Study of natural degradation effect on lignocellulose fibers of archaeological cedar wood: monitoring by Fourier Transform Infrared (FTIR) spectroscopy

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Abstract. The present work aims at elucidating the changes in the chemical composition of Moroccan cedar wood during exposure time to the natural degradation process. Correlation of these changes with certain physical properties and performance of this polymeric material were proposed. Four archaeological *Cedrus atlantica* wood samples dating from the 16th, 17th, 19th and 21st centuries were analyzed using Fourier Transform Infrared spectroscopy. The infrared spectroscopic analyses demonstrated in detail the significant changes that occurred in different molecular groups of lignocelluloses fibers, as evidenced by the decrease of band intensities related to the carbohydrates and lignin. The influence of the natural degradation process on these fibers was enhanced by the gradual decline in fingerprint (1800-800cm^{-1}) related to the cellulose amount accompanied by the detection of new carbonyl band at 1650cm^{-1} attributed to the C=O quinone suggesting the lignin's oxidation.

1 Introduction

Wood is a hydroscopic bio-polymer composite [1] consisting of an interconnecting matrix of lignocellulose fibers; cellulose (homopolymer made up of (1→4)-*β*-D-glucopyranose units), hemicellulose (composed of carbon monosaccharide units) and lignin (heteropolymer of guaiacyl, syringyl and p-hydroxyphenyl units) [2–5]. In addition, wood composed of biomolecules with low molecular weight (extractives) [6, 7].

The lignocellulose fibers are the most abundant biopolymers on earth and promoted as high-durability consumer products; however their degradation under non-controlled environmental conditions constitutes a source of troubles [8]. These fibers are part of a group of biomaterials which are known to suffer from deterioration and degradation processes that are induced by temperature, humidity, solar radiation, fungus, insects, etc. [8]. The consequences of these on wood are apparent as reduction of its physical and chemical performance characteristics.

To monitor the degradation process primarily attributable to the decomposition of the lignocellulose fibers and to display supportive information about their structures, Fourier Transform Infrared spectroscopy (FTIR) was carried out by many researchers. It has been used in previous studies as a prevailing technique for studying the wood molecular structure and characterizing the lignocellulose fibers [9]. Furthermore, it is widely used as qualitative technique for analyzing biomaterials such as wood due to its capacity of providing abundant information on functional groups in each sample, opening the way to monitor the principal chemical pathway responsible for their deterioration.

In this view, the objective of this study is to investigate changes occurring in the structure of Moroccan cedar (*Cedrus atlantica*) wood as an endemic and long-lived tree species [10] using FTIR spectroscopy. The studied samples are four archaeological objects which are dated back to the 16th, 17th, 19th and 21st centuries.

2 Materials and methods

2.1 Considered cedar samples

Four samples were extracted from four historical objects manufactured from Moroccan cedar (*Cedrus atlantica*) wood taken from the National Park of Tazekka (WGS84: 34°6′0″N, 4°11′0″W) which is situated near of Taza city (Middle Atlas of Morocco). The degraded

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samples were extracted from the outside surface of wood specimens and the non-degraded ones were extracted at 1cm of depth under the wood specimen surface. Table 1 presents the characteristics of the studied wood samples.

Table 1. Description of samples of archaeological cedar (*Cedrus atlantica*) wood.

Sample	Age	Actual state
A	21st	non-degraded
B	19th	
C	17th	
D	16th	
A'	21st	degraded
B'	19th	
C'	17th	
D'	16th	

2.2 FTIR spectroscopy

The FTIR transmission spectra tests were recorded using BRUCKER VERTEX 70® spectrometer coupled to a Hyperion® microscope. Scanning of the samples was performed according to Platinum diamond ATR (Attenuated Total Reflectance). The selected wavenumber region corresponds to the domain laying between 4000cm^{-1} and 400cm^{-1}. The resolution was fixed at 4cm^{-1}. 16 scans were averaged at each position. During analysis, the humidity and temperature of the room were controlled. In addition, the spectra were baseline corrected and normalized to the highest peak that was set to the absorbance of 1.5.

