



Sorption of anionic polysaccharides by cellulose

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ABSTRACT

The sorption of anionic polysaccharides pectin, alginate, and xanthan with cellulose were investigated in presence of calcium. Calcium sorption to cellulose was limited by the carboxyl group content in fibers. Atomic Absorption Spectroscopy (AAS) analysis was used to measure the calcium in cellulose fibers and chemical oxygen demand (COD) analysis reveals that the divalent ions calcium can bind the polysaccharide onto cellulose fibers. The amount of calcium and polysaccharide bound in Ca^{2+} /polysaccharide modified cellulose fibers was 5.8–12.5 mM Ca^{2+} /kg fibers and 1500–2400 mg polysaccharide/kg fibers, respectively. Fourier Transform Infrared Spectroscopy–Attenuated Total Reflectance (FTIR–ATR) analysis confirmed the presence of polysaccharide on calcium containing cellulose fibers. The results of alizarin dyeing experiments at the end of polysaccharide sorption further confirmed the presence of calcium in Ca^{2+} /polysaccharide modified cellulose fibers. The basic phenomenon of interaction of soluble ionic polysaccharide and cellulosic fibers in presence of divalent cations such as calcium is a key to understand biological functions and technological applications.

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1. Introduction

Polysaccharides are complex carbohydrate polymers consisting of two or more monosaccharide units. Cellulose is a natural biodegradable homopolysaccharide with the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, consisting of a linear chain of β (1 → 4) linked D-glucose units (Emsley & Stevens, 1994; Hon, 1994). The amorphous regions of cellulose have greater accessibility to solvent or solution penetration than crystalline regions and act as an insoluble carbohydrate type ligand (Fitz-Binder & Bechtold, 2009). Cellulose has many dissociable groups which also influence the adsorption and strength properties of cellulose fibers (Horvath & Lindstrom, 2007).

Pectin is a family of complex heterogeneous polysaccharides, usually amorphous with degree of polymerization around 200–400 units (Calafell, Klug-Santner, Guebitz, & Garriga, 2005; Rolin, Nielsen, & Glahn, 1998). The major constituent of pectin is a linear sequence of 1,4-linked α -D-galacturonic acid units. The galacturonic acid unit determines the functional properties of the

pectin (Yadav, Yadav, & Yadav, 2007). Alginate is a collective term for a family of linear 1,4-linked α -L-guluronic- β -D-mannuronans of widely varying composition and sequential structure. The degree of polymerization of alginate is between 300 and 1500 units (Shirai, Hashimoto, & Irie, 1989). The main sources of this water soluble polysaccharide are various species of marine brown algae (Davis, Volesky, & Mucci, 2003; Zhang et al., 2004).

Xanthan gum is a microbial extracellular heteropolysaccharide. Xanthan contains a cellulosic backbone, with a trisaccharide side chain on every second glucose residue (Stokke, Christensen, & Smidsrod, 1998). The molecular weight of xanthan gum is very high ($>10^6$), the polymer contains D-glucose, D-mannose, D-glucuronate as well as acetyl, and pyruvate units (Argin-Soysal, Kofinas, & Lo, 2009; Hamcerencu, Desbrieres, Popa, Khokh, & Riess, 2007).

These polysaccharides have wide range of applications in many fields such as biological function, food, textile, paper, pharmaceuticals, agricultural, paint, and petroleum industries (Kennedy & Bradshaw, 1984; Sabra & Deckwer, 2005; Sandford, Cottrell, & Pettitt, 1984; Sikorski, Mo, Skjak-Break, & Stokke, 2007). Therefore adsorption of these polysaccharides to cellulose fibers will offer many advantages because of their biological activity, non toxicity, biodegradability, and biocompatibility.

The structure of the different polysaccharides used in this study is shown in Fig. 1.

The interactions of polysaccharide with cellulose have recently been gained considerable attention and the polysaccharide/cellulose interactions were suggested by some authors (Chanliaud & Gidley, 1999; Mishima, Hisamatsu, York, Teranishi, & Yamada, 1998; Rakkolainen et al., 2009; Teeri, Brumer, Daniel,

Abbreviations: CV, Viscose; CLY, Lyocell; RH, Relative humidity (%); MC, Moisture content (%); DM, Demineralised; PS, Polysaccharide; COD, Chemical oxygen demand; AES, Atomic emission spectroscopy; AAS, Atomic Absorption Spectroscopy; MB, Methylene blue; FTIR–ATR, Fourier Transform Infrared Spectroscopy–Attenuated Total Reflectance; ESEM, Environmental scanning electron microscopy.

