Extraction, Purification, and Applications of Hemicellulose

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Abstract: In addition to cellulose and lignin, hemicellulose is an important biomass material. Recently, hemicellulose and its derivatives and materials have attracted increasing attention owing to their unique structures, improved properties, and promising application potential, and many reports on the extraction, isolation, and modification of hemicellulose are currently available. We summarized the recent developments of hemicellulose and its derivatives and materials by focusing on the extraction, purification, and modification of hemicellulose. The synthesis of hemicellulose-based derivatives and materials was also reviewed. Various methods of extracting, isolating, and modifying hemicellulose were discussed. Remaining challenges related to hemicellulose extraction, purification, and application were mentioned, and directions for further research on hemicellulose were proposed.

Keywords: hemicellulose; extraction; purification; modification; application

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1 Introduction

Lignocellulose consists of cellulose, hemicellulose, and lignin. Hemicellulose is a heteropolymer consisting of several monosaccharides such as D-xylose, L-arabinose, D-glucose, D-galactose, D-mannose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid, D-galacturonic acid, various O-methylated neutral sugars, and a trace of L-rhamnose and L-trehalose [1]. Hemicellulose closely attaches to the cellulose surface

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by hydrogen bonding and van der Waals forces and connects to lignin by ferulic acid, forming the hemicellulose-ester-ferulic acid-ether-lignin bridge structure. Compared with cellulose and lignin, hemicellulose exhibits low molecular weight, average polymerization degree (80−200), and multibranching. Moreover, hemicelluloses prepared from different species such as hardwood, softwood, and grass exhibit different chemical structures [2]. Hardwood hemicelluloses are mainly glucuronoxylan or 4-O-methyl-glucuronoxylan, which contain some acetyl groups. Softwood hemicelluloses are mainly galactose glucose mannan or O-ethyl-galactose glucose mannan. Xylan® arabinosuronate (or arabinose-4-O-methylglyoxylan) is an important grass hemicellulose, only a small amount of which exists in softwood. Hemicellulose is widely used as a raw material for preparing feed yeast, furfural, xylose, and xylitol [3] and has many potential biomedical and food applications owing to its active hydroxyl groups and bioactivity [4−5]. In addition, the biotechnological production of alcohol from renewable hemicellulose has attracted global attention [6−7].

Owing to its chemical structural characteristics, raw hemicellulose is usually extracted from biomass and then isolated to obtain high-purity hemicellulose, after which it is modified into derivatives and further used to synthesize hemicellulose-based materials [8]. Recently, rapid progress has been made in extracting, isolating, and modifying hemicellulose [9], and the synthesis and potential applications of hemicellulose-based derivatives and materials has been extensively reported [10]. For example, as early as 2008, Hansen and Plackett [10] summarized the development of hemicellulose-derived sustainable films and coatings for foodstuffs and biomedical applications by focusing on both the oxygen and water-vapor permeabilities of hemicellulose films. Farhat et al [11] reviewed water-resistant hemicellulose-based materials, summarized methods isolating/separating hemicellulose from biomass, reviewed most methods hydrophobizing hydrophilic hemicelluloses, and developed applications targeting at water-resistant hemicellulose.

This article provides an overview of extracting, purifying, and modifying hemicellulose. The properties and applications of hemicellulose-based derivatives and materials are reviewed. Some recent examples are cited to introduce the development of hemicellulose and its derivatives and materials. Finally, challenges related to cleanly and efficiently separating hemicellulose from biomass and efficiently converting hemicellulose into chemicals and materials are acknowledged and directions for further research on hemicellulose are proposed.

2 Extraction of hemicellulose

Traditional methods of extracting hemicellulose from biomass include alkali and organic solvent extractions [12]. Some newer methods have also been reported, such as H_2O_2, steam explosion, microwave-assisted, and ultrasonic-assisted extractions [13].

2.1 Alkali extraction

Alkali extraction is the most used method of extracting hemicellulose from biomass because it breaks the ester and ether bonds between hemicellulose and lignin and between hemicellulose and hydroxycinnamic acid, thereby dissolving the hemicellulose from the cell wall. In 2009, different hemicelluloses were extracted from the mildly ball-milled cell walls of lignified barley straw and maize stems using three organic solvents (90% neutral dioxane, 80% HCl-containing dioxane, and dimethyl sulfoxide) and an aqueous alkaline solution (8% KOH) [14]. The obtained hemicelluloses were then comparatively analyzed. The hemicelluloses extracted using 8% KOH were composed of arabino-(4-O-methyl-D-glucurono) xylans and exhibited partially depolymerized polysaccharides dissolved by cleaving the polymer glycosidic bonds and saponifying the polymer ester groups. Hemicellulose was also extracted from wheat straw by cold alkaline extraction at 40℃ for 90 min and was subsequently separated by ethanol precipitation [15]. The 100 g/L cold alkaline solution and subsequent ethanol precipitation extracted 56.1% and 39.4% of all the hemicellulose from the raw material,

respectively. Alkaline extraction and direct delignification were also used to recover hemicelluloses from the raw materials [16]. The delignified hemicelluloses was used to produce colorless films, and the high Ara/Xyl ratio improved the film formability. Recently, Zhao et al [17] isolated hemicelluloses from the apical, middle, and basal segments of *Neolamarckia cadamba* using KOH extraction. The authors obtained (4-O-methyl) glucuronoxylan of the primary hemicellulose and trace concentrations of high-molecular-weight mannan and xylan from the middle and basal segment stems. More recently, hemicellulose-based polysaccharides were isolated from *Salvia miltiorrhiza* roots using 8% NaOH solution [18]. The 4-*β*-D-Xylp main chain exhibited optimally inhibitory activities, suggesting that biologically active hemicellulose-based polysaccharides have promising biomedical applications.

2.2 H_2O_2 extraction

Alkaline H_2O_2 extraction is an environmentally friendly method of separating hemicellulose because it readily decomposes into hydroxyl and superoxide-anion radicals in alkaline environments, which can oxidize the lignin structure, form hydrophilic groups, and break the chemical bonds between lignin molecular units to remove the lignin and separate the hemicellulose. Hemicellulosic moieties were extracted from opium poppy and cotton stalks using various concentrations of NaOH and H_2O_2 [19]. The 3.0% H_2O_2 extracted 3.2% of all the hemicelluloses in the opium poppy stalks. The authors demonstrated that alkaline peroxide was an effective agent for solubilizing hemicelluloses from opium poppy and cotton stalks. In addition, hemicellulose was extracted from the rice straw and husk in Egyptian agricultural waste using 4% NaOH at 90℃ and was subsequently purified using 5% H_2O_2 [20]. The sulfated soluble hemicelluloses exhibited the highest degree of sulfation, low total carbohydrate content, and biological activities such as anticoagulation at 31.25 μg/mL and fibrinolytic activity lysis above 80% at 2000 μg/mL compared standard (Hemoclar®). Obviously, this research favored the high-value applications of hemicellulose extracted from agricultural wastes. More recently, He et al [21] provided models of hemicellulose transportation from different corn stalk tissues to alkaline H_2O_2 solution. Hemicellulose dissolution was mainly influenced by the alkali-soluble hemicellulose content and tissue density, and all the hemicellulose dissolution processes were physical-mass-transfer dominated. The authors also analyzed the alkali dissolution characteristics and mechanism of bagasse-pith-derived hemicellulose extracted using atmospheric NaOH-H_2O_2 [22]. The optimal alkali concentration of 100 g/L maximized the hemicellulose extraction yield, which was attributed to the ratio of the hydrate hydrodynamic diameter to the cellulosic-microfiber intersheet distance, and the obtained activation energy of 22.19 kJ/mol was attributed to the diffusion-controlled process.