3 Results and discussions

Spectra acquired using ATR-FTIR spectroscopy (see Fig. 1) allowed to study the chemical structure of the tested specimens. This was performed by identifying the functional groups of the different analyzed wood samples. Fig. 1 gives the FTIR spectra in the case of the non-degraded cedar wood samples. The strong peak related to the stretching vibration of alcohol-bonded hydroxyl groups ν(OH) is detected in the interval 3700-3000cm^{-1}. It can be observed that it decreases as sample's age increases. This suggests the drop of the hydrogen bond existing in the cellulosic chains under the natural ageing process [11]. Moreover, this range contains a mixture of *inter-* and *intra-* molecular hydrogen bonds which condition different properties of lignin and native cellulose. They are caused by the enlargement of the OH band in the FTIR spectra, as observed clearly in all spectra of analyzed samples (Fig.1). Kubo and al. [12] reported that at around 3560-3550cm^{-1} (Fig. 1), an intramolecular hydrogen bond was observed in a phenolic group in lignin, as well as a multiple formation of this bond between phenolic groups and their combinations with alcoholic groups.

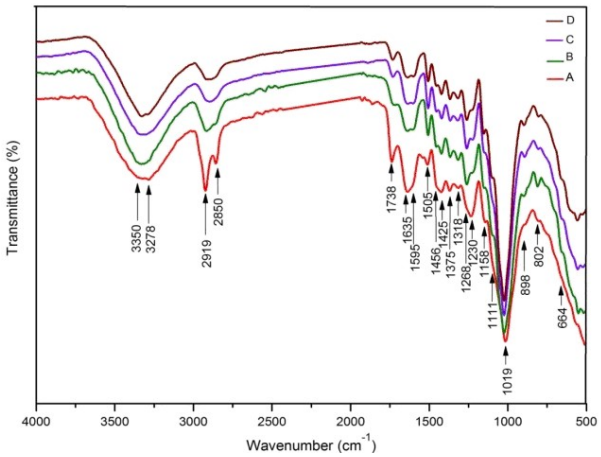

Fig. 1: FTIR spectra of non-degraded samples (A, B ,C and D) of cedar (*Cedrus atlantica*) wood.

In the spectrum of the recent sample dated back to the 21st century (Fig. 1A), the weak shape observed at 3695cm^{-1} is indicative of free OH (hydroxyl) probably related to the absorbed water bound. A higher dehydration of wood constituents resulted from exposure to the high temperature for an extended duration could justify the important decline of this band in all spectra related to the C and D oldest samples from the 17th and 16th centuries, respectively (Fig.1C and 1D). The same trend was observed for the characteristic band of water deformation vibrations (δOH) detected at 1635cm^{-1} (Fig. 1) [9,13-14]. The detection of a peak at 3278cm^{-1} is attributed to the intermolecular hydrogen bonds of type O(6)H·O(3). This confirms the presence of the monoclinic I_β cellulose [15], while the triclinic I_α form appeared absent in the obtained spectra because no band has been recorded at 3213cm^{-1} [13,16-17]. It can be observed that the intensities of these bands decreased proportionally with both the age of sample and the degradation level. This change indicates that microcrystalline structure of cellulose started to present some modifications.

For each sample, when comparing IR spectra of the non-degraded samples and the spectra of degraded ones, many changes were noticed (Fig. 2). The main changes were detected in the spectra region of 3800-2750cm^{-1} and the fingerprint range between 1800 and 800cm^{-1}, because they reflect the essential modifications of molecular structure of the wood components exposure to the process of natural degradation. In the spectra range 3000-2800cm^{-1}, the dominant bands at 2919 and 2850cm^{-1} were assigned to (sp^3) C-H stretching vibration related to methyl and methylene groups (νCH_3 and $\nu_{as}CH_2$ at 2919cm^{-1} and $\nu_{s}CH_2$ at 2850cm^{-1}) [18]. These two bands are clearly visible in spectra of samples A', B' (Fig. 2A' and 2B') and C (Fig. 1C), while they shift to lower intensities and disappear in

spectra of C' and D' degraded samples from the 17th and 16th centuries (Fig. 2C' and 2D'), respectively. This attribution is confirmed by the deformation of CH_2 (CH_2-C=C) bending [14] and CH_3 deformation in lignin observed between 1466-1400cm^{-1} [17].

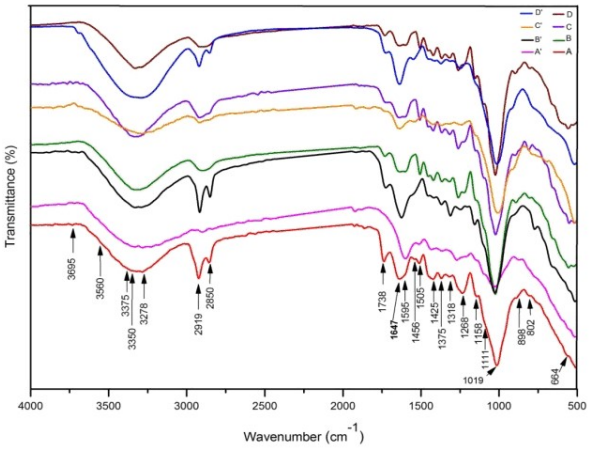

Fig. 2: FTIR spectra of degraded (samples A', B', C' and D') and non-degraded (samples A, B, C and D) cedar (*Cedrus atlantica*) wood.

It can be seen that the bands observed at 1738cm^{-1} and 1456cm^{-1} which are related to non-conjugated C=O stretch of ester and asymmetric deformation of C-H bond of xylan (hemicelluloses), respectively, retain their intensities for the majority of the FTIR spectra and disappear in spectra of the oldest samples from the 17th and the 16th centuries (C' and D' in Fig. 2). This observation indicates that hemicelluloses are less vulnerable to degradation compared to the other wood polymers (cellulose and lignin).

During the oxidation of cellulose, the intramolecular recombination of alcohols groups and oxidative acidic groups results in the generation of new cyclic ester type lactone identified by bands at 1732-1715cm^{-1} [14]. For δ-lactone type (six membered ring), the C=O carbonyl band occurs in the region of 1760-1720cm^{-1}, while saturated γ-lactone (five membered ring) displays a band between 1795-1760cm^{-1}. In our spectra, lactones are characterized by another strong band at 1111cm^{-1} attributed to the C–(C=O)–O link [14,19]. The signals of these bands were drastically reduced in the absence of the broad absorption at 1620-1635cm^{-1} in the case of D' degraded wood dating from the 16th century sample. This may indicate the higher desorption of water which could be generated by thermal degradation due to long exposure to the high temperature during many years. In this regard, several mechanism pathways of cellulose decay have been investigated by researchers. As reported by Aydinli and al. [20], the degradation of the cellulose can proceed via different reaction routes; the chemical degradation (oxidation, hydrolysis, and alkaline degradation), thermal degradation (high levels of temperature), and radiation (ultraviolet-visible radiation, and high energy radiation). For example, during hydrolysis of the *β*-(1–4) glycosidic bonds, the polymeric structure of cellulose changed through reorganization of the hydrogen bonds (transformation from crystalline to amorphous form), causing the changes in the bands detected between 1300-1500cm^{-1} which are related to a combination involving bending vibrations of C–O–H, O–C–H, C–C–H and those of H–C–H (in-plane) [21].