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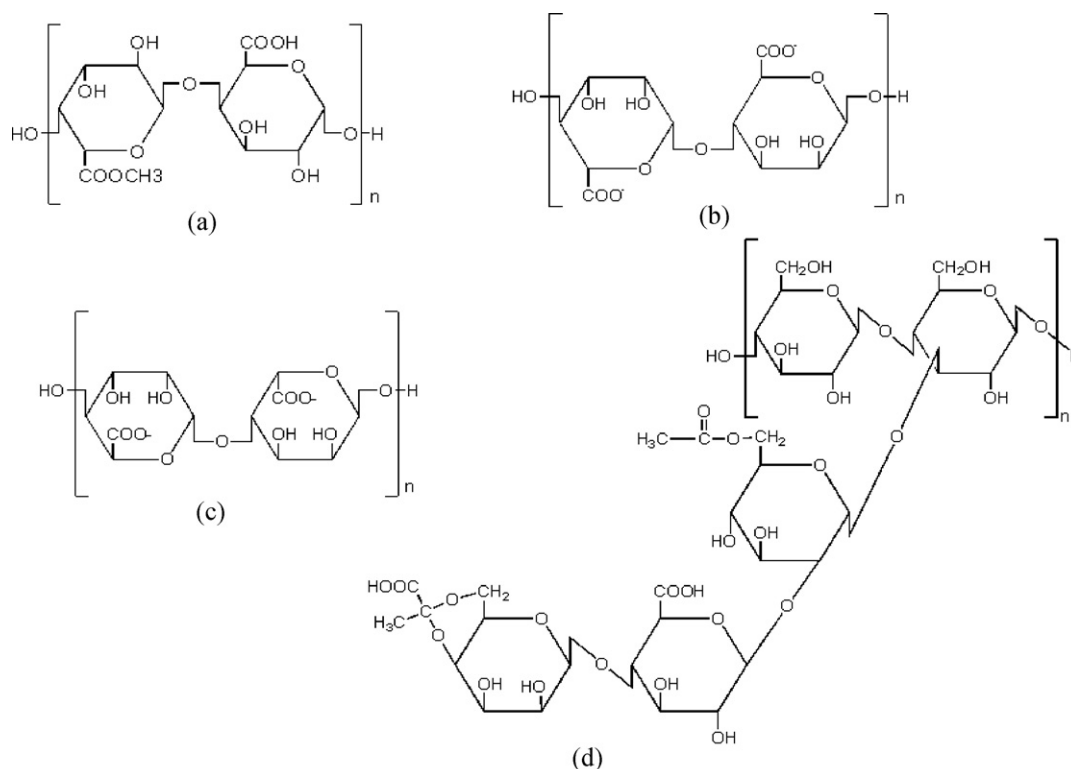


Fig. 1. Polysaccharides used for sorption on regenerated cellulose fibers: (a) pectic acid unit, (b) mannuronic acid unit of alginate, (c) guluronic acid unit of alginate, and (d) xanthan gum.

& Gatenholm, 2007; Torre, Rodriguez, & Saura-Calixto, 1992; Zykwiniska, Ralet, Garnier, & Thibault, 2005; Zykwiniska et al., 2007; Zykwiniska, Thibault, & Ralet, 2008). Moreover, due to the electrostatic repulsion between negatively charged cellulose and anionic polysaccharide, it is difficult to bind the anionic polysaccharide to cellulosic fibers. Therefore, addition of divalent cation in the system may increase the binding capacity of anionic polysaccharide to cellulose fibers. In our experiment, the interactions between polysaccharides and cellulose have performed in presence of calcium. If the divalent cation such as calcium is first adsorbed onto a cellulosic surface, the calcium adsorbed cellulose surfaces are expected to attract the negatively charged polysaccharide molecules. Here the function of calcium is to mediate the charge interactions between the negatively charged polysaccharides and the anionic cellulose surface so that the polysaccharides molecules can absorb to the fiber surface. Ca^{2+} ions are also used as a chelating agent for polysaccharides (Dario, Hortencio, Sierakowski, Neto, & Petri, 2011; Kohn, 1975).

In the present work, at first we bound the calcium in cellulose fibers and then the sorption of polysaccharides pectin, alginate, and xanthan on calcium adsorbed cellulose fibers were performed. This investigation was evaluated for the sorption of polysaccharides to cellulose fibers and determined the amount of polysaccharide and calcium on cellulose substrates by COD and AAS analyses. After sorption experiment the properties of the modified cellulose fibers were also investigated by ESEM, FTIR, carboxyl group content and alizarin dyeing.