2.3 Hydrothermal extraction

In hydrothermal synthesis, water is used as a solvent to prepare materials in a sealed pressure vessel. Hemicellulose can also be hydrothermally extracted. For example, Thomsen et al [23] hydrothermally extracted wheat straw at pilot plant using a three-step reactor system and recovered a high hemicellulose yield. First, the wheat straw was presoaked at 80℃. Then, hemicellulose was extracted at 170−180℃. In the third step, the cellulose enzymatic convertibility was improved at 195℃. The maximum hemicellulose recovery (83%) was achieved at the highest water addition (600 kg/h), and a low hemicellulose recovery (33%) and high glucose yield were obtained during anhydrous enzymatic hydrolysis. Gallina et al [24] hydrothermally extracted hemicellulose at pilot scale using a flow-through reactor and obtained hemicellulose yields of 38.8% and 41.7% from lab and pilot scale extractions, respectively (170℃). Moreover, the yields (9.3%−40.6%) increased and molecular weights (1417−4078 Da) decreased with increasing temperature. Liu et al [25] developed two-step hydrothermal and alkali isolation of hemicelluloses from Chinese quince fruit. Increasing the hydrothermal extraction temperature from 120 to 150℃ increased the

xylose yield from 58.2% to 62.2% in the solid residue and hydrolyzed arabinose and mannose. Moreover, the hemicellulose exhibited a backbone consisting of D-xylose residues with a *β*-(1→4)-linkage at 30% ethanol. More recently, Monteiro et al [26] hydrothermally extracted depolymerized hemicellulose from mango-seed shell to produce xylooligosaccharides for prebiotic applications. Their method yielded 393.44 mg xylooligosaccharides/g xylan at 2.5 MPa and 15 min, and adding a trace of xylose (8.81 mg/g xylan) resulted in a hemicellulose conversion of 40.2%.

Rissanen et al [27] studied the kinetics, mass transfer, and modeling of hemicelluloses extracted from spruce sapwood using pressurized hot water at 120−170℃ in a batchwise-operated cascade reactor. An activation energy of approximately 120 kJ/mol was obtained for both chip sizes. This research quantitatively and qualitatively analyzed the processes occurring during extraction. Formic-acid-containing hot water was used to extract hemicellulose from birch (*Betula pendula*) sawdust at 170℃ [28]. The maximum combined yield of the xylose and furfural was approximately 70 mol% of the total hemicellulose content. Furthermore, the hydrolysis of hemicellulose to xylose and furfural was increased by the formic acid. In addition, hot pressurized water pretreatment was applied to extract the hemicellulose from 10 different tree species using a batchwise-operated cascade reactor at 160℃ for 5 to 80 min [29]. The highest yield was obtained with eucalyptus wood (40.3 wt%) for 80 min.

Our group systematically extracted and isolated hemicellulose by hydrothermal pretreatment. For example, as early as 2012, hemicellulose was extracted using hydrothermal pretreatment from triploid *Populus tomentosa* Carr. in dimethylformamide solvent [30] to obtain high-molecular-weight hemicellulosic fractions exhibiting a high Uro/Xyl ratio (Table 1); namely, the more-branched hemicelluloses. The hemicellulosic fractions were mainly composed of (1→4)-linked *α*-D-glucan and (1→4)-linked *β*-D-xylan attached with traces of hemicellulose-derived branched sugars. Then, hemicelluloses exhibiting different branches and molecular weights were extracted from sweet-sorghum stem using an aqueous alkali solution [31]. The sorghum-stem-derived hemicelluloses were mainly L-arabino-4-O-methyl-D-glucurono-D-xylan. Usually, the higher the molecular weight of the hemicellulose, the higher its thermal stability.

Table 1 Neutral sugars and uronic acids (relative percentage of hemicellulosic sample, *w*/*w*) and Uro/Xyl ratios of hemicellulosic fractions. Reprinted from ref. [30]

Sugars/%	Hemicellulosic fractions					
	H_0	H_{10}	H_{30}	H_{50}	H_{70}	H_{100}
Rhamnose	1.42	0.06	0.03	0.34	0.24	0.49
Arabinose	1.40	0.20	0.52	0.62	5.12	8.19
Galactose	3.22	2.13	2.43	1.29	3.86	19.26
Glucose	40.74	63.04	55.38	58.39	53.41	63.40
Xylose	52.91	33.20	39.48	35.89	34.55	7.00
Uronic acids	0.29	1.36	2.15	3.46	2.76	1.58
Uro/Xyl	0.01	0.04	0.05	0.10	0.08	0.23

Hemicelluloses were also extracted from sweet-sorghum stem by integrating hydrothermal pretreatment and alkaline post-treatment [32] to prepare alkali-soluble hemicelluloses exhibiting the highest yield of 60.6% and a more linear structure owing to the residue hydrothermally pretreated at 130℃ for 1 h. Experimental results confirmed the homogeneous alkali-soluble hemicelluloses with integrated process, compared with that from the nonpretreated. In 2017, water- and alkali-soluble hemicelluloses were hydrothermally extracted using water and alkaline solutions (NaOH or KOH), respectively [33]. The scheme for hydrothermally extracting hemicelluloses from triploid *Populus tomentosa* Carr. using distilled water and alkaline solution is shown in Fig. 1. Briefly, hemicelluloses were extracted from holocellulose using either distilled water of 30 mL or 1 mol/L KOH or 1 mol/L NaOH aqueous solutions at 160℃ for 12 and 24 h, respectively. The hemicelluloses extracted using the alkaline solutions exhibited relatively high molecular weights compared with the hemicelluloses solubilized in distilled water. The hemicellulosic fractions reportedly exhibited a major structure consisting of (1→4) -linked *β* -D-xylan and a minor

structure consisting of (1→4)-linked α-D-glucan with traces of substituted sugars and glucuronic acid attached. The experimental results indicated the effectiveness of the alkalis (NaOH and KOH) as extractants. The hemicelluloses were then hydrothermally extracted with ethanol [34]. A high ethanol concentration (45%−80%) favored the isolation of hemicelluloses with more side chains and lower glucose contents. The authors concluded that the hydrothermal ethanol process was a promising pretreatment strategy for isolating and extracting hemicellulose.

