Preparation, Characterization, and Application of Cationic Xylan-based Aerogel

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Adsorption is one of the most significant approaches for treatment of wastewater. An adsorbent with high mechanical strength, good renewability, and high efficiency is expected for practical applications. In this paper, a cationic xylan-based aerogel composed of xylan, polyvinyl alcohol, and agarose was fabricated to adsorb pectin, which is a typical anionic trash substance in the papermaking white water. The freeze-drying method was used to prepare the aerogel. A cationic xylan-based aerogel with high mechanical strength (34.676 MPa at 50% strain) was obtained. FT-IR results illustrated that the hydrogen bonds between three components contributed to the formation of aerogels. The addition of cationic xylan led to a slight decrease of crystallinity and thermostability of the aerogels. The maximum adsorption capacity of anionic pectin was 19.52 mg/g. Moreover, the aerogels maintained a high pectin-adsorption capacity after five recycles. This new cationic xylan-based aerogel offers potential possibilities for the development of value-added hemicellulosebased materials and the purification of papermaking white water in practical applications.

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INTRODUCTION

The discharge of effluent from the papermaking industry grows continuously with the increase of output of paper and paperboard. In order to minimize water consumption and effluent discharge due to environmental concerns, it is required to increase the closure of whitewater systems in modern papermaking. However, large amounts of detrimental substances with high anionic charge, which are introduced with bleached high-yield pulp and deinked pulp, accumulate with the increasing closure of whitewater (Miao et al. 2013, 2014). The anionic substances are mainly composed of galacturonic acids, glucuronic acids, oxidized lignin, fatty acids, and resin acids (Hubbe et al. 2012). The accumulated anionic substances can disturb the charge balance of papermaking wet-end, and thus the runnability of paper machine and the paper quality are adversely affected (Dunham et al. 2002; Lindström et al. 1977; Zhang et al. 1999; Hubbe et al. 2012). Therefore, in order to alleviate the negative influence of anionic substances, plenty of techniques such as chemical fixing or neutralization and biological degradation have been employed (Hubbe et al. 2012; Miao et al. 2013). Nevertheless, both chemical and biological approaches need additional cost for chemical additives or enzymes. So, it is essential to explore alternative, economical and effective methods for removing anionic substances and thus increase the degree of whitewater closure, paper machine runnability, and paper quality.

Nowadays, adsorption has been recognized as one of the most promising techniques because of its lower cost, superior efficiency, and easy operation for treatment of various effluents (Lu *et al.* 2017; Guan *et al.* 2020). As a porous three-dimensional solid material, aerogel has been considered a promising adsorbent for contaminants in wastewater, on account of its ultralow density, high specific surface, renewable utilization, and excellent mechanical property (Chen *et al.* 2015; Zhu *et al.* 2018; Guan *et al.* 2020). An aerogel can be prepared in various shapes and sizes based on its different applications from various raw materials. In recent years, the bio-based aerogel has attracted increasing attention such as lignocellulose-based aerogel, collagen-based aerogel, and chitosan-based aerogel due to the depletion of petroleum resources (Kadib and Bousmina 2012; Lu *et al.* 2014; Guan *et al.* 2020; Lv *et al.* 2021). However, hemicellulose-based aerogel has rarely been reported in recent years, especially the cationic hemicellulose-based aerogel for adsorbing the impurities in processing water.

Hemicelluloses, one of the three major cell wall components of lignocellulosic biomass besides cellulose and lignin, can be produced annually at about 60 billion tons (Naik *et al.* 2010). They have attracted abundant attention due to their renewability, biodegradability, biocompatibility, and non-toxic properties (Zhang *et al.* 2011; Li and Pan 2018; Gao *et al.* 2023). Nowadays, hemicelluloses are mainly used for manufacturing pulp and paper products in practical applications, and some high value-added hemicelluloses-based functional composites including hydrogels, aerogels, films, drug delivery, and sensor due to their above properties also have been reported (Sun *et al.* 2013; Alekhina *et al.* 2014; Anthony *et al.* 2015; Chen *et al.* 2016; Rao *et al.* 2019; Guan *et al.* 2020). However, the native hemicelluloses process has relatively narrow application fields because of the chemical and physical natures of hemicelluloses. Chemical modification of hemicelluloses provides a better manner for fabricating functional composites with unique properties and wider applications. Cationization is a practical and feasible way to introduce functional amino groups and enables hemicelluloses-based composites as efficient adsorbents for anionic contaminants in wastewater.