2. Materials and methods

2.1. Materials

Pectin (P9135, citrus fruit, galacturonic acid $\geq 74.0\%$), sodium alginate (A2158, brown algae, β -D-mannuronic acid) and gum xan-

than (G1253, *Xanthomonas campestris*) were of analytical grade and used as received without further purification (Sigma Aldrich, St. Louis, USA). All other chemicals – calcium chloride, hydrochloric acid, sodium hydroxide, sodium acetate, sodium carbonate, acetic acid, ammonia, sulphuric acid, alizarin dye ($\text{C}_{14}\text{H}_8\text{O}_4$), methylene blue ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$), and boric acid were of analytical grade (Merck, Darmstadt, Germany; Fluka, Buchs, Switzerland; Carl Roth GmbH Germany). Lyocell staple fibers (CLY) TENCEL[®] and Viscose[®] (CV) both of titer 1.3 dtex, length 38 mm, without spin finish were kindly supplied by Lenzing AG (Lenzing, Austria). The fibers were conditioned in a standard atmosphere at $65 \pm 2\%$ relative humidity (RH) and $20 \pm 2^\circ\text{C}$ for a minimum period of 48 h prior to use.

2.2. Demineralization (DM) of the fibers

To remove any Ca^{2+} present in fibers, samples (1 g) were immersed in 5% (w/w) hydrochloric acid (100 mL) at 40°C and agitated for 1 h, washed thrice in deionised water (100 mL) for 5 min each, followed by neutralization in 0.01 M sodium acetate solution (100 mL) for 2–3 min. The fibers were rinsed again in deionised water (100 mL) for 5 min and dried in ambient condition for 24 h.

2.3. Calcium sorption onto cellulose

The demineralised fibers sample (1 g) was immersed and agitated in 8 mM and 32 mM calcium chloride solution (40 mL) 1 h at 40°C , and pH 9. The pH of this solution was adjusted by 9 mM acetic acid and 25% ammonia solution. The wet fibers were then centrifuged at $4000 \times g$ for 10 min to remove excess solution, washed thrice in deionised water (100 mL) for 5 min each and dried in ambient condition for 24 h.

2.4. Polysaccharide sorption onto cellulose

Polysaccharides (PS) pectin, alginate and xanthan were dissolved in deionised water and the concentration of polysaccharide for sorption experiment was 0.5 g/L and pH 10 adjusted with 0.2 M NaOH. The calcium pre-treated samples (1 g) were immersed in polysaccharide solutions (50 mL) at 30 °C and agitated for 24 h. The soaked fibers were then centrifuged at 4000 × g for 10 min to remove excess polysaccharide solution and dried in ambient condition for 24 h.

2.5. Measurements

For determination of the moisture content in cellulose fibers a conditioned fiber sample (0.5 g) was weighed accurately (W_c) and dried for 4 h at 105 °C. The dried samples were allowed to cool in P_2O_5 desiccators for 24 h and reweighed (W_d). The moisture content was calculated according to Eq. (1).

$$MC (\%) = \frac{W_c - W_d}{W_c} \times 100 \quad (1)$$

Calcium content in fibers and residual solutions was measured by Atomic Absorption Spectrometer (Hitachi-Polarized Zeeman, Japan) in emission mode (wavelength 422.7 nm, Air-C₂H₂ flame). To measure the calcium in fiber, the fiber was extracted (40 °C, 1 h) with 5% hydrochloric acid solution to remove the calcium from fibers. The samples were then quantified directly based on its concentration. For calibration stock solutions of CaCl₂·2H₂O (100 mg/L) was used to make calibration solutions in range of 0.1–1.0 mg/L Ca²⁺. 5% HCl was used to dilute the stock solution and each sample to prevent the formation of calcium carbonate. All glassware and containers were thoroughly cleaned with 5% hydrochloric acid prior to use. At least three repetitions were made for the determination of calcium in each step.

Polysaccharide content in the modified cellulosic fiber was measured by the chemical oxygen demand (COD) method described in BS ISO 15705 (2002). The COD test is used to measure the amount of oxygen required to decompose the organic materials present in a sample with a strong chemical oxidant. To measure the polysaccharides bound in fiber, at first the fiber was extracted with 1% (w/w) sulphuric acid solution to remove the polysaccharide from the fibers. Then the polysaccharide extracted solution (2 mL) was pipette thoroughly into the COD digestion tube. The COD tube was then heated in a thermo reactor at 148 °C for 2 h and the residual dichromate was determined by measuring the absorbance of the digested solution in a photometer (SQ 300, Merck, Darmstadt, Germany) at 585 nm. The COD (expressed as “milligram of O₂ per liter”) was then measured by the following equation ($R^2 = 0.9969$, standard error, $\varepsilon = 0.0075$), obtained from the calibration curve of reference potassium hydrogen phthalate.

