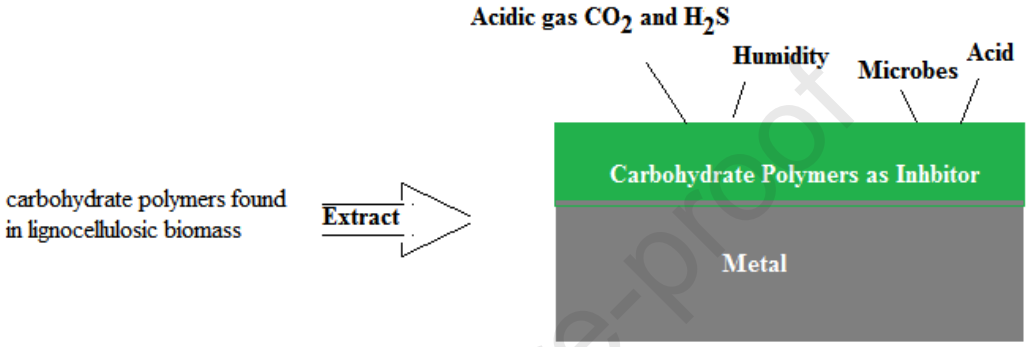


Figure 4. Carbohydrate polymers for corrosion inhibition process for metal in corrosive medium.

It has been observed that Chitosan (*CH*) and its *5-chloromethyl-8-hydroxyquinoline* derivative (*CH-HQ*) perform inhibition efficiency of 78% and 93% for the acidic corrosion of mild steel [51] with a very low amount of 10^{-2} *g/L* of derivative. Such a high inhibition capacity of *CH-HQ* can be associated with its large molecular size as well as the presence of polar functional groups, which increases its solubility in polar electrolytes including mineral acids *HCl and* H_2SO_4. DFT study on *CH* and *CH-HQ* established the mechanistic part of metal protection in corrosive media by directly relating their macromolecular weights, chemical composition and electronic structures [51]. It is worth mentioning here that the synthesis of *CH-HQ* involved water as a solvent which is a green solvent [48].

Substituted/modified CH chitosans [49], [51], exudate gums [53], carboxymethyl and hydroxyethyl cellulose [55], starch, pectin and pectates [56], [57], have been employed for

anticorrosion performance of metals and alloys in acidic environment by using experimental techniques and theoretical calculations. These studies reveal that cellulose [55] and CH chitosan [51] contain free amine and hydroxyl groups and thus capable of chelation of metal ions and are readily coordinated at the metal/solution interface by using their lone pair of electrons. Further, polarization graph, impedance parameters and surface morphology by using scanning electron microscopy shows that the presence of tannins, cellulose, and polycyclic compounds enhance a protective layer of inhibitors film formation over the metal surface, thus decreasing corrosion [54].

The [51] inhibiting effect of pure and derived carbohydrate biopolymers as eco-friendly inhibitors against metallic corrosion have been reviewed through recent reports. Further, the literature shows that the theoretical and computational studies established a clear relation between the performance of carbohydrate polymeric with their molecular structures [48, 51, 56].

2.3 Applications of natural polymers in food science

Utilization of common cellulose strands which have been extricated from cornhusks unexpectedly by Reddy and Yang [58, 59] exhibited effectively. Filaments arranged from cornhusks are not just critical for horticulture, fiber, food and vitality needs of the individual however these are likewise eco-friendly [58].

Cellulose strands acquired from agro based materials have the piece, properties and structure that make them appropriate for utilizations, for example, composite, material, mash and paper make and these are similarly a lot less expensive as these are set up from horticultural results. Results created from the development of corn, wheat, rice, sorghum, grain, sugarcane, pineapple, banana and coconut are the significant wellsprings of agro-based biofibers [59].

Nanofibrillated cellulose as the strengthening stage and kappa-carrageenan have been utilized to create nanocomposite films where as nanofibrillated cellulose have effectively been blended from short stable cotton strands by chemo-mechanical cycle. Different weight percentage of the bionanocomposites of the NFC into a KCRG (in the range of 0.1 to 1 %) grid utilizing an answer projecting technique there portrayal was done as far as warm properties (DSC), morphology (SEM), water fume transmission rate (WVTR), oxygen transmission rate (OTR), X-beam diffractograms (XRD), and malleable properties [60].