Different from cellulose, which is a linear homopolysaccharide of glucose, hemicelluloses are branched heteropolysaccharides and composed of different neutral and acidic monosaccharides (Li and Pan 2018). Especially due to the lower molecular weight, hemicellulose alone is unable to prepare unique aerogels. In order to enhance the formability and strength of hemicelluloses-based aerogel, other components should be added. As a semicrystalline polymer, polyvinyl alcohol (PVOH) is often used as an additive to enhance mechanical properties of biomass-based materials due to its excellent mechanical properties, high hydrophilicity, biodegradability and biocompatibility (Hong et al. 2014; Ai et al. 2021; Joshi et al. 2022). PVOH-based aerogels with excellent properties have been utilized for water-oil separation, adsorption of metal ions, treatment of wastewater, and flame retarding (Kim et al. 2015; Zhang et al. 2019; Wang et al. 2021; Yang et al. 2022a; Joshi et al. 2022). PVOH microcrystals can be formed through freezing operation, in which PVOH molecular chains are entangled and form hydrogen bonds with other substances (Chen et al. 2010). Agarose is a copolymer with alternant linkages of 1,3linked β-D-galactose and 1,4-linked 3,6-anhydrous-L-galactose (Pierre and Pajonk 2002). The agarose gel with relatively larger pores can be prepared through lateral aggregation of agarose chains based on the hydrogen bonds (Griess et al. 1998). The multifunctional agarose-based aerogels can be obtained through combining agarose with organic or inorganic compounds (Wu et al. 2019; Yang et al. 2022b).

Xylan is the principal component of the hemicelluloses in hardwood and agriculture residues with a content of 20-35% (Willför *et al.* 2005). In the present study, the cationic xylan-based aerogel combined with PVOH, and agarose was successfully fabricated by freeze-drying approach for the first time, in which the PVOH as reinforcement phase and agarose as gelling phase. The composite aerogel was subsequently applied to adsorb the anionic pectin which was considered as the typical representative of anionic substances present in white water of paper industry. The characterizations of cationic xylan/PVOH/agarose aerogel were conducted by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscope (SEM), and mechanical properties. Finally, the adsorption of aniconic pectin with the obtained composite aerogel was investigated.

EXPERIMENTAL

Materials

The bagasse xylan was purchased from Shanghai Yuanju Biotechnology Co., LTD in China. The cationic xylan (CX) with a substitution degree of 0.81 was prepared in lab by radical polymerization using acryloxyethyl trimethyl ammonium chloride as the cationic monomer and potassium persulfate as the initiator at 70 °C for 3 h. The cationic xylan was washed with ethanol and separated by centrifugation. The molecular weight (Mw) of cationic xylan was 25033 g/mol. Polyvinyl alcohol (alcoholysis degree of 98-99%) was purchased from Macklin Chemical Reagents Co., Ltd. Agarose, pectin, and poly(diallyldimethylammonium chloride) whose concentration was 1.0051×10^{-3} mol/L were supplied by Aladdin Reagents Co., Ltd. All the reagents used in this experiment were all analytical-grade reagents. All experiments were performed using deionized water.

Preparation of Cationic Xylan-based Aerogel

Cationic xylan-based aerogel, whose total weight was set as 2.0 g, was prepared by the following procedure. First, the agarose and PVOH were respectively dissolved in deionized water by homogeneously stirring in an oil bath, resulting in two transparent solutions of 3% agarose (w/v) and 4% PVOH (w/v). The PVOH and agarose solutions were mixed at a fixed mass ratio of 1:1, and the total volume of the mixture was 50 mL. Then the mixture was stirred for 5 min at 120 °C and for another 15 min at 90 °C. Subsequently, the cationic xylan was added into the above mixture and continued stirring for 10 min at 90 °C. Finally, the gel solution was transferred into a Teflon mold and cooled to room temperature. Then the gel solution was pre-frozen at a refrigerator under -24 °C, which was followed with quick-freezing by liquid nitrogen. The CX/agarose/PVOH aerogel was successfully prepared after final freeze-drying at -60 °C for 48 h. The control aerogel was prepared by a similar method just without addition of cationic xylan.

Characterization of Cationic Xylan-based Aerogel

Mechanical properties of aerogel were determined by a tension & compression testing machine (KJ-1065B, Kejian, Dongguan, China). The cylindrical aerogel with the dimension of 25×20 mm (diameter×height) was placed in the fixture of the testing machine. The upper pressure plate was adjusted to the top surface of aerogel. Then the loading rate and strain was set at 1 mm/min and 50%, respectively. Five parallel tests were conducted for each kind of aerogel sample.

FT-IR spectra of aerogels were recorded on a Nicolet iS20 equipment (Thermo Fisher Scientific, America). The aerogel samples were pre-dried and ground with potassium bromide into powder uniformly before test. The resolution was 4 cm⁻¹, and the spectra range was 400 to 4000 cm⁻¹.

The crystallinity of aerogels was determined based on the area of diffraction peaks with X-ray diffraction method on a D8 Advance spectrometer (Bruker, French). The samples were scanned in the range of 10 to 80° of 2θ with a step size of 10°/min.

Scanning electron microscope (SEM) (Tescan Mira, Czech) was used to characterize the structural morphology of aerogels. The aerogel samples were golden-coated prior to SEM observed. The porosity of aerogels was calculated by Image-Pro Plus 6.0 based on the SEM images.

