



Lignin and derivative charcoals: Functional groups involved in the adsorption phenomenon

M. El Marouani¹, N. El Hrech², J. El Jastimi^{1,3}, A. El Hajji¹, L. Rghioui¹, S. Sebbahi^{1*}, S. El Hajjaji¹, F. Kifani-Sahban⁴

1. Laboratory of Spectroscopy, Molecular Modeling, Materials, Nanomaterials, Water and Environment, (LS3MN2E-CERNE2), Faculty of Sciences, Mohamed V University, Av Ibn Battouta, B.P. 1014, Rabat 10000, Morocco

2. Laboratory of Nanostructures, Nanomaterials, Process Engineering and Environmental, Department of Chemistry, Faculty of Sciences, Mohamed V University, Av Ibn Battouta, B.P. 1014, Rabat 10000, Morocco

3. Laboratory of Chemistry, Biochemistry and Molecular Biology, Faculty of Medicine and Pharmacy, Mohamed V University, Av Mohammed Belarbi El Alaoui, Rabat, Morocco

4. Laboratory of Thermodynamic and Energetic, Physical Department, Faculty of Sciences, Mohamed V University, Av Ibn Battouta, B.P. 1014, Rabat 10000, Morocco

Received 07 Dec2016,
Revised 18 Jun2017,
Accepted 21 Jun 2017

Keywords

- ✓ Lignin;
- ✓ Carbonization;
- ✓ Pre-oxidation with air;
- ✓ Activation by CO₂;
- ✓ Infrared Spectroscopy;
- ✓ Functional groups;

S Sebbahi
sebbahi_seloua@yahoo.fr
+212 6 61397964

Abstract

This work focuses on the characterization of raw lignin and its derivative charcoals by infrared spectroscopy. Derivative charcoals are obtained by carbonization of lignin and by activation of chars with or without pretreatment. Carbonization is carried out at 400, 600 and 800°C under nitrogen. The residence time of the carbonaceous residues at above mentioned temperatures is 2 hours. Pre-oxidation of char is made under air at 245°C for 6 hours. The activation is performed under carbon dioxide at 700°C for 30, 45 and 60 minutes. The effects of temperature of carbonization and of the duration of activation on the surface functional groups of coals and activated carbons were examined. The oxygenated groups originally present in the lignin are aliphatic and cyclic ethers, carbonyl, methoxyl and hydroxyl groups of phenolic and primary and secondary aliphatic alcohols. Functional groups undergo a substantial loss when carbonization temperature increases. Carbonization leads to the decrease in aliphaticity and the increase in aromaticity and the development of a plastic phase by crazing. During pre-oxidation and activation, there is a formation of carbonyl groups and appearance of other oxygenated groups. It follows a better resolution of the bands and a decrease in the thermoplastic nature. The best resolution of the bands and the oxygenated functional groups necessary for adsorption are obtained in the case of lignin carbonized at 600°C and activated at 700°C for 60 min. It is also the case of lignin carbonized at 600°C, pre-oxidized at 245°C for 6h then activated at 700°C for 30 min.

1. Introduction

Lignin is one of the constituents of the organic fraction of the wood and the second aromatic polymer most abundant in the nature after cellulose. Lignin is a three-dimensional macromolecule of phenolic, very complex and amorphous nature. It comes from the polymerization of the three phenylpropanols units named *p*-hydroxyphenyl (H), guaiacyl (G) and silyngyl (S) units. These components result from the oxidative radical dehydrogenation of the three monolignols (e.g. *p*-coumaryl-, coniferyl- and sinapyl-alcohols) which are connected via carbon-carbon and ether linkages (figure 1).

Pulp and paper industries discharge huge amount of black liquor with high lignin content. This latter is a source of energy, chemical products and can be valued as charcoals and activated carbons [1-3]. Our research works showed that carbonization of lignin gives a good yield in coal [4].

Activation of the lignin carbonaceous residue leads to an activated carbon whose properties and the characteristics are comparable to those of commercial activated carbon considered as reference. Activated carbon has an adsorption capacity defined among other things by its functional groups of surface. Among the methods of characterization of the latter, infrared spectroscopy is frequently used. It is in this part that we are interested in this work. Thus, the objective of the present research study is to determine the optimal conditions favorable to the formation of functional groups involved in the phenomenon of adsorption based on a characterization by infrared spectroscopy of raw lignin and its derivative charcoals.