$$COD (mg O_2/L) = \frac{\text{absorbance}}{4.427 \times 10^{-4}} \quad (2)$$

The polysaccharide content in the modified cellulose fiber was then determined by using the following relationship between COD and polysaccharide concentrations obtained from calibration curves of polysaccharides, Fig. 2.

$$COD (mg O_2/L) = (910.15 \pm 55.59) \times \text{concentration of pectin (g/L)} \quad (3)$$

$$COD (mg O_2/L) = (676.16 \pm 20.72) \times \text{concentration of alginate (g/L)} \quad (4)$$

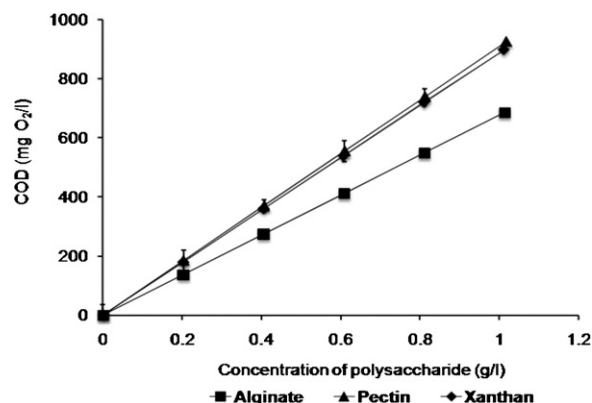


Fig. 2. COD values of polysaccharides – alginate, pectin, and xanthan as a function of polysaccharide concentrations. Each data point is the mean of three repetitions.

$$COD (mg O_2/L) = (887.56 \pm 17.21) \times \text{concentration of xanthan (g/L)} \quad (5)$$

Infrared spectra of a series of polysaccharide modified sample were recorded with an FTIR spectrometer (Brucker, Vector 22, Germany) equipped with an ATR attachment (Universal ATR, Brucker, Vector 22, Germany). All the spectra were obtained by an accumulation of 32 scans, with a resolution of 4 cm⁻¹ at 400–4000 cm⁻¹.

For ESEM observation, the calcium–polysaccharide modified samples were mounted on aluminum stubs with black carbon tape and were observed with an environmental scanning electron microscope (LX 30 ESEM-FEG, Philips, the Netherlands) in an accelerating voltage of 20 kV.

The carboxyl group content of the modified fiber was measured by the methylene blue sorption method (Philipp, Rehder, & Lang, 1965). 0.3 g/L methylene blue (25 mL) and borate buffer (25 mL) pH 8.5 were added to 0.25 g fiber sample at 30 °C and agitated for 24 h. The fiber was then taken out and methylene blue solution (2.5 mL) and 0.1 M HCl (5 mL) were added in a 50 mL volumetric flask and filled to 50 mL by deionised water. The absorbance of the solution was then measured at 664.5 nm by means of a double beam spectrophotometer (Hitachi U-2000, Japan). The carboxyl content of the demineralised and polysaccharide modified sample was then determined from the calibration curves of methylene blue.

For alizarin dyeing, 0.2 mM alizarin in 0.1 M NaOH (100 mL) was added to fiber sample (1 g) at 30 °C for 1 h. Afterwards, fibers were rinsed thrice in 4.7 mM Na₂CO₃ (100 mL) for 5 min each to avoid color change due to pH and dried at ambient condition for 24 h. The alizarin dye exhaustion was determined by Spectrophotometer (Hitachi U-2000, Japan). The absorbance of the diluted dye solution was measured at the wavelength of maximum dye absorption and the exhaustion of dye was measured from the calibration curve of alizarin.

The CIE LAB color strength (K/S) measurement was determined by spectrophotometer (Konica Minolta, CM-3610d, Japan). The CIE LAB color space, illumination viewing angle was 10° with D65 illuminant.

3. Results and discussion

The fibers were analyzed for the calcium content before and after polysaccharide sorption. The data of the calcium analysis are shown in Fig. 3 (a – shows the calcium content in fiber before

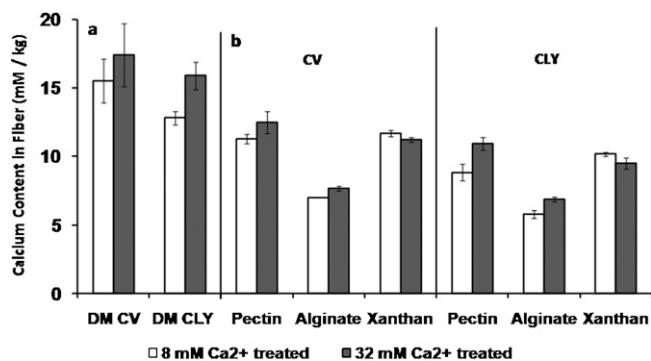


Fig. 3. Calcium content in cellulose fibers (a) before polysaccharide sorption, (b) after polysaccharides sorption as a function of polysaccharide type and Ca^{2+} concentrations in treatment solution.