On the other hand, lignin component displays two peaks at 1595 and 1505cm^{-1} (Fig. 1) attributed to C=C aromatic skeletal vibration in aromatic ring (benzene) which over the guaiacyl-syringyl matrix [14,22-23]. According to Acherar and al. [24], the out-of-plane deformation of the CH aromatic was observed at the wave number 664cm^{-1}. These peaks were significantly weakened in spectra of degraded samples (Fig. 2A', B', C' and D'), which is indicative of a reduction of lignin amount due probably to its decay and alteration. We can confirm this hypothesis by the formation of newly carbonyl groups at 1647cm^{-1} which refer to the quinone chromophore [25] resulting from the oxidation of phenol groups in lignin matrix exposed to effect of degradation factors on the surface of wood samples [26-27]. Analysis of this band related to the C=O carbonyl groups becomes even more complex because it is overlapped with the OH deformation of adsorbed water detected at 1620-1635cm^{-1} [12-13].

This mechanism produced, through transformation into *p*- and/or *o*-quinonoid structures (low-molecular weight products) which contain carbonyl-conjugated phenolic hydroxyl groups. This transformation occurs by cleavage of the side or by demethylation and yields formation of chromophoric structures as quinone. Previous FTIR studies showed that, under dry air conditions, lignin is partially oxidized resulting in an increase of the amount of carbonyl groups [27-30].

Lignin content was also evaluated by studying characteristic bands of guaiacyl and syringyl units. According to Pandeya and al. [31], the syringyl moiety (major unit of hardwood lignin) absorbs at 1230cm^{-1} while the guaiacyl (major unit of softwood lignin) absorbs near 1268 and 1230cm^{-1}. Simultaneously, our results show that the presence of these two bands in all non-degraded spectra (Fig. 1) gives us the information about the kind of wood that we study. It can be inferred that the specie of our samples is softwood. The absence of the peak at 1230cm^{-1} in all degraded wood samples (Fig. 2) indicates that syringyl moieties degrade at a faster rate than guaiacyl moieties.

The peaks observed at 1375 and 1158cm^{-1} which are related to C-O-C vibration and C-H deformation of carbohydrates [32], respectively, have intensities that decrease upon prolonged exposure indicating degradation of carbohydrates.

The result of degradation process affecting the structure of crystalline cellulose can be estimated from the absorption intensity at 1425 and 1318cm^{-1} which characterize the CH_2 bending vibration of amorphous and crystalline cellulose I , C-H deformation in cellulose and hemicelluloses (absorption bands assigned to polysaccharides) respectively [31,33]. The decline of the intensities of these bands is related to the decrease of the crystallinity feature of cellulose and, consequently, it can be confirmed that the degradation

mechanism caused an increase of the disordered fraction of cellulose.

Moreover, the bands detected at 898 and 802cm^{-1} (900-700cm^{-1}) correspond to the polar compounds and rocking of longue chains –$(CH_2)_n$– as well as the out of plane deformation in substituted phenolic [26]. This region is also known for containing characteristic bands of the I_β as well as of the I_α cellulose form [32]. Consequently, the decline of the intensities of these bands indicates the destruction of crystalline cellulose fraction during the degradation process.

4 Conclusions

FTIR analysis was recognized to have a big potential and prospective in diagnostics and characterization of qualitative and quantitative changes on the structure of lignocelluloses fiber of cedar wood. It has the capacity to identify the amorphous and crystalline cellulose, hemicelluloses, and lignin. Chemical modifications and structural changes of samples exposed to the natural degradation process were investigated in this work by using FTIR spectroscopy. The obtained results have shown visible decreases in the peak intensities related to lignin, cellulose and hemicellulose components accompanied by the generation of new conjugated carbonyl groups detected at 1650cm^{-1} (conjugate C=O type quinone) which resulted from lignin oxidation and at 1738cm^{-1} (C=O lactone, C=O ester) because of cellulose degradation. Degradation process occurred preferentially in the structure of cellulose; besides, the lignin was more resistant to the degradation.

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