Width of filaments assumes a significant function to discover various applications especially in food bundling items. All-cellulose nanocomposite film have been created from sugarcane bagasse nanofibers utilizing N,N-dimethylacetamide/lithium chloride dissolvable and considered as a multi-execution material with potential for application in cellulose-based food bundling attributable to its promising properties. Thermo gravimetric examination affirmed that warm steadiness of the ACNC was somewhat not as much as that of the unadulterated cellulose nanofiber sheet. Rigidity of the fiber sheet, nanofiber sheet and ACNC arranged with 10 min disintegration time were 8, 101 and 140 MPa, separately [61].

Cellulose stubbles have likely applications in the fields of composites as a strengthening stage, just as in drug and optical enterprises as added substances have been extricated from the branch-barks of mulberry by a soluble base treatment at 130 °C and hence a sulphuric corrosive hydrolysis. The compound organizations examination, AFM picture, FT-IR, XRD results showed that width of stubbles is in the middle of 20 to 40 nm and the hemicelluloses and lignin were taken out widely in the cellulose hairs, with a crystallinity of 73.4%, which has expanded its potential applications in the fields of composites as a fortifying stage, just as in drug and optical enterprises as added substances [62].

Bacterial cellulose (BC), which is a microbial polysaccharide with multifunctional properties has critical potential in food fixing and uses for thickening and gelling, settling,

water-official and as a pressing material and potential applications in the food industries. It has a noteworthy potential as a food fixing taking into account its high immaculateness and furthermore as a nano-scale fiber it can shape a 3D network structure [63].

Whey protein detaches/cellulose filaments have been acquired by consolidating arrangement of cellulose strands with corrosive instigated gelatinous of whey protein in the concurrent cycle. Flowerlike miniature/nanostructures have been seen on the outside of the recovered cellulose strands made out of ammonium copper sulphate hexahydrate. These cellulose/WPI filaments finds enormous applications in medication, tissue building and as a material for dynamic fixings discharge [64].

Microcrystalline cellulose (MCC) finds use in food, drug, clinical, restorative and polymer composites ventures and is getting impellent as a result of extending solicitation of alternatives to non-unlimited and insufficient fossil materials. Starting late Haafiz et al. gathered a review on methods for withdrawal and depiction of microcrystalline cellulose (MCC) which fuses new sources, new division measures, new meds incite new sorts of MCC materials for industrialization. Odds of MCC-based composite polymers for what's to come are presented and discussed [65].

Food bundling lies at the very heart of the advanced food industry and not many nourishments are sold unpackaged. In ongoing past cutting edge data on the exhibition of bioplastics materials, zeroing in on food bundling has been accounted for. Some bundling materials, for example, particular kinds of plastic, polythenes, and styrofoam can deliver poisons when they are warmed and can be hazardous to shoppers. Report gives a diagram of the fundamental materials utilized for delivering biobased films, their impediments, arrangements thereof, potential applications and a best in class on bioplastics effectively utilized as a food bundling material [66].

Guar gum is a novel agrochemical handled from endosperm of bunch bean. It is utilized as Guar gum is utilized as a purgative. It is additionally utilized for treating the runs, fractious entrails condition, heftiness, and diabetes; for lessening cholesterol; and for forestalling solidifying of the supply routes. In assembling, guar gum is utilized as a coupling operator in tablets, and as a thickening specialist in salves and creams. It is mainly utilized as thickener and stabilizer. Khatkar *et al*. has distributed an article centres around creation, preparing, structure, properties, food applications and medical advantages of guar gum [67].

The utilization of novel nanostructured materials has pulled in impressive enthusiasm for the food business for their usage as profoundly useful fixings, superior bundling materials, preparing helps, and food quality and security sensors. As of late the capacity to create non-woven mats made out of nanofibers that can be utilized in food applications is starting to be researched. For food applications, the filaments may discover utilizes as fixings in the event that they are made exclusively out of palatable polymers and GRAS fixings, , as dynamic bundling materials or as handling helps and sensors [68].

As of late the planned employments of tree gum polysaccharides and their nanostructures in different parts of food, water, vitality, biotechnology, condition and medication enterprises, have earned a lot of consideration. Notwithstanding broad uses of tree gums in food, there are generous non-food uses of these business gums, which have increased inescapable consideration because of their accessibility, auxiliary assorted variety and noteworthy properties as 'green' bio-based sustainable materials. Tree gums are reachable as normal polysaccharides from different tree genera having uncommon properties, including their inexhaustible, biocompatible, biodegradable, and non-poisonous nature and their capacity to go through simple substance adjustments [69].