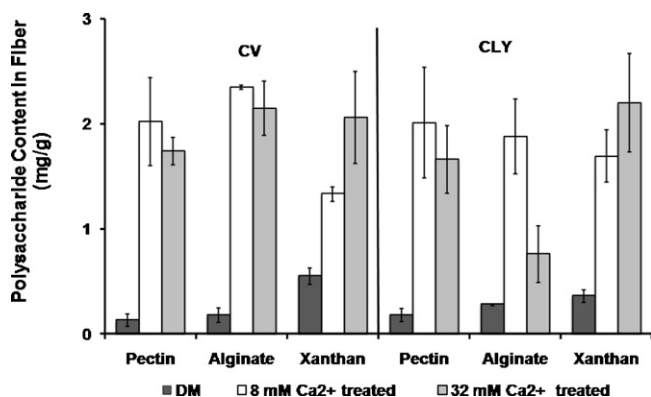


Fig. 4. Sorption of polysaccharides in cellulose as a function of polysaccharide type and Ca^{2+} concentrations in treatment solution.

polysaccharide sorption and b – shows the calcium content in fiber after polysaccharide sorption). Calcium binding in CV and CLY fibers did not increased significantly with increasing calcium concentrations in solution. It is apparent from Fig. 3(a) that CV fiber exhibited higher ability for Ca^{2+} binding than CLY fiber. Calcium binding ability in CV and CLY fibers became saturated by 8 mM Ca^{2+} concentration, as a results the binding of Ca^{2+} by 32 mM Ca^{2+} concentration in CV and CLY fibers did not increase significantly. The amount of calcium bound in cellulosic fibers indicates a remarkable affinity of Ca^{2+} ions in the cellulose fibers.

Fig. 4 shows the sorption of different polysaccharides on calcium containing cellulose fiber. The concentration of polysaccharide in solution was 0.5 g/L, from this concentration the amount of each polysaccharide adsorbed on calcium containing cellulose fiber was observed between 1.5 mg/g and 2.4 mg/g of fibers. It can be seen

from Fig. 4 that, virtually there is very little adsorption of anionic polysaccharides onto the anionic cellulosic (DM) fibers. When calcium was present in cellulose fibers, the binding of polysaccharide to cellulosic fibers increased compared to calcium free (DM) fibers. In this case it is predicted that Ca^{2+} ion building the bridges to link through functional groups of polysaccharides and cellulose surfaces. Hence, it can be concluded that due to the presence of calcium in cellulose fibers, the fibers were enable to adsorb more polysaccharides on cellulose. There was no significant influence of calcium concentrations on binding of polysaccharides to cellulose.

The 32 mM calcium treated CLY fibers show comparatively low alginate content in fibers, compared to pectin and xanthan. However, in CV fibers the sorption of alginate was higher compared with pectin and xanthan and also compared with CLY fibers. This higher binding capacity of alginate to CV fibers compared with CLY probably due to the differences in surface area of CV and CLY. Binding of polysaccharides to cellulose is also a function of time, initial concentration of polysaccharides in solution, temperature, cellulose surface area available, cation binding ability and also depend on the cellulose crystallinity index and their character and structure (Venkateswaran, 1970; Zykwiniska et al., 2005).

Fig. 3(b) shows the amount of calcium present in cellulosic CV and CLY fibers after polysaccharides sorption. Cation exchange capacity of the polysaccharides is a key parameter for their interactions with divalent cations (Debon & Tester, 2001). It can be seen from Fig. 3(b) that less than 50% of calcium transported from fiber to polysaccharide solution during polysaccharide sorption and rest of the calcium is still remained in cellulose fibers. Alginate significantly drawn more calcium from fibers, compared to pectin and xanthan. This is probably due to the tendency of alginate to form gel in presence of Ca^{2+} ions (Sikorski et al., 2007; Yang, Zhang, Peng, & Zhong, 2000). However, this effect was not observed for pectin and xanthan, because the interaction of pectin and xanthan with calcium ions is very little (Dario et al., 2011; Torre et al., 1992). Moreover, the binding capacity of divalent cations with polysaccharide is also depends on the free carboxyl groups present in polysaccharide (Debon & Tester, 2001). So, it can be said that Ca^{2+} plays an important role as a chelating agent to bind the negatively charged polysaccharides to the negatively charged cellulose and also bridging with polysaccharides in solution.

In support of this polysaccharide sorption in cellulose fibers, environmental scanning electron microscopy (ESEM), Fig. 5 was used to see the fiber surface structural arrangement in Ca^{2+} /polysaccharide modified fiber compared with the structure of untreated and calcium treated cellulose fibers. From Fig. 5 it can be seen that the Ca^{2+} /polysaccharide modified fiber is similar to the untreated and only calcium treated fibers. Diameter measurements on the electron micrographs with an image processing software yielded values of: (a) untreated fiber: $11.64 \pm 0.85 \mu\text{m}$, (b) 8 mM Ca^{2+} treated fiber: $11.98 \pm 0.80 \mu\text{m}$, (c) Ca^{2+} -polysaccharide treated fiber: $12.08 \pm 0.81 \mu\text{m}$. A one-way ANOVA test yielded

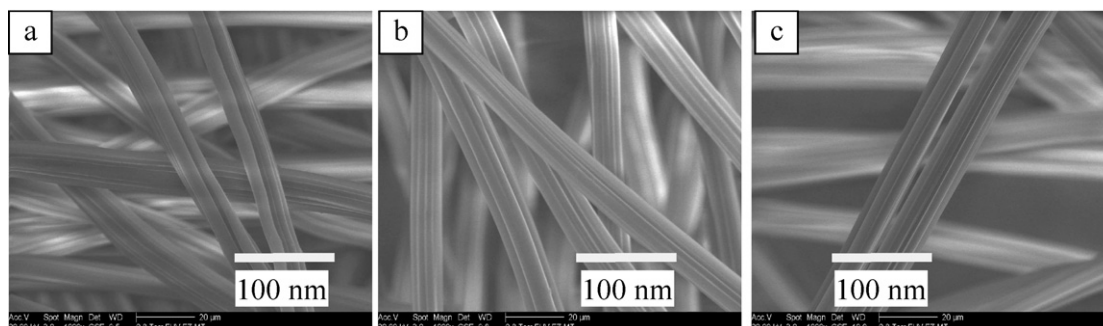


Fig. 5. Representative examples of ESEM images of (a) untreated (DM) CV, (b) 8 mM Ca^{2+} treated CV, and (c) Ca^{2+} /pectin treated CV fibers at 1000 \times magnifications.