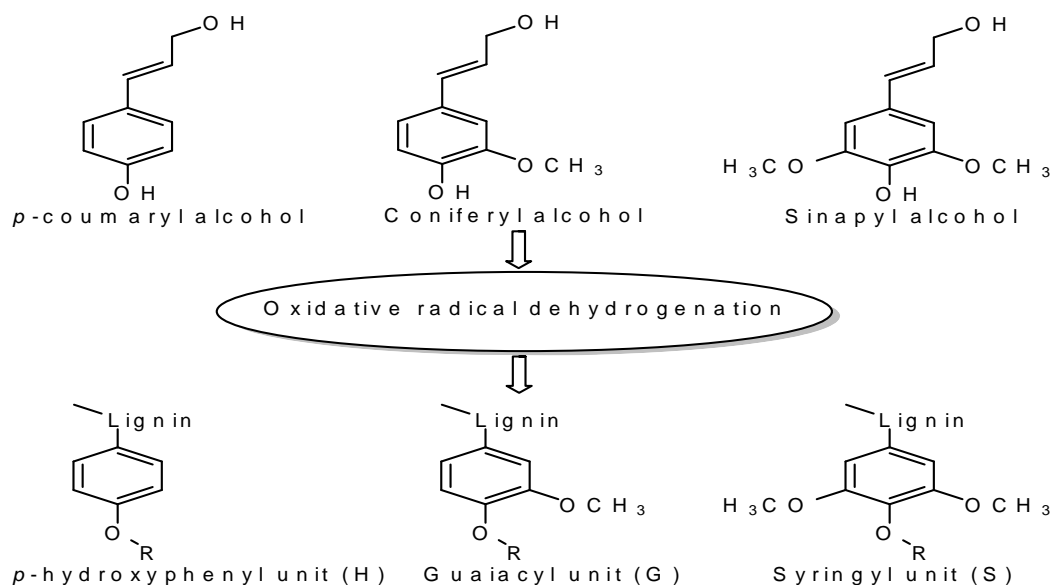


Figure 1: Simplified representation of the three units of lignins and their precursors

2. Materials and experimental methods

2.1. Materials: Raw lignin and derivative charcoals

In this work, we used the lignin in the form of powder of a particle size less than 0.250 mm, marketed by Aldrich (France). Its extraction is done using the Kraft process. Derivative charcoals are: lignin char obtained by carbonization of lignin under inert atmosphere and the activated carbon of lignin obtained by physical activation preceded or not by air pre-oxidation.

2.2 Carbonization procedure

Carbonization of lignin was carried out in a tubular furnace under nitrogen flow rate of 30 cm³/min. Lignin is heated from room temperature to different final temperatures of carbonization with a heating rate of 10°C/min. The selected temperatures are 400°C, 600°C and 800°C. Residence time of the carbonaceous residue in each of the above temperatures is 2 hours. Prepared coals are referred to as CL400, CL600 and CL800.

2.3 Procedure of pre-oxidation

The samples of lignin carbonaceous residue are pre-oxidized in the furnace where the carbonization is carried out too. Operation consists of treating the samples under an air flow rate of 25 cm³/min at selected temperature for a fixed duration. Duration of pre-treatment is 6 hours and pre-oxidation temperature is 245°C. Choice of the duration and the aforementioned temperature has been the subject of previous work [4]. The sample obtained under these conditions is called CL600 (245°C,6h,air).

2.4 Activation procedure

Activation of the pre-oxidized or not charcoals is performed in the same furnace where pre-oxidation and carbonization also perform. The carbonaceous residues, in powder form are activated in carbon dioxide with a partial pressure equal to 1. Once the sample is placed in the oven, it is treated from room temperature to the temperature of activation under nitrogen and with a heating rate of 10°C/min. When the activation temperature is reached and remains constant, nitrogen is interrupted and the carbon dioxide is introduced with a flow rate of 24 cm³/min. The sample is kept at the temperature of activation during a fixed time. At the end of the reaction, cooling is carried out under nitrogen. Only are known the masses before and after each treatment. Activated and pre-oxidized then activated samples thus obtained are referred to respectively as CL600 (700°C,tact,CO₂) and CL600 (245°C,6h,air) (700°C,tact,CO₂) where tact represents the duration of activation. Temperature and activation times examined are respectively 700°C and 30, 45 and 60 minutes.

2.5 Spectral characterization

The apparatus used for the characterization by infrared spectroscopy is a Bruker-Tensor 27, which operates in reflection mode. This apparatus is equipped with a Globar source that emits radiation in the region of mid-infrared and of a DLaTGS detector. In the unity of Attenuated Total Reflection (ATR), enough of the sample is

placed, without prior preparation, on the crystal. In our analyses, the crystal used is the germanium crystal, which allows the acquisition between 4000 and 600 cm^{-1} in wave number. The number of scans is 20 with a resolution of 4 cm^{-1} . The device is controlled by OPUS software.