2.4 Steam explosion extraction

Steam explosion was used to extract biomass by high-temperature and high-pressure steam, which produces an "explosion" effect through instant pressure relief to separate biomass components. Steam explosion was used to isolate hemicellulosic polysaccharides from *Lespedeza crytobytrya* stalks [35]. The hemicellulosic fractions were obviously degraded after steam explosion. Alkaline deresination and sulfuric acid-catalyzed steam explosion were combined to extract hemicellulose from slash pine sawdust [36]. The results showed that 90% of the hemicelluloses were extracted at 200℃ for 5 min of deresination combined with a high glucan recovery from the steam explosion. Chadni et al [37] investigated effect of steam explosion conditions (e. g., severity factor and pH value of presoaking medium) on the selective extraction of hemicelluloses from spruce sawdust. The highest yield was obtained at a severity factor of 3.65, and the high extraction selectivity of high-molecular-weight hemicelluloses was attributed to the impregnation medium. Mihiretu et al [38] developed steam explosion pretreatment to extract xylan-rich biopolymers from sugarcane trash and aspen wood at 176−204℃ for 3−17 min. It achieved the maximum xylan yields of 51% and 24% for sugarcane trash and aspen wood at 204℃ for 10 min. The authors indicated that the steam explosion pretreatment with alkali impregnation of lignocelluloses was a feasible biorefinery approach to coproduce xylan biopolymers and bioethanol. Moreover, the steam explosion pretreatment was suggested as a feasible biorefinery approach to produce hemicellulose with high efficiency and high yield.

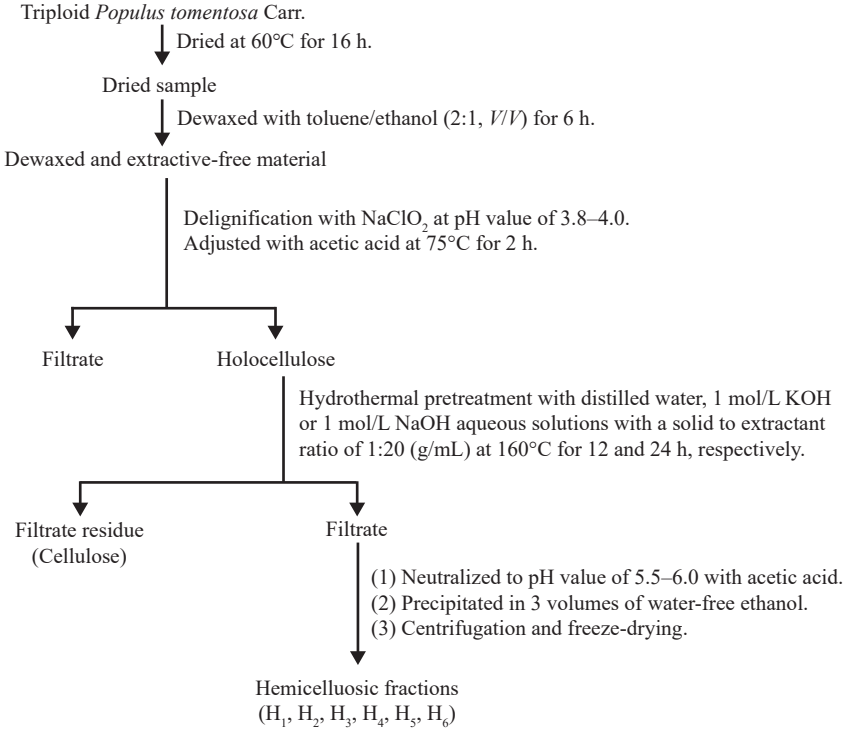

Fig. 1 Scheme for extracting hemicelluloses from Triploid *Populus tomentosa* Carr. Reprinted from ref. [33].

Therefore, steam explosion pretreatment is a promising strategy for the industrial application.

2.5 Microware-assisted extraction

Microwave-assisted extraction has the advantages of fast, high efficiency, low cost, and high yield, which has been widely used in the extraction of hemicellulose. The microwave-induced pressurized hot water was developed for the coproduction of xylan-based biopolymers and bioethanol from aspen wood sawdust and sugarcane trash [39]. It yielded the maximum xylan extraction of 66% for aspen wood sawdust and 50% for sugarcane trash, and a monomeric xylose extraction of below 7% for both feedstocks. Microwave-assisted extraction was also used for the selective extraction of high-molecular-weight hemicelluloses from spruce sawdust [40]. The yield of hemicellulose increased with increasing microwave power in both mediums. The high extraction selectivity depended on the sawdust impregnation medium, which isolated high-molecular-mass acetylated galactoglucomannans (Mw ≈ 41 kDa) in water and high-molecular-mass arabinoglucoronoxylans (Mw ≈ 66 kDa) in the basic medium. Microwave-assisted hydrothermal extraction was also applied to hemicelluloses derived from tobacco-based biomass [41]. The maximum yields of 118.57 and 120.33 mg/g were obtained for the leaf and stem, respectively. It produced a hemicellulose yield of 105.15 mg/g at 200℃ without holding. The Mw values of precipitated hemicelluloses decreased from 143.5 to 13.25 kDa with increasing temperature and holding time. Authors indicated that the microwave-assisted hydrothermal extraction process opens new avenues for a sustainable tobacco-based biorefinery.

2.6 Ultrasonic-assisted extraction

The ultrasonic-assisted extraction has the advantages of high yield, short time, and low temperature due to cavitation effect of mechanical effect, thermal effect, and chemical effect, which has been widely used in the extraction of hemicellulose. The extraction effect of hemicellulose can be improved in the process of ultrasonic-assisted alkali treatment. As early as 2003, the ultrasonic-assisted alkali treatment was used to extract the 27.1%−28.1% of the original hemicelluloses from wheat straw [42]. It found xylose as a predominant sugar in all the hemicellulose, a noticeable amount of 4-O-methyl-D-glucuronic acid (6.0%−7.0%), and a high molecular weight. Then, the ultrasound-assisted alkali extraction was developed to isolate the hemicellulosic fractions of the partially delignified fast-growing poplar wood [43]. It released 75.5% of the original hemicelluloses using ultrasonic-assisted alkali treatment. After that, the ultrasonic-assisted alkali treatment was reported to extract the hemicelluloses from *Eucalyptus grandis* using 5% KOH solution at 50℃ for 3 h [44]. The yield of hemicelluloses was observed to be increased from 2.6% to 19.6% as the increase in ultrasonic time from 5 to 35 min. It achieved the highest yield of hemicelluloses (95.2%) at 30 min ultrasonic time. The ultrasonic-assisted alkali treatment induced the hemicelluloses with slightly low molecular weights (74510−66770 g/mol) and higher contents of xylose (83.95%−84.96%). An ultrasound-assisted procedure was also applied to the extraction of hemicelluloses from grape pomace at 20℃ [45]. Authors obtained the maximum extraction yield of hemicelluloses and found the close agreement between experimental and predicted values. The ultrasound-assisted extraction was suggested be a good option for the extraction of hemicellulosic polysaccharides from grape pomace at industrial level.