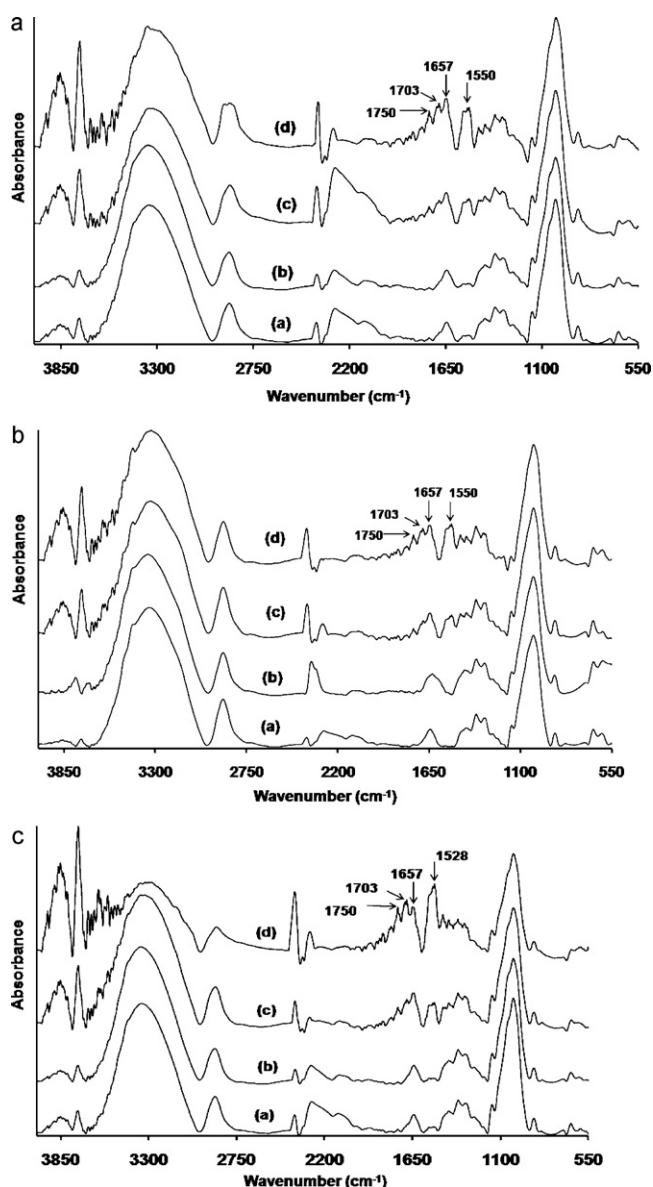


Fig. 6. (a) FTIR spectra of cellulose fibers: (a) untreated (DM) CV, (b) 8 mM Ca^{2+} treated CV, (c) only pectin treated CV, and (d) Ca^{2+} /pectin treated CV fiber. (b) FTIR spectra of cellulose fibers: (a) untreated (DM) CLY, (b) 8 mM Ca^{2+} treated CLY, (c) only alginate treated CLY, and (d) Ca^{2+} /alginate treated CLY fiber. (c) FTIR spectra of cellulose fibers: (a) untreated (DM) CV, (b) 8 mM Ca^{2+} treated CV, (c) only xanthan treated CV, and (d) Ca^{2+} /xanthan treated CV fiber.

a p -value of 0.744, indicating that the differences were not significant.

On the basis of the assumptions that the fibers are uniform cylinders, there was homogenous polysaccharide sorption on fibers and that polysaccharide density may be approximated at 1 g/cm^3 ; the thickness of polysaccharide layers on fibers were estimated at 7 nm (pectin), 8 nm (alginate) and 5 nm (xanthan) with Eq. (6):

$$T = \frac{d}{2\pi r} \times p \frac{1}{\rho} \times 10^{-6} \quad (6)$$

where, T =thickness of polysaccharide layer (nm), d =fiber linear density ($1.3 \text{ dtex} = 1.3 \text{ g}/10,000 \text{ m}$), r =fiber radius (m), p =average polysaccharide content on fiber (g/g), ρ =polysaccharide density (approximated at 1 g/cm^3).

The estimated polysaccharide layers were less than 10 nm on cellulose fibers, and were not detectable due to the limiting resolution of ESEM. However, it could be predicated that the

Table 1

Moisture content, carboxyl group and alizarin exhaustion (%) of different pre-treated CV and CLY fibers. Results are expressed as the mean of three values \pm standard deviation.

Sample	Moisture content (%)	COOH content (mmol/kg fiber)	Alizarin exhaustion (%)
<i>Demineralised</i>			
CV	9.2 ± 0.3	18.1 ± 1.1	10.8 ± 0.5
CV + pectin	9.8 ± 0.2	22.9 ± 0.3	8.8 ± 0.4
CV + alginate	9.6 ± 0.3	20.8 ± 0.7	1.6 ± 0.2
CV + xanthan	10.0 ± 0.1	22.9 ± 0.9	4.4 ± 0.8
CLY	8.3 ± 0.1	20.9 ± 0.9	11.3 ± 0.0
CLY + pectin	8.9 ± 0.1	24.7 ± 0.6	7.9 ± 0.8
CLY + alginate	9.4 ± 0.4	23.5 ± 1.0	1.7 ± 0.1
CLY + xanthan	9.7 ± 0.2	22.8 ± 0.6	4.8 ± 0.6
<i>Demineralised and treated with 8 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$</i>			
CV	9.3 ± 0.1	19.4 ± 0.2	79.1 ± 1.7
CV + pectin	10.2 ± 0.1	18.8 ± 0.9	59.4 ± 0.7
CV + alginate	10.4 ± 0.2	19.2 ± 3.2	39.4 ± 1.0
CV + xanthan	10.2 ± 0.0	20.2 ± 3.9	67.6 ± 0.4
CLY	8.5 ± 0.0	21.6 ± 1.0	67.3 ± 0.9
CLY + pectin	9.3 ± 0.0	20.0 ± 1.2	50.4 ± 0.2
CLY + alginate	9.1 ± 0.1	20.5 ± 3.4	34.8 ± 1.3
CLY + xanthan	9.4 ± 0.3	18.5 ± 3.3	55.6 ± 0.4

polysaccharide layers uniformly distributed on cellulose surfaces, as there was no agglomeration or precipitation of polysaccharides or calcium ions on Ca^{2+} /polysaccharide modified fiber surfaces observed.

The FTIR-ATR spectra of treated and untreated cellulosic fibers are shown in Fig. 6(a–c). In comparison with the spectrum obtained from the untreated (DM), calcium treated and only polysaccharide treated fibers, in can be seen that the Ca^{2+} /polysaccharide treated fibers [Fig. 6(a–c), d] have the obvious characteristic peaks in the range $1700\text{--}1750 \text{ cm}^{-1}$ and in the range $1650\text{--}1550 \text{ cm}^{-1}$ due to the carbonyl ($\text{C}=\text{O}$) and the carboxyl group (COOH) group of polysaccharides. The Ca^{2+} /polysaccharide treatment caused shifts of the COO^- peaks indicating the interaction between the cellulose molecules and polysaccharide chains.