The advancement of regular cellulose specialized strands from soybean straw with properties like the common cellulose filaments have been accounted for. Around 220 million

tons of soybean straw accessible on the planet consistently could supplement the side-effects of other significant food crops as reasonable, plentiful and every year inexhaustible hotspots for common cellulose filaments. Utilizing the rural side-effects as hotspots for strands could assist with tending to the worries on the future cost and accessibility of both the common and engineered filaments in current use and furthermore help to increase the value of the food crops [70].

Acquaintance of multifunctional properties with cellulose fiber network by various nano/miniature particles have been accounted for. Arrangements can be applied on cellulosic surfaces by basic arrangement projecting strategies or by plunge covering for enormous zone applications. Many potential applications can be envisioned for this methodology, for instance, food and current packaging, record affirmation, reactant cellulosic layers, textronic (electrofunctional materials), electromagnetic devices, affirmation of significant files, and antimicrobial injury repairing things [71].

2.4 Drug delivery applications

In addition to the benefits of sustainability, these “green” raw materials, (natural polymers including lignocellulosic biomass) offer great potential as cellulose-derivatives for drug delivery systems and can be explored either for the development of agricultural formulations e.g., pesticides or fertilizers or for pharmaceutical drug delivery systems. Moreover, with a hierarchical structure comprising cellulose, hemicelluloses and lignin these natural polymers are an excellent source in terms of variety, unique bio-renewability, biodegradability, biocompatibility, nontoxicity and chemically accessibility of the substrates for the modified bioactive materials [72-74]. In this section we discuss the formation of advanced materials from lignocellulosic biomass for bioactive delivery in pharmaceuticals and in agriculture Figure 5.

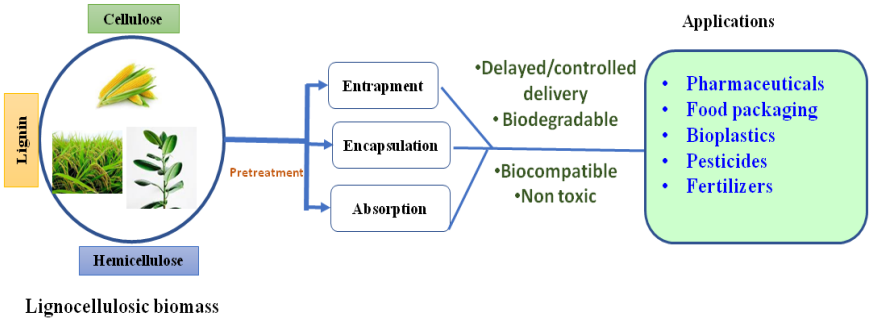


Figure5. Potential applications of lignocellulosic biomass in food and drug delivery

2.4.1 Delivery of pharmaceutical active ingredients

A variety of lignin-based encapsulation systems have been developed for sustainable release of drugs/active constituents, initiate the specific interaction and control the amount of drug released within the host. Different methods such as entrapment, encapsulation, adsorption, covalent binding, anti-solvent precipitation, interfacial polymerization/cross linking, template utilization, self-assembly, sonication, mechanical shearing etc are explored for loading active substances into lignin materials [75-76]. For example, Larraneta and coworkers [80] worked on lignin-based hydrogels synthesized by lignin esterification with poly(ethylene glycol) (PEG)and poly(methyl vinyl ether-co-maleic acid) and loaded with hydrophobic drug curcumin in the hydrogel. These hydrogels showed sustained delivery of the curcumin for four days and also demonstrated the reductions in adherence of microbes in comparison to the polyvinyl chloride, the most commonly used medical material for reducing and preventing health care acquired infections [77]. Other study showed high internal phase emulsions (HIPEs) were prepared and using sulfomethylation modification techniques the

polarity and conformation was adjusted. Also the stabilization of oil-in-water HIPEs was carried out through emulsification via enzymatic hydrolysis lignin and alkyl polyglycoside (APG) under neutral conditions, demonstrating higher surface elasticity as well as stability. These encapsulates were further explored for the enhanced delivery and protection of curcumin, the results showed higher UV protection in comparison to curcumin diffused in bulk oil as well as encapsulates also demonstrated good inhibitory activity against microbe (*S. aureus*) [78]. Similarly, the hydrogels formed by reactive extrusion methods showed a strong pH dependent swelling ability used to control diffusion rates of water and small molecules in and out of the gel for drug delivery [79]. Li *et al*. [80], modified lignin with anionic surfactant alkali lignin (AL) to synthesize the microstructure via interaction of sodium dodecyl benzenesulfonate (SDBS) with quaternized alkali lignin (QAL). This led to the formation of SDBS/QAL (sodium dodecyl benzenesulfonate/quaternized alkali lignin) complex that self-assembled itself in ethanol/water solution into lignin colloidal spheres (LCSs) and further encapsulated avermectin (AVM) were capable of demonstrating antiphotolysis [80].