2.6 Microscopic characterization

The characterization by transmission electron microscope (TEM) is done on a fine powder, using TECNAI G2/FEI equipment, high voltage (120 KV), provided with a CCD camera. The resolution is 0.35 nm and the enlargement varies from 150 to 500000 x. The characterization by scanning electron microscopy (SEM) of the lignin residues is made on a scanning electron microscope, GEOL JSM T330.

2.7 Characterization by X-ray diffraction

The powder diagrams of raw lignin and lignin char are recorded with a diffractometer Siemens D5000 type using $\text{K}\alpha_1$ ray of copper ($\lambda = 1.5406 \text{ \AA}$).

2.8 Measurement of specific surface area

Specific surface area measurements are made on a micrometer ASAP 2010. The degassing of samples is carried out at 250°C under a mixture of He (70 %) and N_2 (30 %) for 2h.

3. Results and discussions

The infrared spectra of raw lignin and its derivative charcoals are illustrated in figures 2, 3 and 5. The assignment of the fundamental vibrations of raw lignin, its carbonaceous residues and its activated carbons with or without pre-treatment are grouped in tables 1 and 2. The assignment of vibration bands was made on the basis of previous work carried out on the compounds of the same family [5-32] and on the basis of the interpretation of the infrared spectra that we have performed for raw lignin and for CL600 [33].

3.1 Infrared spectrum of raw lignin

Identification of the main functional groups of raw lignin is given in the following:

Vibrations of (O-H) groups

The $\nu(\text{O-H})$ stretching vibration appears on the IR spectrum of the raw lignin as a wide and intense massif centered around 3410 cm^{-1} and having two shoulders at 3600 and 3287 cm^{-1} (figure 2). The latter's are attributed to the hydroxyl alcoholic groups in phenolic and aliphatic structures [17-21]. The thin absorption of medium intensity observed at 1417 cm^{-1} is related to the vibration of $\delta(\text{O-H})$ in-plane deformation of phenolic hydroxyl groups [7, 18]. The thin and weak band at 667 cm^{-1} is assigned to the $\gamma(\text{O-H})$ out-of-plane deformation of primary and secondary aliphatic hydroxyl groups and/or phenolic hydroxyl groups (table 1) [7].

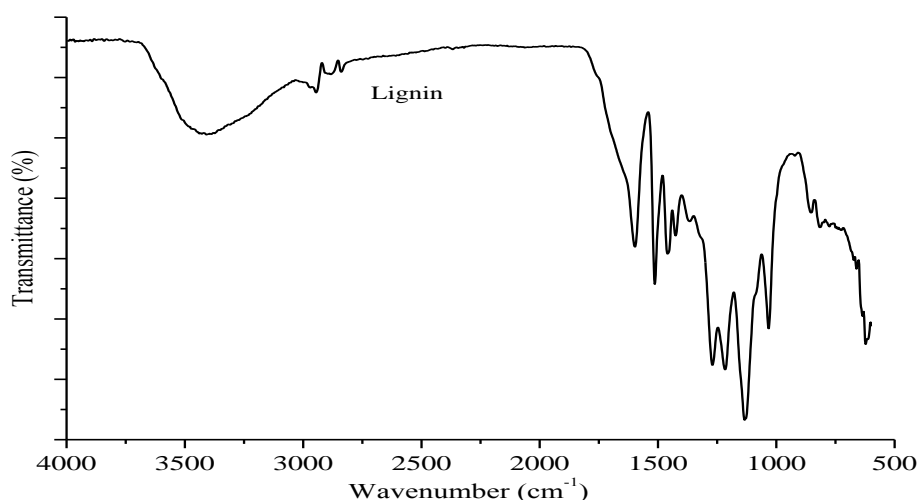


Figure 2: Infrared spectrum of raw lignin

Vibrations of (C-H) groups

The bands between 2975 and 2800 cm^{-1} correspond to the $\nu(\text{C-H})$ asymmetric and symmetric stretching vibrations of aromatic methoxyl groups ($-\text{OCH}_3$) and of methylene groups ($-\text{CH}_2$) of side chains [17-20]. The asymmetric and symmetric vibrations of CH_3 in-plane deformation group are respectively located at 1444 and 1361 cm^{-1} [17-20]. The band recorded at 1444 cm^{-1} can also be attributed to the vibration of CH_2 in-plane deformation group [17-20]. The $\gamma(\text{C-H})$ out-of-plane vibration in benzene of guaiacyl type gives rise to bands located at 843 and 796 cm^{-1} [17-20].

Vibrations of (C=O) groups

The shoulder located at 1740 cm^{-1} is related to the $\nu(\text{C=O})$ stretching vibration of carbonyl groups [20], indicating the presence of the hydroxycinnamates, such as *p*-coumarate and ferulates [34].