The thermogravimetric analysis of aerogels was carried out by a STA449F3 simultaneous thermal analyzer (Netzsch, Germany). About 20 mg of the aerogel sample was heated from 25 to 500 °C at a heating rate of 20 °C/min. The apparatus was continually flushed with a nitrogen flow of 50 mL/min.

The specific surface area and the pore size of aerogels were determined according to the nitrogen adsorption method by using an ASAP 2460 volumetric gas adsorption instrument (Micromeritics, America) at 25 °C. The aerogels were air-dried prior to the measurements.

The density and the porosity of aerogels was calculated according to the following equation (1) and equation (2), respectively (Chen *et al.* 2011),

$$\rho = m \times (h\pi)^{-1} \times (d/2)^{-2} \tag{1}$$

$$P = (1 - \rho/\rho') \times 100\%$$
 (2)

where *P* is the porosity of aerogel (%); ρ is the density of aerogel (g/cm³); ρ' is the density of mixture of agarose, PVOH, and cationic xylan (g/cm³); *m* is the dry weight of aerogel (g), *h* is the height of aerogel (cm), *d* is the diameter of aerogel (cm).

Adsorption of Pectin with Cationic Xylan-based Aerogel

The adsorption experiment was performed as follows. Firstly, the aerogel was added into 50 mL pectin solution of 0.5 g/L, and then the solution was shaken at certain temperature until reaching the adsorption equilibrium. Next, the solution was filtered by a membrane (pore size of $0.22 \,\mu$ m), and the cationic demand of filtrate was determined by a charge titration instrument (PCD-03, BTG, Sweden) using poly (diallyldimethyl-ammonium chloride) as standard titrant. The concentration of pectin before and after adsorption was calculated based on the cationic demand value according to the standard equation as shown in Fig.1. The amount of adsorbed pectin by aerogel was calculated water and ethanol, and then was reused after freeze-drying,

$$q = (C_0 - C_x) V/m$$
 (3)

where *q* is the amount of adsorbed pectin (mg/g); C_0 and C_x is the initial and equilibrium pectin concentration (mg/L), respectively; *V* is the volume of pectin solution (mL); *m* is the dry weight (g) of aerogel.



Fig. 1. Standard curve of concentration and cationic demand of pectin solution

RESULTS AND DISCUSSION

Physical Characteristics of the Aerogels

In the present investigation, the total weight of the CX/agarose/PVOH composite aerogel was set to 2.0 g, and the mass ratio of agarose and PVOH was fixed to be 1:1. The weight of cationic xylan was changed as the mass ratio in the CX/agarose/PVOH composite aerogels. The mass ratio of cationic xylan was increased while the weight of agarose and PVOH was proportionally decreased in order to take full advantage of the xylan. For example, the CX_{2.5}/agarose/PVOH referred to the mass ratio of CX:agarose:PVOH was 2.5:1:1, namely the absolute weight of CX, agarose, and PVOH was 1.11 g, 0.445 g, and 0.445 g, respectively.

The physical structure of CX/agarose/PVOH aerogel was an important factor affecting its practical application. The CX/agarose/PVOH aerogels were characterized based on the density, porosity, pore diameter, and specific surface area, as shown in Table 1. It can be found that the addition of cationic xylan decreased the density and the pore diameter of the CX/agarose/PVOH aerogels, but the specific surface area was increased. Though the porosity of the composite aerogels was decreased slightly, the values of porosity exceeded 93% which was higher than that of PVOH aerogel (Nabipour *et al.* 2020). The results indicated that the addition of cationic xylan was conducive to the formation of micropore structure of the composite aerogels. However, the decreased specific surface aera of CX/agarose/PVOH aerogel was found when the mass ratio of cationic xylan exceeded 2.5. It may be caused by the decreased content of agarose leading to the poorer microgelation.

The mechanical strength of the aerogel is another significant property for its practical application. Fig. 2A displays the strain-stress curves of the CX/agarose/PVOH aerogels under compressive mode. Apparently, the addition of cationic xylan improved the mechanical property of the CX/agarose/PVOH aerogels compared with that without cationic xylan. The compressive strength and elasticity of CX/agarose/PVOH aerogels increased initially and then decreased with the increase of mass ratio of cationic xylan. When the mass ratio of cationic xylan was 2.5, the compressive stress of CX_{2.5}/agarose/PVOH aerogel reached the maximum value of 34.7 MPa at 50% strain, and the stress remained 54.7% relative to the first compressive stress (Fig. 2B), though the aerogel was reciprocally compressed for 50 times. The mass ratio of cationic xylan was

further increased to 3, whereas the mechanical strength of CX₃/agarose/PVOH was decreased. It might have been induced by the decreased weight of the other two components because the agarose contributed to the gelatinization and the PVOH contributed to the strength of CX/agarose/PVOH aerogels. Moreover, the larger pore size may be responsible for the decreased mechanical strength of CX₃/agarose/PVOH aerogels. The stress of all the CX/agarose/PVOH aerogels was distinctly higher than that reported in the literature (Guan *et al.* 2020), in which the aerogel was prepared with dialdehyde xylan and chitosan, and the maximum stress of the dialdehyde xylan/chitosan aerogel was only 0.38 MPa.

Aerogel Sample	Density (g/cm ³)	Porosity (%)	Pore Diameter (nm)	Specific Surface Area (m²/g)
agarose/PVOH	0.087	94.63	5.8004	0.7118
CX ₁ /agarose/PVOH	0.065	94.51	5.5093	0.8237
CX _{2.5} /agarose/PVOH	0.062	93.82	4.4551	1.7888
CX ₃ /agarose/PVOH	0.064	93.41	5.3288	1.0816

Table 1. Physical Characteristics of the Composite Aerogels



Fig. 2. The stress and strain of the aerogels

FT-IR Analysis of the Composite Aerogels

The FT-IR spectra of agarose/PVOH aerogel and three CX/agarose/PVOH aerogels are shown in Fig. 3. In the four composite aerogels, there are three components of PVOH, agarose, and cationic xylan, and they process plenty of hydroxyl groups (Yan *et al.* 2021). The cationic xylan also has some amino groups. The adsorption band around 3400 cm⁻¹ corresponds to the stretching of hydroxyl groups of xylan, agarose, and PVOH. The peaks at 1041, 1043, 1048, and 1090 cm⁻¹ in CX/agarose/PVOH aerogels were attributed to the stretching vibration of C-O-C ether bond providing evidence of the ether linkages present in cationic xylan (Ren *et al.* 2007). The addition of cationic xylan led to the appearance of the peak of 890 cm⁻¹, which was the characteristic bond of β -glycosidic bond between the xylose units (Ren *et al.* 2007; Kong *et al.* 2018). The band at 2931 cm⁻¹ was attributed to the symmetric C-H vibration (Wang *et al.* 2016). The peaks at 1435, 1446, and 1470 cm⁻¹ were assigned to the methyl group in ammonium. There was a strong sharp absorbance around 1720 cm⁻¹, which was the characteristic peak of carbonyl group from uronic acid (Liu *et al.* 2011). The peaks around 1650 cm⁻¹ were attributed to the H-O-H angle vibration originated from hydrogen bonds among the three components by freeze-drying method (Haxaire *et al.* 2003; Guan *et al.* 2014). It can be found that the intensity of the absorption band around 3430 cm⁻¹ became weaker than that of the agarose/PVOH aerogel with the increase of mass ratio of cationic xylan in the composite aerogels, indicating that the decrease of -OH groups. This may be caused by the decreased amount of agarose and PVOH. Furthermore, the absorption frequency around 3430 cm⁻¹ moves toward the lower wave number confirming the formation of hydrogen bonds between cationic xylan, agarose, and PVOH (Yan *et al.* 2021). As there are no other new peaks observed, it can be deduced that there was no chemical interaction among agarose, PVOH, and cationic xylan. Therefore, it can be inferred that cationic xylan, agarose, and PVOH have a physical interaction with the forming of hydrogen bonding.



Fig. 3. FT-IR spectra of the composite aerogels

Crystallinity of the Composite Aerogels

The X-ray diffraction technique was used to determine the variations in crystalline structure as a result of addition of cationic xylan to the agarose/PVOH aerogel. Figure 4 shows the X-ray diffraction patterns of the composite aerogels. As to the agarose/PVOH aerogel, the diffraction peak at 2θ = 19.9°, which is a typical fingerprint of PVOH and represented the obvious semicrystalline phase of PVOH, was observed (Yan *et al.* 2021). The addition of cationic xylan changed the X-ray diffraction patterns of composite aerogels. All the aerogels of CX/agarose/PVOH exhibited a crystalline structure with peaks angle around 2θ =10.6°, 12.2°, 22.0°, and 24.5°. In Li and Xiang's study, the deacetylated xylan also has the same XRD patterns as the authors' study (Li and Xiang 2022). The diffraction

peak of cationic xylan at 2θ = 19.9° overlapped with that of PVOH (Peng *et al.* 2011). Compared with the agarose/PVOH aerogel, it is noticeable that the crystallinity of CX/agarose/PVOH aerogels decreased obviously with the increasing amount of cationic xylan, as shown in Table 2. The decreased crystallinity was mainly caused by the decreased amount of PVOH in the CX/agarose/PVOH aerogels. Moreover, the hydrogen bonds formed by -OH and -O- in cationic xylan with the O-H group in PVOH would destroy the ordered PVOH molecular chain, thereby reducing the crystallinity of PVOH and CX/agarose/PVOH aerogels. As reported in Yan's investigation, the formation of hydrogen bonds between -OH and -O- in agarose with the O-H group in PVOH decreased the crystallinity of PVOH (Yan *et al.* 2021). The decreased crystallinity was also beneficial for the improvement of flexibility, as shown in Fig. 2A.



Fig. 4. X-ray diffraction patterns of the composite aerogels

 Table 2. Crystallinity of the Composite Aerogels

Aerogel Sample	agarose/PVOH	CX ₁ /agarose/PVOH	CX _{2.5} /agarose/PVOH	CX ₃ /agarose/PVOH
Crystallinity (%)	62.66	51.53	51.25	50.36

Thermal Properties of the Composite Aerogels

The composite aerogels were also characterized by thermogravimetry (TGA) to determine thermal stability. The typical TGA-DTG curves of the two composite aerogels were shown in Fig. 5. In the TGA curves (Fig. 5A), small weight losses were observed below 100 °C due to the apparent evaporation of absorbed water from the aerogels (Guan *et al.* 2020). The gently weight losses of four aerogels were observed during 100 °C and 250 °C.



Fig. 5. TGA thermogram curves (A) and DTG curves of the composite aerogels (B)

From 250 to 400 °C, the weight losses increased obviously. However, there was still more than 17.0% of residual masses left when the temperature reached 500 °C from the TGA curves of the four composite aerogels. The onset decomposition temperatures of four aerogels were all below 100 °C. It can be also found from Fig. 5B that the maximum decomposition temperatures of the three aerogels were all at around 375 °C, while the maximum decomposition rate of agarose/PVOH aerogel at 425 °C was higher than that of CX/agarose/PVOH aerogels, indicating that the thermal stability of agarose/PVOH aerogel was higher than that of CX/agarose/PVOH aerogels. The lower thermal stability of CX/agarose/PVOH aerogel might be due to the addition of cationic xylan.

Microstructure of the Composite Aerogels

The microstructure of the composite aerogels was demonstrated by scanning electron microscopy (SEM) images (Fig. 6). As shown in the figures, compared with the agarose/PVOH aerogel, a more regular porous structure of the CX/agarose/PVOH aerogels was found, indicating the three-dimensional network was successfully formed from cationic xylan, PVOH, and agarose during the gelation process. The crosslinking reaction among three components of the composite aerogels mainly resulted from the formation of hydrogen bonds which interpenetrated three-dimensional CX/agarose/PVOH network, offering large amounts of channels for the movement of pectin (Yan *et al.* 2021). Interestingly, the CX_{2.5}/agarose/PVOH aerogel had more and smaller intact pores, which was consistent with its higher specific surface area. The results showed that the proportion of CX had a greater impact on the pore structure of aerogels. This porous structure of aerogels could provide an important prerequisite for the adsorption of anionic substances present in papermaking white water. As shown in Fig. 6C, it can also be found that the composite aerogel was very light that could be placed on the surface of the grass leaf.

Adsorption of Pectin with Cationic Xylan-based Aerogel

The adsorption capacities of the composite aerogels for removal of aniconic pectin and the optimized adsorption process were demonstrated in Fig. 7. As shown in Fig. 7A, the CX_{2.5}/agarose/PVOH aerogel had the highest adsorption capacity of pectin reaching 19.52 mg/g among the four composite aerogels when they were used for adsorbing anionic pectin at 25 °C and initial pectin concentration of 0.5 mg/mL for 60 min. The optimized adsorption parameters, which are shown in Fig. 7 (B-D), were as follows: temperature of 40 °C, time of 60 min, and initial pectin concentration of 0.5 mg/mL.

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Fig. 6. SEM images (A) agarose/PVOH aerogel, (B) CX_1 /agarose/PVOH aerogel, (C) $CX_{2.5}$ /agarose /PVOH aerogel, (D) CX_3 /agarose/PVOH aerogel



Fig. 7(A, B). The optimization of adsorption process of pectin with the composite aerogels



Fig. 7(C, D). The optimization of adsorption process of pectin with the composite aerogels

As is well known, it is very significant for solid adsorbents to carry out continuous operation in industrial practice. The reusability of aerogel is thus very important for its continuous practical application. The relative adsorption efficiency of $CX_{2.5}$ /agarose/PVOH aerogel after five cycles is illustrated in Fig. 8. It was observed that the relative adsorption efficiency retained more than 81% of the original adsorption efficiency after the fifth cycle. The decrease of the relative adsorption efficiency after recycling may be induced by the breakdown of pore structure leading to the reduction of available adsorbing sites during the extraction process.



Fig. 8. Recycling performance of CX_{2.5}/agarose/PVOH aerogel

CONCLUSIONS

1. The cationic xylan-based aerogels were successfully fabricated by freeze-drying technique. The three-dimensional network structure of aerogels was proved by the scanning electron microscopy (SEM) images. The hydrogen bonds were responsible for the formation of aerogels. The addition of cationic xylan led to the decrease of crystallinity and thermal stability of the composite aerogels.