Alqahtani *et al*. [81] evaluated the lignin nanoparticles (LNPs) as oral drug delivery candidate, where the curcumin loaded LNP system was developed to demonstrate increased bioavailability of curcumin as compared to unformulated curcumin, thus lignin nanoparticles were considered as an effective system for oral drug delivery, used mainly to enhance low solubility and limited bioavailability of drug molecules [81].

In 2018, Liu *et al*. [82] designed a core-shell structure (Pec-8PUH NPs) using pectin-eight-arm polyethylene glycol-ursolic acid/hydrooxy campothecin nanoparticle for stabilizing and dispersing particles. These formed Pec-8PUH NPs showed improved water-solubility, controlled drug release, enhanced cellular cytotoxicity, with shortened blood retention time

and comparatively better cellular uptake than free drugs, in synergistic manner with ursolic acid (UA) and 10-hydroxycamptothecin (HCPT) [82].

In addition lignins are also explored as precursors in fabrication of nanotubes with affinity-binding and for adsorption applications [81]. Lignin nanotubes (LNTs) were synthesized from the lignin on a template of sacrificial alumina membrane by Ten and his coworkers. These lignin nanotubes are explored to transfer of deoxyribonucleic acid (DNA) into cervical (HeLa) cancer cells and found that lignin nanotubes are more effective in comparision to carbon nanotubes [83]. Researchers from other groups reported methotrexate adsorption on sugarcane bagasse soda lignin, silica gel and iron/silica nanocomposite that were explored against rheumatoid arthritis *in vivo* in albino rats [84]. Encapsulation of magnetic nanocarriers (Fe_3O_4 nanoparticles) into double layers of polysaccharide shells were developed by Hosseni et al., 2020. The first shell of nanocarrier, was composed of cross-linked salep polysaccharide, attached to fluorescence dye and doxorubicin (chemotherapy agent) followed by a second shell of PEGylated carboxymethyl cellulose. The formed nanocarriers loaded with drugs showed enhanced biocompatibility, pH sensitivity and regulated drug release when experimented with MCF-7 (breast) cancer cells [85]. In another study, the hollow nanoparticles (LHNPs) were prepared by grafting β-cyclodextrin (β-CD) onto the enzymatic-hydrolysis lignin to form cyclodextrin-enzymatic-hydrolysis lignin. With the modified lignin, the hollow nanoparticles (LHNPs) were prepared through self assembly process. Further, the formed LHNPs were used to encapsulate the hydroxycamptothecin (HCPT), an antitumor drug. These CD-LHNPs (cyclodextrin hollow nanoparticles) demonstrated higher porosity, specific surface area, low cytotoxicity, enhanced encapsulation capability, and sustained-release of the drug [86]. In another paper they discussed the encapsulation of the drug, DOX (doxorubicin hydrochloride) within lignin based hollow nanoparticles. They proposed that π-π interactions and hydrogen bonding contributed towards

encapsulation of hydrophilic drug doxorubicin hydrochloride by lignin hollow nanoparticles. Drug (doxorubicin hydrochloride) encapsulation was improved due to increased pore volume and surface area of LNPs helped towards better cellular uptake as well as accumulation of the drug DOX in cervix cancer cells [87]. Similarly, to improve the delivery of drug trans-resveratrol (a poor water soluble and light unstable drug) film for merging poly (L-lactide) (PLLA) with lignin-based functional filler was developed via process of ring-opening polymerization on alklin lignin with D-lactide. Further, drug (trans-resveratrol) was loaded on poly (L-lactide) /lignin-graft-PDLA films. The LG-g-PDLA (lignin-based filler) variation may control the release behaviours of trans-resveratrol that performed good in exhibiting better mechanical, light barrier properties and uniform distribution properties of drug [88]. Ressi et al., 2018 synthesized nanofiber-based wound dressings by developing a gel containing lignin nanofibers. The surface was modified by arginine molecules through electrostatic interaction. The wounds treated by using these hydrocolloid wound dressings showed accelerated closure of wound, increased re-epithelialization, deposition of collagen and angiogenesis as compared to lone treatment of lignin nanofibers gel and arginine solution in animal model [89].