3 Purification of hemicellulose

Hemicellulose usually contains some low-molecular-weight lignin, salt, and other impurities. Therefore, hemicellulose must be purified to obtain uniformly structured high-purity hemicellulose. The common purification methods include column chromatography, membrane separation, and solvent precipitation. In a previous review, Peng et al [46] summarized the isolation, purification, and bioconversion of hemicellulose. They presented numerous isolation and purification strategies including alkali peroxide

extraction, organic solvent extraction, steam explosion, ultrasound-assisted extraction, microwave-assisted extraction, column chromatography, and membrane separation. Egues et al [47] reported the separation and purification of hemicellulose from corn waste by ultrafiltration. The 10-kDa retentate liquor fraction exhibited the highest hemicellulose concentration (6.10 g/L). Ultrafiltration was used to improve the physicochemical characteristics of the original liquor. Liu et al [48] compared the performance of ultrafiltration and nanofiltration for concentrating hemicelluloses and found that nanofiltration gave much better rejection rates for organic compounds than ultrafiltration and that activated carbon adsorption and ion-exchange resin pretreatment removed much more total phenolic compounds and acetic acid than nanofiltration. Bokhary et al [49] used ultrafiltration to recover and purify hemicelluloses from thermomechanical pulp mill water. The authors used three hydrophilic ultrafiltration membranes with different molecular weight cutoffs (5, 10, and 30 kDa) for hemicellulose recovery and purification and recovered above 95% and approximately 89% of the 5- and 10-kDa hemicelluloses, respectively. They obtained the highest hemicellulose purity (80%) using the 10-kDa membrane. More recently, Hliavitskaya et al [50] proposed Praestol 859-assisted ultrafiltration membranes to improve separation performance and antifouling stability. The Praestol 859 reportedly increased the membrane pure-water flux from 51 to 68 L/(m^2·h) without decreasing membrane retention and decreased the "solvent-nonsolvent" exchange rate. The authors found that the Praestol 859-modified membrane increased the flux 2−6 times, increased the fouling recovery ratio, and improved the cleaning efficiency without decreasing the membrane rejection of the hemicellulose reference components (91.5%−93.0%). Besides ultrafiltration, air sparging reportedly increased the flux of alkaline-extracted wheat-bran hemicelluloses [51] and purified two alkaline hemicellulose solutions. Air sparging increased the average flux from 52 to 151 L/(m^2·h) during ultrafiltration for 2 h. More importantly, the cost was reduced from 1375 to 1122 €/t hemicelluloses when air sparging was conducted prior to membrane filtration.

4 Modification of hemicellulose

Hemicellulose is usually hydrophobic owing to its chemical structure, and different hemicelluloses exhibit different chemical properties and molecular structures, thereby limiting their industrial applications. The shortcomings of hemicellulose can be overcome by modification, such as etherification, esterification, and crosslinking [52−53]. Moreover, modification improves the physicochemical properties of hemicellulose, such as molecular weight, solubility, surface tension, biological activity, and thermal stability [54].

4.1 Etherification

Etherification is an important modification method used to improve the application potential of hemicelluloses. In 2007, Ren et al [55] prepared etherified hemicelluloses from sugarcane bagasse using 2,3-epoxypropyltrimethylammonium chloride and NaOH as a catalyst in aqueous solution. The overall yield ranged from 35.2% to 41.9% and the degree of substitution ranged from 0.14 to 0.33 by changing the experimental conditions. The authors found that the thermal stability of the hemicellulosic ethers decreased after chemical modification, and the etherified hemicelluloses exhibited low molecular weights. Moreover, the authors found that the hemicelluloses were etherified and quaternized mainly at the C-3 position. Nypelo et al [56] reported the etherification of wood-based hemicelluloses for wetting, hygroscopicity, and interfacial activity and found that hygroscopicity decreased with modification to butylated grades and that the degree of modification determined the interfacial tension of the aqueous hemicellulose solutions.

4.2 Esterification

Esterification is another important modification method used to improve the application potential of hemicelluloses. Sun et al [57] esterified hemicelluloses

with various acyl chlorides in a homogeneous system consisting of N, N-dimethylformamide and lithium chloride and using 4-(dimethylamino) pyridine as a catalyst and triethylamine as a neutralizer. The authors stearoylated >90% of the free hydroxyl groups in the native hemicelluloses at 75℃ for 40 min and found minimal degradation of the macromolecular hemicelluloses during the reactions. Then, the authors homogeneously esterified xylan-rich hemicelluloses with maleic anhydride in a 1-butyl-3-methylimidazolium chloride ionic liquid using LiOH as a catalyst [58]. The structures of the hemicellulosic derivatives contained carbon-carbon double bonds and carboxyl groups. Later, Wang et al [59] explored the reaction behavior of hemicelluloses during homogeneous phthalation in an ionic liquid and found the phthalation degree of hemicellulose ranged from 16.37% to 52.14%. The authors indicated that the hemicellulose side-chains were easily phthalated compared to the main chains.

4.3 Acetylation

Acetylation refers to the process of transferring acetyl groups to hemicellulose side chains. Ren et al [60] acetylated wheat straw hemicelluloses with acetic anhydride using iodine as a catalyst in 1-butyl-3-methylimidzolium chloride ionic liquid. The yield ranged from 70.5% to 90.8% and the degree of substitution ranged from 0.49 to 1.53 for the acetylated hemicelluloses. Approximately 83% of the hydroxyl groups in the native hemicelluloses were esterified under the preferred reaction conditions. Mugwagwa and Chimphango [61] used an alkali-organosolvo pretreatment on wheat straw to enhance the hemicellulose modification and compatibility with reinforcing fillers. The enhanced acetylation and filler compatibility and the enhanced hydrophobicity were attributed to minimizing the degree of acetylation, the uronic acid content, and the arabinose/xylose ratio. The hemicellulose films exhibited a high water contact angle (68.1°), and the acetylated nanocellulose-reinforced films exhibited a high tensile strength and Young's modulus of 10.6 and of 590.2 MPa, respectively. Moreover, chemical modification was used to improve the processability of hemicellulose, resulting in a remarkable (95.3%–99.7%) biodegradation for value-added applications by the ring-opening graft-polymerization of ε-caprolactone [62]. The poly-(ε-caprolactone) grafting onto hemicellulose was reported to enhance the mechanical properties and hydrophobicity of the materials.

5 Applications of hemicellulose-based materials

As an important biomass, hemicellulose can be used as raw material to synthesize hemicellulose-based materials such as hydrogels, films, and composites [63–64]. In 2008, Lindblad et al [65] prepared hemicellulose-based hydrogels by radically polymerizing 2-hydroxyethyl methacrylate or poly(ethylene glycol) dimethacrylate with oligomeric hydrosoluble hemicellulose modified with well-defined methacrylic functions. The hydrogels exhibited predominantly solid-like behavior. Edlund and Albertsson [66] fabricated hydrogel microspheres from the major softwood hemicellulose (polysaccharide acetylated galactoglucomannan) loaded with either a small hydrophilic substance or a macromolecular protein (e. g., bovine serum albumin) and afforded diffusion-controlled release *in vitro*. Zhang et al [67] prepared temperature/pH dual-sensitivity reed-hemicellulose-based hydrogels through low discharge electrolysis plasma. The authors found that the phase-transition temperatures were at approximately 33℃. Moreover, the hydrogel was more sensitive to temperature and pH value and exhibited high deswelling ratio. Zhang et al [68] synthesized highly reusable reed-hemicellulose-based hydrogels using glow-discharge electrolysis plasma for the adsorption of heavy metal ions from aqueous solutions. Discharge voltage and time both played an important part in the adsorption of the reed-hemicellulose-based hydrogels, which followed the pseudo-second order and Langmuir isotherm model. Then, the authors fabricated a high-performance superabsorbent hydrogel using waste-hemicellulose lye [69]. The formation mechanism of the

composite hydrogel and its interpenetrating polymer network structure represented the synergistic effect of poly(vinyl alcohol) and bentonite.