Vibrations of (C=C) groups

The stretching vibration for $\nu(\text{C=C})$ in aliphatic chain causes the shoulder at about 1640 cm^{-1} [10, 32]. While the skeletal $\nu(\text{C=C})$ vibrations in aromatic rings, they are represented by four bands at about 1593, 1565, 1509 and 1454 cm^{-1} [17-21]. These are characteristic bands of the lignins of guaiacyl-syringyl type [35].

Vibrations of (C-O) groups

As regards the $\nu(\text{C-O})$ stretching vibrations, strong band at 1269 cm^{-1} is due to the cyclic ether groups [18, 19, 22]. Faix and Beinhoff [36] attributed this band to the breathing vibration of guaiacyl core. The $\nu(\text{C-O})$ stretching vibrations of phenols and/or cyclic ethers in the guaiacyls were attached to the signal detected at 1204 cm^{-1} [18, 19, 22]. The very strong absorption at 1120 cm^{-1} is attributed to $\nu(\text{C-O})$ of the secondary alcohol ($-\text{R}_2\text{CH-OH}$) and/or aliphatic ether [18, 19]. This band can also be attached to the breathing vibration of syringyl core. However, for Faix [37], the presence of this band indicates that the lignin is GSH-type. As for the strong absorption located at 1018 cm^{-1} , it is assigned to the vibration of $\nu(\text{C-O})$ valence of the primary alcohol (R-OH) [18, 19].

According to the above analysis, the main oxygenated groups originally present in the lignin are aliphatic and cyclic ether, carbonyl, methoxyl groups, phenolic hydroxyl groups and primary and secondary aliphatic hydroxyl groups. In addition, this lignin is composed of guaiacyl (G) and syringyl (S) units (GS-type). These units are the main components of hardwood lignins [38, 39].

3.2 Evolution of functional groups during carbonization

Figure 3 includes the infrared spectra of raw lignin and the lignin residues carbonized at 400, 600 and 800°C. Corresponding residues are respectively appointed CL400, CL600 and CL800.

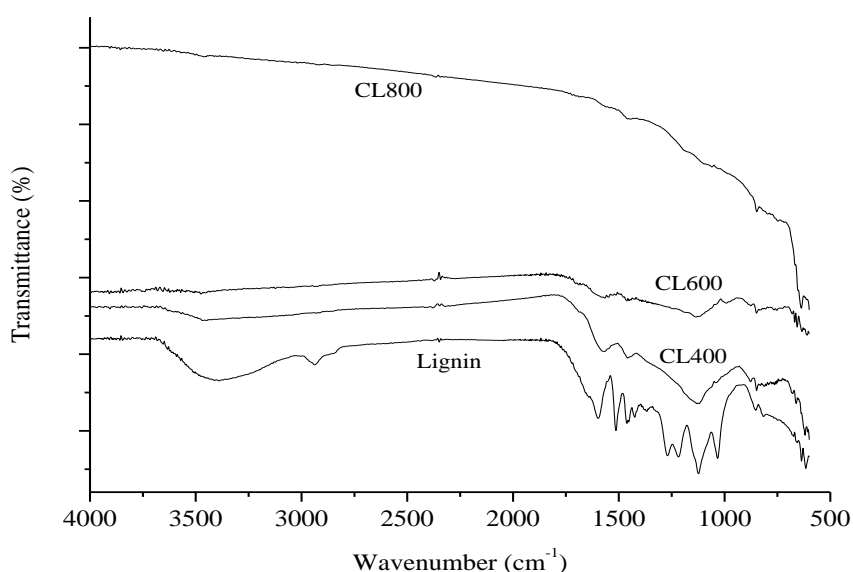


Figure 3: IR spectra of raw lignin and carbonaceous residues obtained at 400, 600 and 800°C

Compared to the spectrum of raw lignin, the spectra of the three coals present a widening of the infrared bands with a reduction in their intensity and a concomitant loss of resolution as carbonization temperature increases. This is due to thermal treatment of lignin. Indeed, carbonization is accompanied by a loss of mass [40] and the development of a plastic phase by crazing [40, 41] that gives to the material its thermal resistance [40] and its amorphous character shown by the diffractograms of X-rays that we have done (figure 4). Indeed, diffractograms do not have a horizontal baseline. This would indicate that the majority of material is amorphous, that the sequence of the samples crystallinity is very low and the structure of these compounds is a turbostratic structure.