The lignin model of dehydrogenated polymer (DHP) was prepared using alginate hydrogel (Alg) showed the antimicrobial potential against several bacterial strains, these lignin models (DHP-Alg) were also found nontoxic against human epithelial cells [90]. Yang and his co-worker prepared hydrogels through a freezing-thaw procedure using polyvinyl alcohol/chitosan containing 1 & 3 percent weight of lignin nanoparticles. These hydorgel demonstrated the synergetic anti-oxidative response and antimicrobial effect against bacterial pathogens [91].

2.4.2 Delivery of agricultural active ingredients

Actives-controlled release of the various formulations for agricultural purposes has various advantages such as economic, low dosages, minimal labor usages, safety and low environmental impact. Lignin-based microparticles are exploited to develop the agricultural actives mostly as economically feasible product that may serve dual functions as fertilizer and carrier material. A method for production of lignin-based microparticles was patented by Asrar and Diang (2010) demonstrating the better controlled release of various agricultural actives (fertilizers, herbicides, and pesticides). They synthesized lignin acetate microparticles loaded with an insecticide (imidacloprid) by using a solvent evaporation method [92].

Usually plant infection is taken care of by routine application of fungicides to diminish chances of infections. Nanocarrier (NC)-mediated drug delivery using least amounts of fungicide was encapsulated within lignin and was used to establish long-term treatment against Esca (fungal grapevine trunk disease). Plants proved to exhibit significantly lower symptoms of infection after several weeks of treatment. Additonally, condition of the plants was further monitored for five years (2014-2018), showed long-term curative efficacy by nanocarrier treatment. In this study, a single trunk was injected with <10 mg fungicide that resulted in the cure of an infected plant. Lignin nanocarrier (NC) release the fungicide degraded by ligninolytic enzymes that were released by fungi associated with Esca on infected plants. *In vitro* & *in planta* (in *Vitis vinifera* L. cv. 'Portugieser') confirmed the specific antifungal activity [93]. Similarly, antagonistic fungi such as *Trichoderma reesei* are considered as potential alternatives against traditional fungicides used in agriculture. Due to reduced self life and unrestrained germination the applications of fungi *Trichoderma* for treatment of grapevine trunk diseases are reduced to only preventive measures. Peil *et al*. formulate a mild and spore-compatible lignin shell encapsulated by spores of mycoparasitic strain of *T. reesei* (IBWF 034-05). The encapsulated spores inhibited the undesired premature germination as well as enabled the application as aqueous self-stabilizing spore dispersal *via*

trunk injection. Initially, encapsulated pores were injected into a plant at resting state without damage; it was observed that spore dispersion remained colloidally stable for months and controlled the plant infection by fungal pathogens [94, 95].

Another study conducted by Ouriques Machado *et al.* synthesized lignin nanocarriers (chemically crosslinked) via aza-Michael addition in miniemulsion and solvent evaporation. Here the cross-linking of lignin was done using bio-based amines (spermine and spermidine). This technique was explored for many fungicides such as pyraclostrobin, azoxystrobin, boscalid and tebuconazole. These fungicides were encapsulated *in situ* by miniemulsion polymerization and established the efficacy to inhibit the growth of *Phaeomoniella chlamydospora* and *Phaeoacremonium minimum* (ligninase producing fungi) responsible for fungal grapevine trunk disease Esca [96]. Zikeli *et al*. [97] isolated lignin from beech sawdust to prepare lignin nanoparticles to entrap cinnamon bark (*Cinnamomum zeylanicum Blume*), common thyme (*Thymus vulgaris L.),* and wild thyme (*Thymus serpyllum L.*) essential oil via., anti-solvent method. Results showed that essential oils were entrapped inside lignin nanoparticles, due to high π-stacking between the many aromatic compounds present in essential oil like thymol, carvacrol and cinnamaldehyde on one side and aromatic lignin units on the other side. Also *in vitro* release of common thyme and wild thyme essential oil from essential oil -loaded lignin nanoparticles was found to be deferred when compared with pure oil application, thus such systems can be explored as biodegradable delivery systems for wood preservation [97].

3. Conclusions

Due to the variety of chemical structure, functionality and properties of naturally occurring biopolymers from lignocellulosic biomass they have gained interest in recent years for use in a variety of applications. Reviewing the application of lignin and carbohydrate polymers in areas such as drug delivery, food industry, corrosion inhibition and catalysis

highlights the wide ranging use these polymers have and they can be sources from renewable resources that do not compete with the production of food.

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Highlights of manuscript

- Waste biomass from different sources
- Catalytic applications of natural polymers
- Carbohydrate Polymers as Corrosion inhibitor
- Food applications of Natural polymers
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Declaration of interests

☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: