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PECTIN QUANTIFICATION FROM CELLULOSIC/LIGNOCELLULOSIC RAW MATERIALS BY FT-IR ATR ANALYSIS

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Abstract: *This paper presents an accurate quantification by FT-IR ATR analyses of pectin content from cotton and flax raw woven fabrics. For this purpose, the investigated samples were exposed to HCl vapours. The relative absorbance of pectin-specific bands was evaluated. The results showed an increase in the band intensity values located at ~ 1735 cm^{-1} and a decrease of the one from ~ 1645 cm^{-1} after the exposure of the samples to HCl vapours due to the transformation of the (COO-) linked with Ca^{2+} groups into acidic carboxylic groups.*

Keywords: cotton fabric, flax fabric, pectin, HCl vapours exposure, FT-IR ATR spectroscopy

INTRODUCTION

Due to their renewable character, textile materials based on natural fibres are gaining more and more ground in the framework of sustainable development policy. Their use in various industrial fields (textiles, construction, automobiles, etc.) implies a decrease in fossil fuels that fall within the lines of sustainable development (Karus et al. 2002, Puşcas et al. 2002, Perepelkin et al. 2005).

Cotton and flax materials get into the category of renewable materials, and their investigation, analysis, and characterization to find environmentally friendly processing methods for obtaining value-added materials can be considered a priority.

Cotton occupies one of the first places in the world in production, at the same time having the highest percentage of cellulose in the composition (Eichhorn et al. 2001, Pursley et al. 2005). The lignocellulosic materials like flax have become interesting in the last decade, due to the possibility of cultivation in areas with lower temperatures in Europe as well as the low costs for crop maintenance because no pesticides are needed (Summerscales et al. 2010).

According to literature data, the chemical composition of investigated materials is: cotton - 86-96% cellulose, 0.7-1.9% pectin, 0.4-1.2% waxes, etc. (Wakelyn et al. 2007); flax - 70-75% cellulose, 3-15% pectin, 8-15% waxes and hemicelluloses, 0.6-4% lignin (Abdel-Halim et al. 2008, Manaia et al. 2019).

Because there are differences in structure, composition, and properties between these raw materials, detailed information on the content of non-cellulosic attendants is needed to find suitable solutions in their processing. For example, pectin, a complex of polysaccharides of 1-4 linked α-D-galacturonic acid molecules, esterified with methanol or as calcium salts (Dochia et al. 2013), must be removed from the substrate to improve the hydrophilic properties of fabrics.

Infrared spectroscopy, due to its versatility, has become one of the most important analytical techniques available to researchers. As shown in previous studies (Dochia et al. 2018a, 2018b, 2018c), the FT-IR ATR spectroscopy can be a simple and rapid technique to obtain data about the structure and constituents of cellulosic and lignocellulosic materials (Dochia et al. 2018a, Wang et al. 2006, Terpáková et al. 2012, Choe et al. 2018, Ouajai et al. 2005). This method allows the identification of specific bands for cellulose and non-cellulosic attendants' functional groups.

Because in the FT-IR ATR spectra there are situations in which the characteristic bands of various vibrations overlap, a specific preparation of the samples (e.g. HCl vapour treatment of natural fibres) is required for a more accurate interpretation of the results (Wang et al. 2006, Choe et al. 2018). At the same time, the FTIR

ATR spectra allow obtaining information related to the amorphous and crystalline structure of the cellulosic polymer from raw materials. This is possible by calculating the Lateral Order Index (LOI) and the Total Crystallinity Index (TCI) using absorbance values (Ciolacu et al. 2011).

The aim of this paper has been the accurate quantification of pectin content from cotton and flax raw woven fabrics by FT-IR ATR analyses. In this purpose, the raw cotton and flax samples were subjected to the action of HCl vapours and the relative absorbance values of pectin specific band were evaluated.

MATERIALS AND METHODS

Materials

Samples from the following fabrics were analysed:

- Raw woven cotton fabric with a width of 150 ± 3 cm, the weight of 200 ± 10 g/m^2, the warp of 100 % cotton yarn with Ne 25/2 and weft of 100 % cotton yarn with Ne 25/1 (denoted as **RC)**;
- Raw woven flax fabric with a width of 120 ± 3 cm, the weight of 220 ± 10 g/m^2 and 100 ± 1 fibres/10 cm warp and weft density (denoted as **RF)**;

Method

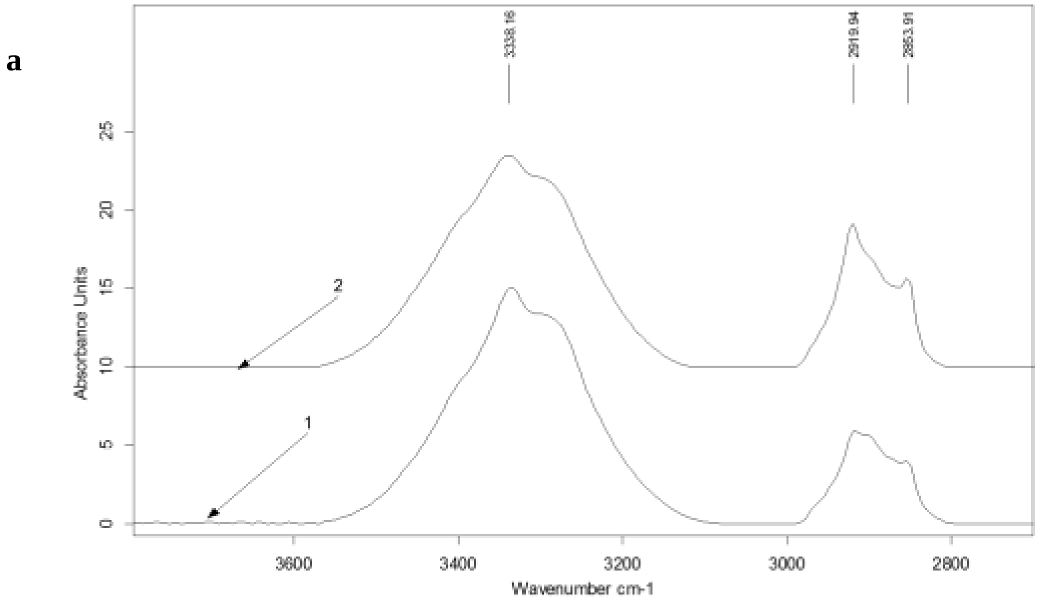
The experiments were made on 3 samples taken from different parts of the fabrics. Before being analysed, the samples were conditioned at 105 ^{0}C in a Sartorius MA 100 balance. In the case of samples subjected to the action of HCl vapours, the time exposure was 1 minute.

FT-IR ATR spectra were obtained with a Bruker Vertex 70 spectrophotometer equipped with the ATR cell. The measurements were carried out on the 600 - 1800 cm^{-1} and 2600 – 4000 cm^{-1} wavelength range with a resolution of 8 cm^{-1} and 100 scans. For the acquisition and processing of data (normalization to the peak at 615 cm^{-1} and baseline correction), the OPUS software was used. Before each measurement, a background calibration was done.

RESULTS AND DISCUSSIONS

Cotton and flax materials present several specific absorption bands for cellulose and non-cellulosic components (lignin, pectin, etc.). Figure 1 a and b presents the FT-IR ATR spectra of the RC and RF samples recorded on 600 – 1800 cm^{-1} and 2600 – 4000 cm^{-1}.

The peak at 3338 cm^{-1} is characteristic of the hydrogen-bonded stretching vibration of the hydroxyl group (OH) from polysaccharides structures (cellulose and hemicellulose). The peaks observed at 2919 cm^{-1} and 2853 cm^{-1} are extra bands given by C-H stretching vibration of noncellulosic components like pectin and waxes which overlap with the specific signal of the same vibrations of cellulose and hemicellulose (Terpáková et al. 2012, Choe et al. 2018, Subramanian et al. 2005).



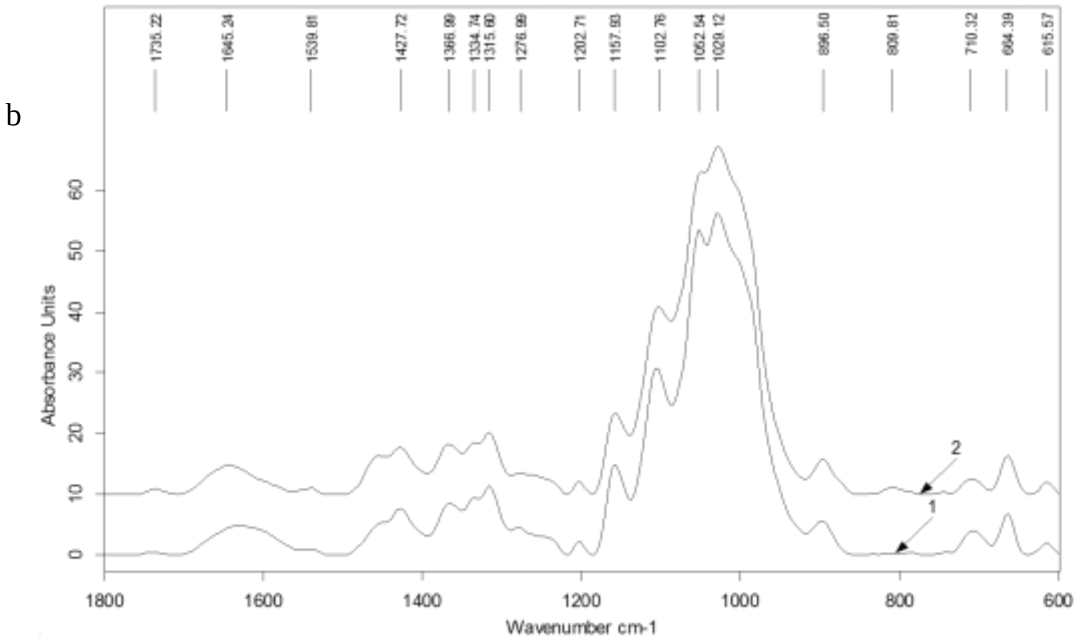


Figure 1. FT-IR ATR spectra of 1- **RC** and 2 - **RF** samples on 2600 - 4000 cm^{-1} range (a) and 600 – 1800 cm^{-1} range (b)

Comparing the extra bands obtained for the two types of samples analysed, it is observed that in the case of flax their intensity is higher than that of cotton. This suggests a higher content of waxes and pectins of the raw lignocellulosic material.

The weak absorbance located in the FT-IR spectrum at 1735 cm^{-1} for cotton and 1737 cm^{-1} for flax can be attributed to C = O stretching of methyl ester and carboxylic acid in pectin and waxes.

Also, the literature mentions that in this FT-IR region the signal of the acetyl group in hemicelluloses occurred (Ouajai et al. 2005). The antisymmetric stretching vibration of the carboxylate group (COO^-) boned with Ca^{2+}, specific for pectin, appears at approximately 1645 cm^{-1} and overlaps with OH bending of absorbed water which is located between 1500-1700 cm^{-1} (Choe et al. 2018).

On 600 - 1500 cm^{-1}, the specific and common bands for cellulose and hemicellulose were registered. The main infrared vibrations recorded on the above interval are presented in Table 1.

The specific bands for lignin from the lignocellulosic samples were observed at 1278 cm^{-1} and 809 cm^{-1} being given by the G ring and aromatic C-H stretching.

Table 1. Main infrared signals on 600 - 1500 cm^{-1} range for the investigated samples (Dai et al. 2010)

Wavenumber (cm^{-1})	Vibration	Compound
1427	HCH and OCH in-plane bending vibration	Cellulose
1366	In-the-plane CH bending	Cellulose Hemicellulose
1315	CH_2 rocking vibration	Cellulose
1278	C=O and G ring stretching	Lignin
1202	C-O-C symmetric stretching	Cellulose Hemicellulose
1157	C-O-C asymmetrical stretching	Cellulose Hemicellulose
1102, 1052, 1028	C-C, C-OH, C-H ring and side group vibrations	Cellulose Hemicellulose
897	COC, CCO and CCH deformation and stretching	Cellulose
809	C-H vibration	Aromatic hydrogen from lignin
710, 664, 615	OH out-of-phase bending	Cellulose

Quantification of pectin content of samples

Accurate quantification of the remanent pectin content of textile substrates it's the main problem for bioscoured materials characterization when the FT-IR ATR technique is used. Bioscouring treatments, which aim the elimination of a large amount of pectin from cellulosic and lignocellulosic materials, involve the use of complexing agents such as EDTA or sodium citrate along with mixture of enzymes (pectatylases, pectinlyase, pectinesterases and polygalacturonases).

Due to their specificity, these enzymes act differently on the pectin polymer. For example, pectinesterases act on methyl ester groups while polygalacturonases, pectin lyases and pectatylases depolymerize the pectic chain on which carboxylate groups are bound to Ca^{2+} ions. On the other hand, complexing agents causes the removal of Ca^{2+} from pectin bridges, destabilizes the cell wall structure and facilitates the pectin elimination under the action of enzymes (Kozlowski et al. 2006).

The band absorbance values around 1735 cm^{-1} cannot provide accurate information on the total amount of pectin from the substrate. The 1735 cm^{-1} FT-IR signal is given only by $COOCH_3$ and COOH groups in acid form, while the pectin fraction in the form of calcium salts of 1-4-D-polygalacturonic acid cannot be quantified in this wavenumber range. On the other hand, due to the overlap of the OH bending of absorbed water with the COO$^-$ band recorded at 1550 cm^{-1} – 1700 cm^{-1}, the accurate quantification of the pectin content in this wavenumber range is quite difficult. (Dai et al. 2010, Ouajai et al. 2005, Dochia et al. 2018c).

To solve this inconvenience, the investigated samples of cotton and flax raw materials were treated with HCl vapour to convert the carboxylate groups from pectin to acid groups.

Figure 2 presents the FT-IR spectra of cotton and flax raw materials after HCl vapour exposure.

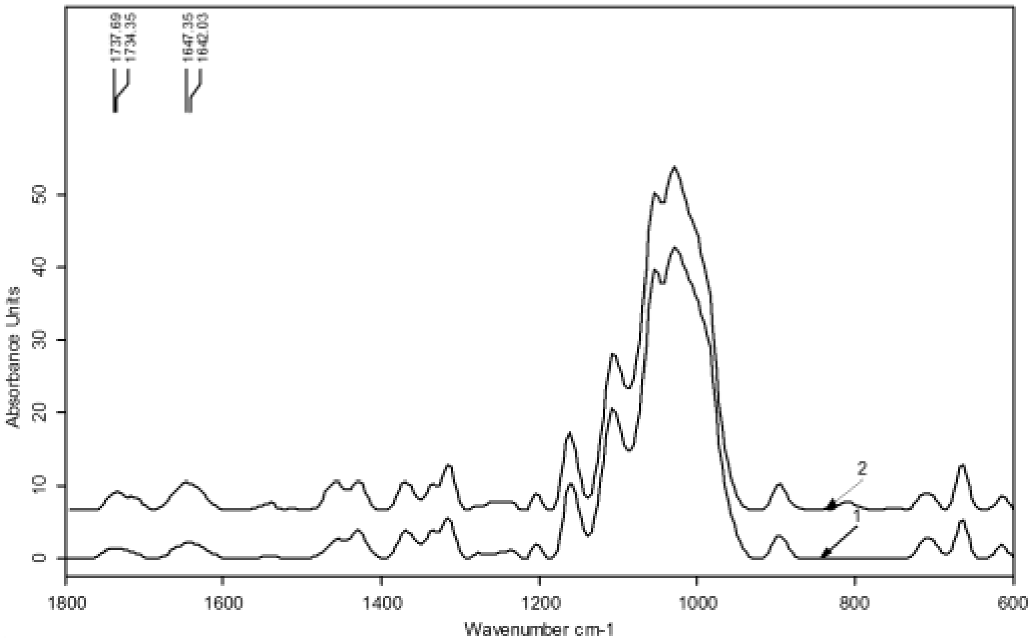


Figure 2. FT-IR ATR spectra of 1- **RC** and 2 – **RF** after HCl vapour exposure

Comparing FT-IR spectrum from Figure 2 with Figure 1b, it can be observed an increase in the band intensity located around 1735 cm^{-1} after the exposure of the samples to the action of HCl vapours.

This behaviour can be attributed to the transformation of COO$^-$ groups from polygalacturonic chains into COOH groups.

Table 2 shows the relative absorbance values of the C=O pectin bands from cotton and flax samples before and after HCl vapour exposure.

Table 2. The relative absorbance values of cotton and flax samples before and after HCl vapour exposure

Samples	Wavenumber (cm^{-1})	*A* (a.u.)*
RC - raw	1735	0.75232
RF - raw	1737	1.47179
RC - HCl	1734	2.96447
RF - HCl	1737	4.63010

* The average value of three determinations

The data show that after the treatment with HCl vapours, the values of the relative absorbance of the C = O vibration band of pectin increased approximately 3 times for both types of investigated materials, this being in accordance with data presented in the literature by Choe et. al. (Choe et al. 2018).

As expected, after the exposure of the samples to the action of HCl vapours, a decrease in the relative absorbance value of the ~ 1645 cm^{-1} band was observed. Thus, in the case of cotton the relative absorbance value decreases from A_{1645} = 5.18473 (a.u.) to A_{1642} = 2.22794 (a.u.) and for flax from A_{1645} = 6.19413 (a.u.) to A_{1647} = 3.70118 (a.u.). The relative absorbance values from Table 2 confirm higher pectin content in flax samples than in cotton, as was previously presented.

In our opinion, after exposing the samples to the action of HCl vapours, the relative absorbance values of the bands located around 1735 cm^{-1} allow a more precise quantification of the pectin amount from textile substrates. This procedure can be recommended for an accurate quantification of the amount of remanent pectin in the textile materials subjected to the bioscouring treatment.

CONCLUSIONS

An accurate quantification of pectin content from cotton and flax raw woven fabrics after exposure to HCl vapours was performed by FT-IR ATR analyses. The relative absorbance of pectin-specific bands was evaluated. The results showed an increase in the band intensity values located at ~ 1735 cm^{-1} and a decrease of the one from ~ 1645 cm^{-1} after the exposure of the samples to HCl vapours due to the transformation of the (COO^-) linked with Ca^{2+} groups into acidic carboxylic groups.

Based on the obtained results, this procedure can be useful for the quantification of the remanent pectin from textile substrates after bioscouring treatment.

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