The reduction of the intensity of the band related to $\nu(\text{O-H})$ is due to a consequent loss of oxygenated alcoholic and phenolic groups [7, 17, 21]. The loss of these groups occurs during the carbonization of all biomasses [7, 9-11, 13, 14, 16, 17, 21, 42, 43]. This loss indicates that these functional groups are thermally unstable [10, 11, 42]. Moreover, the bands corresponding to the stretching vibrations of methyl and methylene groups are no longer discernable in the coals. The loss of these groups is in favor of a reduction in aliphaticity [7-10, 13, 17, 43] and an increase in aromaticity [7, 9, 10, 17, 42, 43]. The development of the latter is supported by the increase of intensity of the aromatic vibrations of $\gamma(\text{C-H})$ out-of-plane deformation and by the appearance of new absorptions at 851 and 750 cm^{-1} attached to these vibrations (table 1) [7, 10, 17, 42, 43].

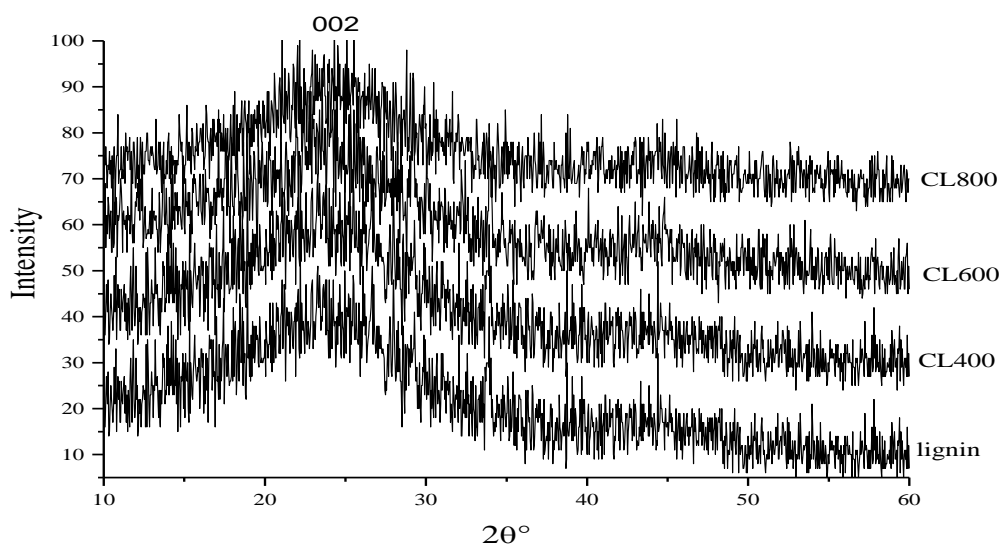


Figure 4: X-ray diffractograms of raw lignin and lignin chars

Regarding $\nu(\text{C=O})$ vibration at 1740 cm^{-1} related to the carbonyl groups, it takes the form of shoulder on the infrared spectra of CL400 and CL600 as in the case of raw lignin (table 1).

The $\nu(\text{C=C})$ stretching vibrations related to the aliphatic functional groups, which appear as shoulder around 1640 cm^{-1} on the IR spectrum of raw lignin, persist in the same form in the case of CL400 and disappear in the case of CL600 and CL800 [10, 43]. However, the skeletal vibrations $\nu(\text{C=C})$ in the aromatic rings that existed in the lignin persist in the three coals [10, 13, 42, 43] with a slight shift to either low or high frequencies (table 1). In this regard, no explanation is advanced in the literature [7, 17].

Finally, the $\nu(\text{C-O})$ stretching vibrations gather in broadband. The intensity of this band decreases when carbonization temperature increases.

Considering this infrared characterization, the continuation of the work will be performed on CL600, seeing that it is the carbonaceous residue which contains the least amount of volatiles matters.

3.3 Evolution of functional groups during activation

Figure 5 contains the infrared spectra of CL600 and CL600 activated at 700°C for 30, 45 and 60 minutes with pre-treatment (b) and without pre-treatment (a). The pre-treatment is carried out under air at 245°C for 6 hours. Figure 5a shows that when the activation time is less than or equal to 45 minutes, resolution and intensity of the bands relating to different groups improve as activation time increases. However, spectrum corresponding to CL600 activated at 700°C for 60 minutes shows a decrease in the intensity of the band assigned to the O-H

group and the appearance of three new bands located at 1722, 1713 and 1695 cm^{-1} attributed to $\nu(\text{C}=\text{O})$ stretching vibrations (table 2). The presence of these vibrations indicates that carbon dioxide reacts with the substrate to form the carbonyl groups. The same result was obtained by Yang and al. [44] and Guo and al. [45].