Guan et al [70] mostly worked on the applications of hemicellulose-based hydrogels. In 2014, they prepared a hybrid hydrogel from hemicelluloses, polyvinyl alcohol, and chitin nanowhiskers by the freeze-thaw technique. The chitin nanowhiskers exhibited an average length and width of approximately 200 and 40 nm, respectively. The hydrogels exhibited the highest compressive stress of 9.6 MPa, and the compressive stress increased with increasing proportion of chitin nanowhiskers. The authors indicated that the packed chains became physically cross-linked by hydrogen bonds among the polymers during the repeated freeze-thaw cycles. Then, the authors prepared a series of hydrogels consisting of semiinterpenetrating polymeric networks composed of hemicellulose-g-poly(acrylic acid) and phosphorylated poly(vinyl alcohol) by radical polymerization using potassium persulphate as an initiator [71]. The hydrogels exhibited a highly porous structure, increased thermal stability, and the maximum equilibrium swelling ratios of 1085 and 87 g/g in distilled water and 0.9 wt% sodium chloride solutions, respectively. The authors also enhanced the mechanical performance of the biocompatible hemicellulose-based hydrogel by the free-radical graft copolymerization of crosslinked quaternized hemicelluloses and acrylic acid in the N, N′-methylenebisacrylamide crosslinking agent [72]. The hemicellulose-based hydrogels did not exhibit any toxicity to cells and they allowed cell growth. More recently, dialdehyde hemicelluloses were synthesized by the oxidation of hemicellulose extracted from straw with $NaIO_4$ [73]. The hydrogels were processed using vacuum freeze-drying to prepare aerogels, exhibiting a finer porous and regular structure owing to the three-dimensional network formed between the dialdehyde hemicelluloses and chitosan during gelation. The maximum compression strength of the obtained aerogel was 0.37 MPa, and the maximum absorption capacity of the Congo red dye was 137.74 mg/g.

Hartman et al [74] developed hemicellulose-based O-acetylgalactoglucomannan oxygen-barrier films that exhibited high resistance to moisture-rich conditions. The oxygen-barrier properties exhibited drastically low moisture sensitivity. Biodegradable films were produced from hemicelluloses mixed with glycerol using citric acid as a crosslinking agent [75]. The citric acid improved the water resistance, water-vapor-barrier properties, and the tensile properties of the films by crosslinking. Different films were formed using hemicelluloses as a matrix and different cellulose nanocrystal and citric acid contents [76]. The cellulose nanocrystals reinforced hemicellulose-based films improved the tensile strength and modulus, water resistance, and water vapor barrier. Polyacrylamide-hemicellulose hybrid films were synthesized through the copolymerization of acrylamide monomers and hemicellulose with the potassium persulfate/N, N, N′, N′-tetramethylethylenediamine redox initiator and the cross-linker N, N-methylene-bis(acrylamide) [77]. The hybrid films exhibited ambient-temperature water solubility, good recyclability, high stretchability, and low oxygen permeability.

Recently, Rao et al [78] fabricated tight, homogeneous, and smooth hemicellulose films for humidity sensing. The films exhibited enhanced mechanical properties owing to graphene oxide. The hybrid films exhibited a high tensile strength of 43.8 MPa and high humidity sensitivity. The storage modulus of the hybrid films changed by an order of magnitude in different humidities. Lucenius et al [79] synthesized composite films made of cellulose nanofibrils and various modified and unmodified polysaccharides. The polysaccharides moderately reduced the repulsive forces and friction between the cellulose surfaces and improved the mechanical properties of the CNF-based composites in wet conditions. Zhang et al [80] prepared functional hemicellulose films exhibiting flexibility, thermoplasticity, and UV-shielding ability using poly (vinyl alcohol) and ZnO. The composite films exhibited moderate tensile strength, good flexibility with the maximum elongation at break of 87.2%, and

increased thermal stability. Moreover, the hemicellulose composite films exhibited a water vapor permeability of 2.08 × 10^{-10} g/(m·s·Pa), an oxygen permeability of 0.95 $cm^3 \cdot \mu m/(m^2 \cdot d \cdot kPa)$, and excellent UV-shielding properties: blocking 99.34% and 99.99% of UV-A and UV-B radiation, respectively. The authors also prepared functional semitransparent packaging films exhibiting acceptable antioxidant activity originating from the direct transesterification of hemicellulose laurate in ionic liquid [81]. The hemicellulose laurate films exhibited excellent hydrophobicity with a water contact angle of approximately 120° and enhanced mechanical properties with tensile strength of 33.9 MPa and elongation at break of 3.09%.

In addition to hemicellulose-based hydrogels and films, hemicellulose has been used to prepare composites for various applications. For example, Gautam et al [82] synthesized hemicellulose-based materials exhibiting good reusability efficiency as malachite green dye adsorbents with a Langmuir adsorption capacity of 456.23 mg/g for the acetylated and dicarboxylated hemicellulosic material. The kinetic and isotherm models matched a pseudo-second order kinetic model and a Freundlich isotherm, respectively. Willfor et al [83] developed a biomimetic composite material consisting of bacterial cellulose and wood-based hemicelluloses. The easier composite hydrolysis could have been related to the substrate nanostructure, particularly the cellulose microfibrils packed into ribbons or bundles. The authors demonstrated that the easier enzymatic hydrolysis of the bacterial cellulose produced in wood-based xylan could overcome biomass recalcitrance through genetic engineering. Shah et al [84] prepared hemicellulose-cellulose composites that mimic plant-cell-wall polymer interactions by synthesizing deuterated bacterial cellulose in glucomannan or xyloglucan. The xyloglucan-cellulose macrofibril dimensions and macrofibrillar network remained relatively unchanged after pretreatment, and the xyloglucan tightly interacted with the microfibrils while the glucomannan only interacted with the macrofibrillar surfaces.

6 Conclusions

Naturally abundant hemicellulose can be applied to chemicals, foods, pharmaceutical drugs, coatings, papers, and other industrial products. This review focused on the rapid progress in hemicellulose extraction, purification, and modification, emphasizing the conversion of hemicellulose into derivatives, chemicals, and materials owing to their diverse range of applications. Many problems related to cleanly and efficiently separating hemicellulose from biomass and to efficiently converting hemicellulose into chemicals and materials must be solved. Current extraction methods should be scaled for industrial application. In addition, research should be conducted on combining purification methods to prepare high-purity hemicellulose. Although many reports on esterified and etherified hemicellulose are currently available, the relationship between the microstructure and properties of pristine and modified hemicellulose should be explored. Moreover, a biofunctionalization pathway should be provided for hemicellulose applications. More importantly, an enormous amount of research effort has gone into nanocellulose and nanolignin, and nanohemicellulose may have a wide range of applications owing to its small size and great properties. We expect that further research will demonstrate the promise of utilizing hemicellulose in a diverse range of industrial applications.