- The cationic xylan (CX)/agarose/poly(vinylalcohol) (PVOH) aerogels had a high mechanical strength. When the mass ratio of cationic xylan, agarose, and PVOH was 2.5:1:1 in the composite aerogel, the compressive stress of aerogel could reach more than 34.0 MPa at 50% strain, and the density and porosity was 0.062 cm³/g and 93.8%, respectively.
- 3. The addition of cationic xylan improved the adsorption capacity of anionic pectin, and the maximum adsorption capacity of pectin could reach 19.5 mg/g for CX_{2.5}/ agarose /PVOH aerogel. Moreover, the aerogel could be effectively recycled, and the relative adsorption efficiency retained more than 81% of the original adsorption efficiency after the fifth cycle.

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REFERENCES CITED

- Alekhina, M., Mikkonen, K. S., Alén, R., Tenkanen, M., and Sixta, H. (2014).
 "Carboxymethylation of alkali extracted xylan for preparation of bio-based packaging films," *Carbohydr. Polym.* 100, 89-96. DOI: 10.1016/j.carbpol.2013.03.048
- Anthony, R., Xiang, Z.-Y., and Runge, T. (2015). "Paper coating performance of hemicellulose-rich natural polymer from distiller's grains," *Prog. Org. Coat.* 89, 240-245. DOI: 10.1016/j.porgcoat.2015.09.013
- Ai, J., Li, K., Li, J., Yu, F., and Ma, J. (2021). "Super flexible, fatigue resistant, selfhealing PVOH/xylan/ borax hydrogel with dual-crosslinked network," *Int. J. Biol. Macromol.* 172, 66-73. DOI: 10.1016/j.ijbiomac.2021.01.038
- Chen, C., Zhu, Y.-H., Bao, H., Yang, X.-L., and Li, C.-Z. (2010). "Physically controlled cross-linking in gelated crystalline colloidal array photonic crystals," ACS Appl. Mater. Interfaces 2, 1499-1504. DOI: 10.1021/am100130n
- Chen, W. -S., Yu, H.-P., Li, Q., Liu, Y.-X., and Li, J. (2011). "Ultralight and highly flexible aerogels with long cellulose I nanofibers," *Soft Matter* 7, 10360-10368. DOI: 10.1039/C1SM0617-9H
- Chen, H., Wang, X., Li, J., and Wang, X.-K. (2015). "Cotton derived carbonaceous aerogels for the efficient removal of organic pollutants and heavy metal ions," *J. Mater. Chem. A*, 3, 6073-6081. DOI: 10.1039/c5ta00299k
- Chen, G.- G., Qi, X.-M., Guan, Y., Peng, F., Yao, C.-L., and Sun, R.-C. (2016). "High strength hemicellulose-based nanocomposite film for food packaging applications," *ACS Sustain. Chem. Eng.* 4, 1985-1993. DOI:10.1021/acssuschemeng.5b01252
- Dunham, A., Sherman, L., and Alfano, J. (2002). "Effect of dissolved and colloidal substances on drainage properties of mechanical pulp suspensions," *J. Pulp Pap. Sci.* 28, 296-310.
- Gao, Y.-N., Guo, M.-K., Wang, D.-D., Zhao, D.-Q., and Wang, M.-X. (2023). "Advances in extraction, purification, structural characteristics and biological activities of

hemicelluloses: A review," Int. J. Biol. Macromol. 225, 467-483. DOI:10.1016/j.ijbiomac.2022.11.099