Table 1: Assignment of the fundamental vibrations of raw lignin and its carbonaceous residues

Vibrational frequencies (cm^{-1})				Functional groups and type of corresponding monolignol (G): Guaiacyl or (S): Syringyl	
Lignin	CL400	CL600	CL800		
3410	3448	3438	-	-	$\nu(\text{O-H})$ stretching vibrations in hydroxyl groups
2972	-	-	-	-	$\nu(\text{C-H})$ stretching vibrations in methyl and methylene groups
2945	-	-	-	-	
2907	-	-	-	-	
2880	-	-	-	-	
2833	-	-	-	-	
1740	1740	1740	-	-	$\nu(\text{C}=\text{O})$ stretching vibrations in carbonyl groups
1640	1676	-	-	-	$\nu(\text{C}=\text{C})$ stretching vibrations in aliphatic groups
1593	-	1593	-	(S)	$\nu(\text{C}=\text{C})$ stretching vibrations in aromatic groups
-	-	1574	-	-	
1565	1565	1556	1565	-	
-	1537	1537	-	-	
1509	-	-	-	(G)	
1454	1454	1454	1454	-	
1444	1444	1444	-	-	$\delta^{\text{as}}_{\text{CH}_3}$ and δ_{CH_2} in-plane deformation vibrations
1417	1417	1417	-	-	$\delta(\text{O-H})$ in-plane deformation vibrations
1361	1352	1361	-	-	$\delta^{\text{s}}_{\text{CH}_3}$ in-plane deformation vibrations
1306	-	1306	-	-	
1269	1269	1269	-	(G)	$\nu(\text{C-O})$ stretching vibrations in ether, alcohol groups
1204	1204	1204	1176	(G)	
1120	1120	1120	-	(S)	
1083	-	1083	-	-	
-	1046	-	1046	-	
1018	1018	1018	-	-	
-	1000	991	-	-	
-	981	981	-	-	
954	954	945	-	-	
907	-	907	-	-	
-	861	851	-	-	$\gamma(\text{C-H})$ out-of-plane deformation vibrations
843	843	843	843	(G)	
796	796	796	787	-	
-	750	750	732	-	
667	667	667	648	-	$\gamma(\text{O-H})$ out-of-plane deformation vibrations
-	-	-	639	-	
-	-	-	620	-	

According to Perezdrienko and al. [46], oxidation of some alcoholic hydroxyl groups into carboxyl and aldehydes groups would be at the origin of the progressive increase in the intensity of $\nu(\text{C}=\text{O})$ absorption band and the decline of the $\nu(\text{O-H})$ band during activation. The formation of carbonyl groups leads to the decrease of the thermoplastic nature and the development of porosity. These phenomena also appear clearly on images taken by SEM (figure 6), by TEM and by the values of the specific surface areas (figure 7).

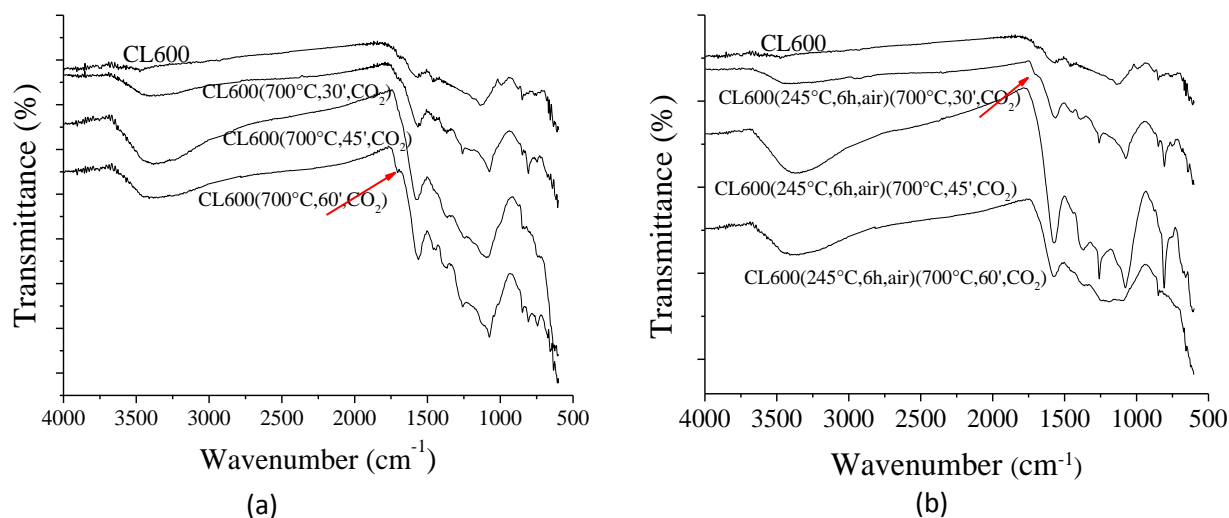


Figure 5: Evolution of functional groups with the activation duration (a) without pre-oxidation (b) with pre-oxidation