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References

[1] Puls J, Saake B. Industrially isolated hemicelluloses. *ACS Symposium Series*, 2004, 864, 24-37.

[2] Kapu N S, Trajano H L. Review of hemicellulose hydrolysis in softwoods and bamboo. *Biofuels Bioproducts & Biorefining-Biofpr*, 2014, 8(6), 857-870.

[3] Mamman A S, Lee J M, Kim Y C, Hwang I T, Park N J, Hwang Y K, Chang J S, Hwang J S. Furfural: Hemicellulose/xylosederived biochemical. *Biofuels Bioproducts &*

Biorefining-Biofpr, 2008, 2(5), 438-454.

[4] Li X M, Pan X J. Hydrogels based on hemicellulose and lignin from lignocellulose biorefinery: a mini-review. *Journal of Biobased Materials and Bioenergy*, 2010, 4(4), 289-297.

[5] Liu X X, Lin Q X, Yan Y H, Peng F, Sun R, Ren J. Hemicellulose from plant biomass in medical and pharmaceutical application: A critical review. *Current Medicinal Chemistry*, 2019, 26(14), 2430-2455.

[6] Girio F M, Fonseca C, Carvalheiro F, Duarte S L, Marques C, Bogel-Łukasik R. Hemicelluloses for fuel ethanol: A review. *Bioresource Technology*, 2010, 101(13), 4775-4800.

[7] Chandrakant P, Bisaria V S. Simultaneous bioconversion of cellulose and hemicellulose to ethanol. *Critical Reviews in Biotechnology*, 1998, 18, 295-331.

[8] Mäki-Arvela P, Salmi T, Holmbom B, Willför S, Murzin D Y. Synthesis of sugars by hydrolysis of hemicelluloses—A review. *Chemical Reviews*, 2011, 111(9), 5638-5666.

[9] Carvalheiro F, Duarte L C, Girio F M. Hemicellulose biorefineries: a review on biomass pretreatments. *Journal of Scientific & Industrial Research*, 2008, 67(11), 849-864.

[10] Hansen N M L, Plackett D. Sustainable films and coatings from hemicelluloses: A review. *Biomacromolecules*, 2008, 9 (6), 1493-1505.

[11] Farhat W, Venditti R A, Hubbe M, Taha M, Becquart F, Ayoub A. A review of water-resistant hemicellulose-based materials: processing and applications. *ChemSusChem*, 2017, 10(2), 305-323.

[12] Sun J X, Sun X F, Sun R C, Su Y Q. Fractional extraction and structural characterization of sugarcane bagasse hemicelluloses. *Carbohydrate Polymers*, 2004, 56(2), 195-204.

[13] Peng P, She D. Isolation, structural characterization, and potential applications of hemicelluloses from bamboo: A review. *Carbohydrate Polymers*, 2014, 112, 701-720.

[14] Jin A X, Ren J L, Peng F, Xu F, Zhou G Y, Sun R C, Kennedy J F. Comparative characterization of degraded and non-degradative hemicelluloses from barley straw and maize stems: Composition, structure, and thermal properties. *Carbohydrate Polymers*, 2009, 78, 609-619.

[15] García J C, Díaz M J, Garcia M T, López F. Search for optimum conditions of wheat straw hemicelluloses cold alkaline extraction process. *Biochemical Engineering Journal*, 2013, 71(1), 127-133.

[16] Egues I, Eceiza A, Labidi J. Effect of different hemicelluloses characteristics on film forming properties. *Industrial Crops and Products*, 2013, 47, 331-338.

[17] Zhao X H, Tong T T, Li H L, Lu H, Ren J, Zhang A, Deng X, Chen X, Wu A M. Characterization of hemicelluloses from *Neolamarckia cadamba* (Rubiaceae) during xylogenesis. *Carbohydrate Polymers*, 2017, 156, 333-339.

[18] Zhao K, Li B, He D M, Zhao C, Shi Z, Dong B, Pan D, Patil R R, Yan Z, Guo Z. Chemical characteristic and bioactivity of hemicellulose-based polysaccharides isolated from *Salvia miltiorrhiza*. *International Journal of Biological Macromolecules*, 2020, 165, 2475-2483.

[19] Cengiz M, Dincturk O D, Sahin H T. Fractional extraction and structural characterization of opium poppy and cotton stalks hemicelluloses. *Pharmacognosy Magazine*, 2010, 6 (24), 315-319.

[20] Ragab T I M, Amer H, Mossa A T, Emam M, Hasaballah A A, Helmya W A. Anticoagulation, fibrinolytic and the cytotoxic activities of sulfated hemicellulose extracted from rice straw and husk. *Biocatalysis and Agricultural Biotechnology*, 2018, 15, 86-91.

[21] He L, Yang S B, Chen D, Peng L, Liu Y, Guan Q, Li J. Hemicellulose transportation from different tissues of corn stalk to alkaline hydrogen peroxide solution. *Cellulose*, 2020, 27, 4255-4269.

[22] He L, Chen D, Yang S B, Peng L, Zhang J, Guan Q, Zhang P. Deep insights into the atmospheric sodium hydroxide-hydrogen peroxide extraction process of hemicellulose in bagasse pith: technical uncertainty, dissolution kinetics behavior, and mechanism. *Ind Eng Chem Res*, 2020, 59 (21), 10150-10159.

[23] Thomsen M H, Thygesen A, Thomsen A B. Hydrothermal treatment of wheat straw at pilot plant scale using a three-step reactor system aiming at high hemicellulose recovery, high cellulose digestibility and low lignin hydrolysis. *Bioresource Technology*, 2008, 99(10), 4221-4228.

[24] Gallina G, Alfageme E R, Biasi P, García-Serna J. Hydrothermal extraction of hemicellulose: from lab to pilot scale. *Bioresource Technology*, 2018, 247, 980-991.

[25] Liu H M, Li Y R, Wu M, Yin H S, Wang X D. Two-step isolation of hemicelluloses from Chinese quince fruit: Effect of hydrothermal treatment on structural features. *Industrial Crops & Products*, 2018, 111, 615-624.

[26] Monteiro C R M, Avila P F, Pereira M A F, Pereira G N, Poletto P. Hydrothermal treatment on depolymerization of hemicellulose of mango seed shell for the production of xylooligosaccharides. *Carbohydrate Polymers*, 2021, DOI: 10.1016/j.carbpol.2020.117274.

[27] Rissanen J V, Grénman H, Willför S M, Murzin D, Salmi T. Spruce hemicellulose for chemicals using aqueous extraction: kinetics, mass transfer, and modeling. *Ind Eng Chem Res*, 2014, 53(15), 6341-6350.

[28] Goldmann W M, Ahola J, Mikola M, Tanskanen J. Formic acid aided hot water extraction of hemicellulose from European silver birch (*Betula pendula*) sawdust. *Bioresource Technology*, 2017, 232, 176-182.

[29] Gallina G, Cabeza Á, Grénman H, Biasi P, García-Serna J, Salmib T. Hemicellulose extraction by hot pressurized

water pretreatment at 160℃ for 10 different woods: Yield and molecular weight. *The Journal of Supercritical Fluids*, 2018, 133, 716-725.

[30] Ma M G, Jia N, Zhu J F, Li S M, Peng F, Sun R C. Isolation and characterization of hemicelluloses extracted by hydrothermal pretreatment. *Bioresource Technology*, 2012, 114, 677-683.

[31] Sun S L, Wen J L, Ma M G, Sun R C. Successive alkali extraction and structural characterization of hemicelluloses from sweet sorghum stem. *Carbohydrate Polymers*, 2013, 92(2), 2224-2231.

[32] Sun S L, Wen J L, Ma M G, Song X L, Sun R C. Integrated biorefinery based on hydrothermal and alkaline treatments: Investigation of sorghum hemicelluloses. *Carbohydrate Polymers*, 2014, 111, 663-669.

[33] Fu L H, Meng L Y, Li Y Y, Ma M G. Comparative study of water-soluble and alkali-soluble hemicelluloses isolated by hydrothermal pretreatment. *Paper and Biomaterials*, 2017, 2(1), 1-9.

[34] Fu L H, Liu S, Li S M, Li Y Y, Ma M G. Characterization of hemicelluloses extracted from *Populus tomenttosa* Carr. by the hydrothermal method with ethanol. *Paper and Biomaterials*, 2017, 2(3), 1-11.

[35] Wang K, Xu F, Sun R C, Jones G L. Influence of incubation time on the physicochemical properties of the isolated hemicelluloses from steam-exploded lespedeza stalks. *Ind Eng Chem Res*, 2010, 49(18), 8797-8804.

[36] Stoffel R B, Neves P V, Felissia F E, Ramos L P, Gassa L M, Area M C. Hemicellulose extraction from slash pine sawdust by steam explosion with sulfuric acid. *Biomass and Bioenergy*, 2017, 107, 93-101.

[37] Chadni M, Grimi N, Bals O, Ziegler-Devin I, Brosse N. Steam explosion process for the selective extraction of hemicelluloses polymers from spruce sawdust. *Industrial Crops & Products*, 2019, DOI: 10.1016/j.indcrop.2019.111757.

[38] Mihiretu G T, Chimphango A F, Görgens J F. Steam explosion pre-treatment of alkali-impregnated lignocelluloses for hemicelluloses extraction and improved digestibility. *Bioresource Technology*, 2019, DOI: 10.1016/j.biortech.2019.122121.

[39] Mihiretu G T, Brodin M, Chimphango A F, Øyaas K, Hoff B H, Görgens J F. Single-step microwave-assisted hot water extraction of hemicelluloses from selected lignocellulosic materials—A biorefinery approach. *Bioresource Technology*, 2017, 241, 669-680.

[40] Chadni M, Bals O, Ziegler-Devin I, Brosse N, Grimi N. Microwave-assisted extraction of high-molecular-weight hemicelluloses from spruce wood. *C R Chimie*, 2019, 22 (8), 574-584.

[41] Yuan Y, Zou P, Zhou J H, Zhang C. Microwave-assisted hydrothermal extraction of non-structural carbohydrates and hemicelluloses from tobacco biomass. *Carbohydrate Polymers*, 2019, DOI: 10.1016/j.carbpol.2019.115043.

[42] Sun R C, Tomkinson J. Characterization of hemicelluloses isolated with tetraacetylethylenediamine activated peroxide from ultrasound irradiated and alkali pre-treated wheat straw. *European Polymer Journal*, 2003, 39, 751-759.

[43] Yuan T Q, Xu F, He J, Sun R C. Structural and physico-chemical characterization of hemicelluloses from ultrasound-assisted extractions of partially delignified fast-growing poplar wood through organic solvent and alkaline solutions. *Biotechnology Advances*, 2010, 28(5), 583-593.

[44] Xu J Y, Yuan T Q, Xiao L, Sun R C. Effect of ultrasonic time on the structural and physico-chemical properties of hemicelluloses from *Eucalyptus grandis*. *Carbohydrate Polymers*, 2018, 195, 114-119.

[45] Minjares-Fuentes R, Femenia A, Garau M C, Candelas-Cadillo M G, Simal S, Rosselló C. Ultrasound-assisted extraction of hemicelluloses from grape pomace using response surface methodology. *Carbohydrate Polymers*, 2016, 138, 180-191.

[46] Peng F, Peng P, Xu F, Sun R C. Fractional purification and bioconversion of hemicelluloses. *Biotechnology Advances*, 2012, 30(4), 879-903.

[47] Egues I, Sanchez C, Mondragon I, Labidi J. Separation and purification of hemicellulose by ultrafiltration. *Industrial & Engineering Chemistry Research*, 2012, 51(1), 523-530.

[48] Liu H T, Hu H R, Jahan M S, Baktash M M, Ni Y H. Purification of hemicelluloses in pre-hydrolysis liquor of kraft-based dissolving pulp production process using activated carbon and ion-exchange resin adsorption followed by nanofiltration. *Journal of Biobased Materials and Bioenergy*, 2014, 8(3), 325-330.

[49] Bokhary A, Maleki E, Liao B Q. Ultrafiltration for hemicelluloses recovery and purification from thermomechanical pulp mill process waters. *Desalination and Water Treatment*, 2018, 118, 103-112.

[50] Hliavitskaya T, Plisko T, Bildyukevich A, Lipnizki F, Rodrigues G, Sjölin M. Modification of PES ultrafiltration membranes by cationic polyelectrolyte Praestol 859: Characterization, performance and application for purification of hemicellulose. *Chemical Engineering Research & Design*, 2020, 162, 187-199.

[51] Thuvander J, Jönsson A S. Techno-economic impact of air sparging prior to purification of alkaline extracted wheat bran hemicelluloses by membrane filtration. *Separation and Purification Technology*, 2020, DOI: 10.1016/j.seppur.2020.117498.

[52] Cheng G P, Duan X W, Jiang Y M, Sun J, Yang S Y, Yang B, He S G, Liang H, Luo Y B. Modification of hemicellulose polysaccharides during ripening of

postharvest banana fruit. *Food Chemistry*, 2009, 115, 43-47.

[53] Zoldners J, Kiseleva T. Modification of hemicelluloses with polycarboxylic acids. *Holzforschung*, 2013, 67(5), 567-571.

[54] Kochumalayil J J, Berglund L A. Water-soluble hemicelluloses for high humidity applications-enzymatic modification of xyloglucan for mechanical and oxygen barrier properties. *Green Chemistry*, 2014, 16, 1904-1910.

[55] Ren J L, Sun R C, Liu C F. Etherification of hemicelluloses from sugarcane bagasse. *Journal of Applied Polymer Science*, 2007, 105(6), 3301-3308.

[56] Nypelo T, Laine C, Aoki M, Tammelin T, Henniges U. Etherification of wood-based hemicelluloses for interfacial activity. *Biomacromolecules*, 2016, 17(5), 1894-1901.