- Griess, G. A., Guiseley, K. B., Miller, M. M., Harris, R. A., and Serwer, P. (1998). "The formation of small-pore gels by an electrically charged agarose derivative," *J. Struct. Biol.* 123, 134-142. DOI: 10.1006/jsbi.1998.4021
- Guan, Y., Peng, F., Bian, J., and Sun, R.-C. (2014). "High strength of hemicelluloses based hydrogels by freeze/thaw technique," *Carbohydr. Polym.* 101, 272-280. DOI: 10.1016/j.carbpol.2013.08.085
- Guan, Y., Rao, J., Wu, Y., Gao, H., Liu, S.-Q., Chen, G.-G., and Peng, F. (2020).
 "Hemicelluloses-based magnetic aerogel as an efficient adsorbent for Congo red," *Int. J Biol. Macromol.*, 155, 369-375. DOI: 10.1016/j.ijbiomac.2020.03.231
- Haxaire, K., Maréchal, Y., Milas, M., and Rinaudo, M. (2003). "Hydration of polysaccharide hyaluronan observed by IR spectrometry I. Preliminary experiments and band assignments," *Biopolymers* 72, 10-20. DOI:10.1002/bip.10245
- Hubbe, M. A., Sundberg, A., Mocchiutti, P., Ni, Y., and Pelton, R. (2012). "Dissolved and colloidal substances (DCS) and the charge demand of papermaking process waters and suspensions: A review," *BioResources* 7(4), 6109-6193.
- Joshi, P., Raturi, A., Srivastava, M., and Khatri, O. P. (2022). "Graphene oxide, kaolinite clay and PVOH-derived nanocomposite aerogel as a regenerative adsorbent for wastewater treatment applications," *J. Environ. Chem. Eng.* 10, article 108597. DOI: 10.1016/j.jece.2022.108597
- Kadib, A., and Bousmina, M. (2012). "Chitosan bio-based organic-inorganic hybrid aerogel microspheres," *Chem. Eur. J.* 18, 8264-8277. DOI: 10.1002/chem.201104006
- Kim, H. M., Noh, Y. J., Yu, J.-S., Kim, S. Y., and Youn, J. R. (2015). "Silica aerogel/polyvinyl alcohol (PVOH) insulation composites with preserved aerogel pores using interfaces between the superhydrophobic aerogel and hydrophilic PVOH solution," *Compos. Part A-Appl. S.*, 75, 39-45. DOI: 10.1016/j.compositesa.2015.04.014
- Kong, F., Guo, Y., Liu, Z., Wang, S., and Lucia, L. A. (2018). "Synthesis of cationic xylan derivatives and application as strengthening agents in papermaking," *BioResources* 13(2), 2960-2976. DOI:10.15376/biores.13.2.2960-2976
- Lindström, T., Söremark, C., and Westman, L. (1977). "The influence on paper strength of dissolved and colloidal substances in the white water," *Sevensk Papperstidn*. 80, 3141-345.
- Li, Z., and Pan, X. (2018). "Strategies to modify physicochemical properties of hemicelluloses from biorefinery and paper industry for packaging material," *Rev. Environ. Sci. Biotechnol.* 17, 47-69. DOI: 10.1007/s11157-018-9460-7
- Li, L., and Xiang, Z. (2022). "Crystallization properties of acetylated β -(1-4)-D-xylan," *Cellulose* 28, 107-115. DOI: 10.1007/s10570-021-04277-9
- Liu, Z., Ni, Y., Fatehi, P., and Saeed, A. (2011). "Isolation and cationization of hemicelluloses from pre-hydrolysis liquor of kraft-based dissolving pulp production process," *Biomass and Bioenergy* 35, 1789-1796. DOI: 10.1016/j.biombioe.2011.01.008
- Lu, J.-B., Xu, K., Yang, J.-M., Hao, Y.-R., and Cheng, F. (2017). "Nano iron oxide impregnated in chitosan bead as a highly efficient sorbent for Cr(VI) removal from water," *Carbohydr. Polym.* 173, 28-36. DOI: 10.1016/j.carbpol.2017.05.070
- Lu, T.-H., Li, Q., Chen, W.-S., and Yu, H.-P. (2014). "Composite aerogels based on dialdehyde nanocellulose and collagen for potential applications as wound dressing

and tissue engineering scaffold," *Compos. Sci. Technol.* 94, 132-138. DOI: 10.1016/j.compscitech.2014.01.020