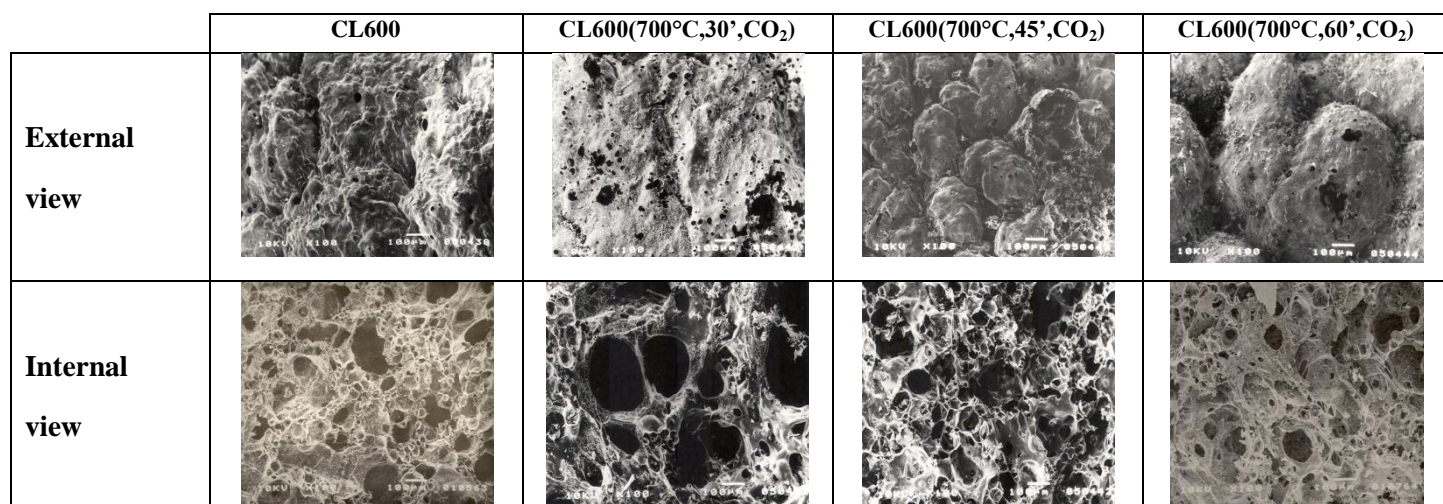


Figure 6: SEM micrographs relating to the internal and external side of CL600 and CL600 activated at 700°C for 30, 45 and 60 minutes (magnification : $\times 100$ and --- : 100 μm)

	CL600	CL600 (700°C,1h,CO ₂)
TEM		
Specific surface areas (m ² /g)	30.28	394.26

Figure 7: Images taken by TEM and specific surface areas of CL600 and activated CL600

At the end of this infrared analysis, it is clear that the formation of oxygen groups by activation under CO₂ depends on the conditions of carbonization and activation. Indeed, the comparison of the different spectra made in the above paragraphs (figures 2 and 4a) indicates that lignin carbonized at 600°C for 2 hours under N₂ then

activated at 700°C for 1 hour under CO₂ is the richest sample in functional groups and especially in carbonyl groups involved in the phenomenon of adsorption (table 2).

Table 2 : Assignment of the fundamental vibrations of CL600, CL600 activated at 700°C for 30, 45 and 60 min and the same activates preceded of a pre-oxidation at 245°C for 6 h

Vibrational frequencies (cm ⁻¹)							Functional groups
CL600	CL600 A30'	CL600 A45'	CL600 A60'	CL600 PO+A30'	CL600 PO+A45'	CL600 PO+A60'	
3438	3350	3338	3407	3370	3352	3370	ν(O-H)as Stretching vibrations in hydroxyl groups
-	-	-	1722	-	-	-	ν(C=O) Stretching vibrations in carbonyl groups
1740	-	-	1713	-	-	-	
-	1695	1695	1695	1695	-	-	
1593	-	1593	1593	-	-	1583	ν(C=C) Stretching vibrations in aromatic groups
1574	1574	1574	1574	-	1574	-	
1556	1556	1556	1556	1565	-	1556	
1537	1537	1537	-	1537	-	-	
-	1518	1518	-1528	1518	-	-	
-	-	1491	1472	1491	1472	1472	
1454	1454	1454	1454	1454	1454	-	
1444	1444	1444	1400	1444	-	-	δ ^{as} _{CH3} and δ _{CH2}
1417	-	-	-	1417	1426	-	δ(O-H)
1361	1361	1361	-1361	1380	1368	-	δ ^s _{CH3}
1306	-	1306	-	1343	-	-	
-	-	-	1287	1278	1287	-	ν(C-O) Stretching vibrations in ether, alcohol groups
1269	1269	1269	1269	-	1260	1260	
-	1250	1250	1250	1250	-	1250	
1204	1185	1195	1185	1195	1185	-	
-	-	-	-	1167	-	1148	
1120	-	1120	1120	-	1120	1111	
1083	-	1083	1083	1065	1078	1074	
-	1056	1056	1046	-	-	1056	
1018	1018	1018	-1018	-	-	-	
991	991	-	-	-	-	-	
981	982	973	-963	963	-	-	
945	945	-	-	935	-	945	
907	-	-	-	-	-	-	
-	-	880	-889	889	-898	880	
851	-	861	-861	861	861	861	
843	843	843	-	843	833	843	
-	833	806	815	788	824	-	
796	787	-	-	-	807	-	
750	722	750	750	-	-	-	
-	-	732	-	722	-	-	
667	667	667	667	676	685	667	γ(O-H) Out-of-plane deformation vibrations
-	-	-	-	657	639	-	