Table 1 shows the moisture content, carboxyl group content and alizarin dye exhaustion (%) of modified fibers. There is no significant difference in moisture content of Ca^{2+} /polysaccharide modified cellulose fibers compared to DM and only polysaccharide treated fibers. The carboxyl group content of cellulosic fibers is directly related to the ions binding capacity of fibers including Ca^{2+} . The carboxyl group content in DM, CV and CLY fibers was 18–21 mmol COOH/kg cellulose fibers. From Table 1, it can be seen that only polysaccharide treated fibers showed slightly higher

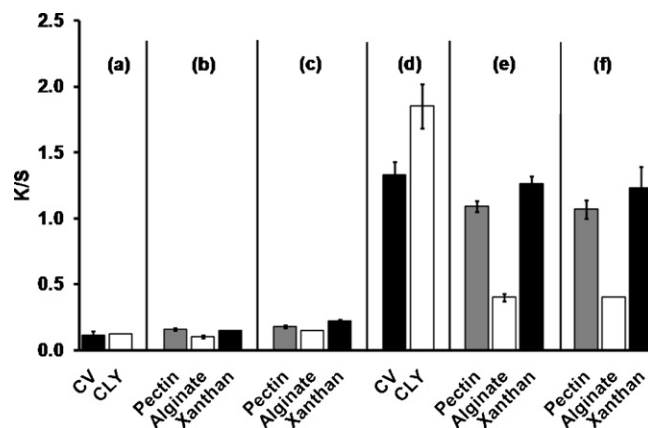


Fig. 7. K/S of a series of alizarin dyed samples: (a) demineralised (DM) CV, CLY, (b) DM CV treated with polysaccharides, (c) DM CLY treated with polysaccharides, (d) calcium treated DM CV and CLY, (e) calcium-PS treated CV, and (f) calcium-PS treated CLY.

carboxyl group content compare to (DM) samples, however the change in carboxyl group content on Ca^{2+} /polysaccharide modified fibers is very marginal. The alizarin dye exhaustion percentage of Ca^{2+} /polysaccharide modified cellulose fibers show significant difference compared to DM and only polysaccharide treated fibers.

In order to confirm the presence of calcium on Ca^{2+} /polysaccharide modified fibers, the K/S of different alizarin dyed samples was performed to see the visual staining effect of fibers in relation with its calcium ions concentrations.

From Fig. 7, it can be seen that the K/S values increased in the fiber because alizarin form complex with Ca^{2+} and fixed on fibers. The K/S function is proportional to the concentration of the dye on the substrate and indicates dye adsorption and fixation. The K/S value of DM and only polysaccharide treated fibers was very marginal compared to Ca^{2+} /polysaccharide modified fibers, and these fibers showed almost colorless after alizarin dyeing because there was no Ca^{2+} present in these fibers. In case of Ca^{2+} /polysaccharide modified fibers, the K/S values increase, because of the complex formation of alizarin with increase in Ca^{2+} concentration of fibers.

4. Conclusions

In this work the sorption ability of anionic polysaccharides to cellulose fibers was studied. As the calcium sorption to cellulose was limited by the carboxyl content, fibers loaded with calcium from 8 mM and 32 mM Ca^{2+} solution did not show differences in polysaccharide sorption. When calcium was present in the fibers as counter ion of the carboxylic groups, sorption of polysaccharide to cellulosic fibers increased, this indicated that the mechanisms of sorption probably involved cation bridging between cellulose and the polysaccharide molecules. The amount of calcium and polysaccharide bound in cellulose fibers was 5.8–12.5 mM Ca^{2+} /kg fibers and 1500–2400 mg polysaccharide/kg fibers, respectively.

FTIR–ATR spectra indicate the presence of polysaccharide on Ca^{2+} containing cellulose fibers. There was no deposition of calcium carbonate on fibers. In presence of water soluble polysaccharide the mobility of Ca^{2+} was increased and Ca^{2+} was released from the fibers into the polysaccharide solution in the order: alginate > pectin > xanthan. The results of the alizarin dyeing experiments at the end of polysaccharide sorption further confirmed the presence of calcium in Ca^{2+} /polysaccharide adsorbed cellulose fibers. The adsorbed behavior of polysaccharides on cellulose fibers in presence of calcium ions was calculated and the thickness of the adsorbed polysaccharide layer was less than 10 nm. The study demonstrated that Ca^{2+} can play a significant role in the interaction between dissolved polysaccharide and cellulose surface.

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