- Lv, Y.-C., Liang, Z.-X., Li, Y.-H., Chen, Y.-C., Liu, K.-Y., Yang, G.-F., Liu, Y.-F., Lin, C.-X., Ye, X.-X., Shi, Y.-Q., and Liu, M.-H. (2021). "Efficient adsorption of diclofenac sodium in water by a novel functionalized cellulose aerogel," *Environ. Res.* 194, article 110652. DOI: 10.1016/j.envres.2020.110652
- Miao, Q., Huang, L., and Chen, L. (2013). "Advances in the control of dissolved and colloidal substances present in papermaking processes: a brief review," *BioResources* 8, 1431-1455. DOI: 10.15376/biores.8.1.1431-1455
- Miao, Q.-X., Zhong, G.-Z., Qin, M.-H., Chen, M.-H., and Huang, L.-L. (2014).
 "Influence of alkaline treatment and alkaline peroxide bleaching of aspen chemithermomechanical pulp on dissolved and colloidal substances," *Ind. Eng. Chem. Res.* 53, 2544-2548. DOI: 10.1021/ie4040785
- Nabipour, H., Nie, S., Wang, X., Song, L., and Hu, Y. (2020). "Zeolitic imidazolate framework-8/polyvinyl alcohol hybrid aerogels with excellent flame retardancy," *Compos. Part A-Appl. S.*, 129, article 105720. DOI: 10.1016/j.compositesa.2019.105720
- Naik, S. N., Goud, V. V., Rout, P. K., and Dalai, A. K. (2010). "Production of first and second generation biofuels: A comprehensive review," *Renew. Sustain. Energy. Rev.* 14, 578-597. DOI: 10.1016/j.rser.2009.10.003
- Peng, X.-W., Ren, J.-L., Zhong, L.-X., and Sun, R.-C. (2011). "Nanocomposite films based on xylan-rich hemicelluloses and cellulose nanofibers with enhanced mechanical properties," *Biomacromolecules* 12, 3321-3329. DOI: 10.1021/bm2008795
- Pierre, A. C., and Pajonk, G. M. (2002). "Chemistry of aerogels and their applications," *Chem. Rev.* 102, 4243-4265. DOI: 10.1021/cr0101306
- Rao, J., Gao, H., Guan, Y., Li, W.-Q., and Liu, Q. (2019). "Fabrication of hemicelluloses films with enhanced mechanical properties by graphene oxide for humidity sensing," *Carbohydr. Polym.* 2018, 513-520. DOI: 10.1016/j.carbpol.2018.12.099
- Ren, J.-L., Sun, R.-C., Liu, C.-F., Lin, L., and He, B.-H. (2007). "Synthesis and characterization of novel cationic SCB hemicelluloses with a low degree of substitution," *Carbohydr. Polym.* 67, 347- 357. DOI: 10.1152/ajplung.00168.2012
- Sun, X.-F., Wang, H.-H., Jing, Z.-X., and Mohanathas, R. (2013). "Hemicellulose-based pH-sensitive and biodegradable hydrogel for controlled drug delivery," *Carbohydr. Polym.* 92, 1357-1366. DOI: 10.1016/j.carbpol.2012.10.032
- Wang, S.-J., Konduri, M. K. R., Hou, Q.-X., and Fatehi, P. (2016). "Cationic xylan-METAC copolymer as a flocculant for clay suspensions," *RSC Adv.* 6, 40258-40269. DOI: 10.1039/C6RA05223A
- Wang, X.-W., Deng, X., Wu, L.-L., Deng, Y.-M., Liu, Q., Li, M., and Li, Z. (2021). "Facile preparation of mechanically strong polyvinyl alcohol/MTMS aerogel composites with improved thermal stability," *J. Nanopart. Res.* 23, 261. DOI: 10.1007/s11051-021-05372-5
- Willför, S., Sundberg, A., Pranovich, A., and Holmbom, B. (2005). "Polysaccharides in some industrially important hardwood species," *Wood Sci. Technol.* 39, 601-617. DOI: 10.1007/s00226-005-0039-4

- Wu, X., Robson, M. E., Phelps, J. L., Tan, J. -S., Shao, B., Owens, G., and Xu, H.-L. (2019). "A flexible photothermal cotton-CuS nanocage-agarose aerogel towards portable solar steam generation," *Nano Energy*, 56, 708-715. DOI: 10.1016/j.nanoen.2018.12.008
- Yang, C., Yang, H., and An, Q. (2022a). "Recyclable CMC/PVOH/MIL-101 aerogels with tailored network and affinity sites for efficient heavy metal ions capture," *Chem. Eng. J.* 447, 2-13. DOI: 10.1016/j.cej.2022.137483
- Yang, X., Jiang, P.-J., Xiao, R., Fu, R., Liu, Y.-H., Ji, C., Song, Q.-Q., Miao, C.-Q., Yu, H.-Q., Gu, J., Wang, Y.-X., and Sai, H.-Z. (2022b). "Robust silica-agarose composite aerogels with interpenetrating network structure by in situ sol-gel process," *Gels* 8, 303-317. DOI: 10.3390/gels8050303
- Yan, T.-T., Zou, Y.-H., Zhang, X.-H., Li, D.-H., Guo, X.-X., and Yang, D.-J. (2021). "Hydrogen bond interpenetrated agarose/PVOH network: a highly ionic conductive and flame-retardant gel polymer electrolyte," ACS Appl. Mater. Interfaces 13, 9856-9864. DOI: 10.1021/acsami.0c20702
- Zhang, X., Beatson, R., Cai, Y., and Saddler, J. (1999). "Accumulation of specific dissolved and colloidal substances during white water recycling affects paper properties," J. Pulp Pap. Sci. 25, 206-210.
- Zhang, Y., Pitkänen, L., Douglade, J., Tenkanen, M., Remond, C., and Joly, C. (2011). "Wheat branarabinoxylans: Chemical structure and film properties of three isolated fractions," *Carbohydr. Polym.* 86, 852-859. DOI: 10.1016/j.carbpol.2011.05.036
- Zhang, Q.-R., Wang, X.-Y., Tao, X.-J., Li, Z.-W., Li, X.-H., and Zhang, Z.-J. (2019). "Polyvinyl alcohol composite aerogel with remarkable flame retardancy, chemical durability and self-cleaning property," *Compos. Commun.* 15, 96-102. DOI: 10.1016/j.coco.2019.07.003.8b00566
- Zhu, L.-T., Zong, L., Wu, X.-C., Li, M.-J., Wang, H.-S., You, J., and Li, C.-X. (2018). "Shapeable fibrous aerogels of metal-organic -frameworks templated with nanocellulose for rapid and large-capacity adsorption," ACS Nano 12, 4462-4468. DOI: 10.1021/acsnano.8b00566

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