[57] Sun R, Fang J M, Tomkinson J. Characterization and esterification of hemicelluloses from rye straw. *Journal of Agricultural and Food Chemistry*, 2000, 48(4), 1247-1252.

[58] Peng X W, Ren J L, Sun R C. Homogeneous esterification of xylan-rich hemicelluloses with maleic anhydride in ionic liquid. *Biomacromolecules*, 2010, 11(12), 3519-3524.

[59] Wang H H, Chen Y T, Wei Y, Zhang A P, Liu C F. Homogeneous esterification mechanism of bagasse modified with phthalic anhydride in ionic liquid. Part 2: Reactive behavior of hemicelluloses. *Carbohydrate Polymers*, 2017, 157, 1365-1373.

[60] Ren J L, Sun R C, Liu C F, Cao Z N, Luo W. Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst. *Carbohydrate Polymers*, 2007, 70(4), 406-414.

[61] Mugwagwa L R, Chimphango A F A. Optimising wheat straw alkali-organosolv pre-treatment to enhance hemicellulose modification and compatibility with reinforcing fillers. *International Journal of Biological Macromolecules*, 2020, 143, 862-872.

[62] Farhat W, Venditti R, Ayoub A, Prochazka F, Fernández-De-Alba C, Mignard N, Taha M, Becquart F. Towards thermoplastic hemicellulose: Chemistry and characteristics of poly-(ε-caprolactone) grafting onto hemicellulose backbones. *Materials and Design*, 2018, 153, 298-307.

[63] Liu H T, Chen T, Dong C H, Pan X J. Biomedical applications of hemicellulose-based hydrogels. *Current Medicinal Chemistry*, 2020, 27(28), 4647-4659.

[64] Smart C L, Whistler R L. Films from hemicellulose acetates. *Science*, 1949, 110(2870), 713-714.

[65] Lindblad M S, Albertsson A C, Ranucci E, Laus M, Giani E. Biodegradable polymers from renewable sources: Rheological characterization of hemicellulose-based hydrogels. *Biomacromolecules*, 2005, 6(2), 684-690.

[66] Edlund U, Albertsson A C. A microspheric system: Hemicellulose-based hydrogels. *Journal of Bioactive and Compatible Polymers*, 2008, 23, 171-186.

[67] Zhang W M, Zhu S, Bai Y P, Xi N, Wang S Y, Bian Y, Li X W, Zhang Y C. Glow discharge electrolysis plasma initiated preparation of temperature/pH dual sensitivity reed hemicellulose-based hydrogels. *Carbohydrate Polymers*, 2015, 122, 11-17.

[68] Zhang W M, Liang Z L, Feng Q L, Wei N, Liu Z Q, Fu N, Zhang Y C. Reed hemicellulose-based hydrogel prepared by glow discharge electrolysis plasma and its adsorption properties for heavy metal ions. *Fresenius Environmental Bulletin*, 2016, 25(6), 1791-1798.

[69] Liu X W, Luan S, Li W. Utilization of waste hemicelluloses lye for superabsorbent hydrogel synthesis. *International Journal of Biological Macromolecules*, 2019, 132, 954-962.

[70] Guan Y, Zhang B, Bian J, Peng F, Sun R C. Nanoreinforced hemicellulose-based hydrogels prepared by freeze-thaw treatment. *Cellulose*, 2014, 21, 1709-1721.

[71] Peng F, Guan Y, Zhang B, Bian J, Ren J L, Yao C L, Sun R C. Synthesis and properties of hemicelluloses-based semi-IPN hydrogels. *International Journal of Biological Macromolecules*, 2014, 65, 564-572.

[72] Qi X M, Chen G G, Gong X D, Fu G Q, Niu Y S, Bian J, Peng F, Sun R C. Enhanced mechanical performance of biocompatible hemicelluloses-based hydrogel via chain extension. *Scientific Reports*, 2016, DOI: 10.1038/srep33603.

[73] Guan Y, Rao J, Wu Y L, Gao H, Liu S Q, Chen G G, Peng F. Hemicelluloses-based magnetic aerogel as an efficient adsorbent for Congo red. *International Journal of Biological Macromolecules*, 2020, 155, 369-375.

[74] Hartman J, Albertsson A C, Sjoberg J. Surface- and bulk-modified galactoglucomannan hemicellulose films and film laminates for versatile oxygen barriers. *Biomacromolecules*, 2006, 7(6), 1983-1989.

[75] Azeredo H M C, Kontou-Vrettou C, Moates G K, Wellner N, Cross K, Pereira P H F, Waldron K W. Wheat straw hemicellulose films as affected by citric acid. *Food Hydrocolloids*, 2015, 50, 1-6.

[76] Pereira P H F, Waldron K W, Wilson D R, Cunha A P, Brito E S D, Rodrigues T H S, Rosa M F, Azeredo H M C. Wheat straw hemicelluloses added with cellulose nanocrystals and citric acid. Effect on film physical properties. *Carbohydrate Polymers*, 2017, 164, 317-324.

[77] Du J, Li C, Zhao Y D, Wang H S. Hemicellulose isolated from waste liquor of viscose fiber mill for preparation of polyacrylamide-hemicellulose hybrid films. *International Journal of Biological Macromolecules*, 2018, 108, 1255-1260.

[78] Rao J, Gao H, Guan Y, Li W Q, Liu Q. Fabrication of hemicelluloses films with enhanced mechanical properties by graphene oxide for humidity sensing. *Carbohydrate Polymers*, 2019, 208, 513-520.

[79] Lucenius J, Valle-Delgado J J, Parikka K, Österberg M.

Understanding hemicellulose-cellulose interactions in cellulose nanofibril-based composites. *Journal of Colloid and Interface Science*, 2019, 555, 104-114.

[80] Zhang X Q, Luo W H, Xiao N Y, Chen M J, Liu C F. Construction of functional composite films originating from hemicellulose reinforced with poly(vinyl alcohol) and nano-ZnO. *Cellulose*, 2020, 27(3), 1341-1355.

[81] Zhang X Q, Xiao N Y, Chen M J, Wei Y, Liu C F. Functional packaging films originating from hemicelluloses laurate by direct transesterification in ionic liquid. *Carbohydrate Polymers*, 2020, DOI: 10.1016/j.carbpol.2019.115336.

[82] Gautam D, Kumari S, Ram B, Chauhana G S, Chauhanb K. A new hemicellulose-based adsorbent for malachite green. *Journal of Environmental Chemical Engineering*, 2018, 6 (4), 3889-3897.

[83] Willfor S, Sugiyama J, Penttila P A, Imai T, Hemming J. Enzymatic hydrolysis of biomimetic bacterial cellulose-hemicellulose composites. *Carbohydrate Polymers*, 2018, 190, 95-102.

[84] Shah R, Huang S X, Pingali S V, Sawada D, Pu Y, Rodriguez M, Ragauskas A J, Kim S H, Evans B R, Davison B H, et al. Hemicellulose-cellulose composites reveal differences in cellulose organization after dilute acid pretreatment. *Biomacromolecules*, 2019, 20(2), 893-903. PBM