At this stage of our work, it is possible to advance that above mentioned temperatures and duration of carbonization and activation are the optimal conditions to elaborate an adsorbent from lignin. The pre-treatment of the carbonaceous residues of lignin in presence of oxygen seems to improve the reactivity of chars [47]. This phenomenon is justified by the results in figure 5b. Indeed, examination of the infrared spectra of figures 5a and 5b shows that most of functional groups, initially present in raw lignin (figure 2), are reformed in the activated carbons. In this analysis, we are particularly interested in the carbonyl group, which is involved in the adsorption phenomenon. The intensity of this band is maximum on the spectrum of the CL600 (700°C,60',CO₂)

sample (figure 5a) and on that of the CL600 (245°C,6h,air) (700°C,30',CO₂) one (figure 5b), which are practically similar.

So without pre-treatment, the time required to have bands with better resolution is 60 min and with pre-treatment, the duration is reduced to 30 minutes. The pre-oxidation allows reducing the activation duration. This was explained in a previous work [47] by the results related to the activation yield of the residue non pre-oxidized and of the residue pre-oxidized at 245°C for 6 hours.

Pre-treatment at 245°C for 6 hours reduced activation time to 50 %, intensifies and improves resolution of bands related to different oxygenated groups. The presence of all of these groups and more particularly that of carbonyl group is of great interest in the phenomena of adsorption. Moreover, adsorption tests of methylene blue and methyl orange that we have done onto raw lignin, on its derivative charcoals and on commercial activated carbon showed that the activated carbon of lignin has adsorption capacities equal and even superior to those of commercial activated carbon.

Conclusions

Characterization by infrared spectroscopy has allowed to identify the different oxygenated groups of raw lignin and to follow their evolution after carbonization and then activation preceded or not with a pre-oxidation.

Oxygenated groups initially present in the lignin are the aliphatic and cyclic ether, carbonyl, methoxyl, phenolic hydroxyl groups and primary and secondary aliphatic hydroxyl groups.

After carbonization, there is decrease in intensity and resolution of the various bands that becomes more important when carbonization temperature increases. Bands related to the vibrations of the aliphatic bindings and the oxygenated groups decrease and those related to the vibrations of the aromatic connections increase. This lead to a thermoplastic character, much more developed for CL800 than for CL400 and CL600.

After pre-oxidation and activation, most initially present functional groups in lignin re-form in its activated carbon. The formation of these groups reduces the thermoplastic nature of coal.

The study based on the activation time has shown that the best resolution of the bands and the essential oxygenated groups for adsorption are obtained in the case of the lignin carbonized at 600°C and activated at 700°C for 60 min. This is also the case of lignin carbonized at 600°C, pre-oxidized at 245°C for 6 h and activated at 700°C for 30 minutes.

Pre-treatment at 245°C for 6 hours reduced activation time to 50 %, intensifies and improves resolution of bands related to oxygenated groups. The presence of all of these groups and more particularly the carbonyl group is of great interest in the phenomena of adsorption.

References

1. Pearl I.A., 'The Chemistry of Lignin', Marcel Dekker, Inc.: New York, (1967) 339.
2. Fengel D. and Wegener G., 'Wood Chemistry, Ultrastructure, Reaction', Kessel Verlag, München (2003).
3. Sjöström E., 'Wood Chemistry: Fundamentals and Application. Academic Press', Orlando (1993) 293.
4. Sebbahi S., Ahmido A., Kifani-Sahban F., El Hajjaji S. and Zoulalian A., *J. Eng.* 2014 (2014) Article ID 972897, 1.
5. Liu Q., Wang S., Zheng Y., Luo Z. and Cen K., *J. Anal. Appl. Pyrol.* 82(1) (2008) 170-177.
6. Zhao J., Xiuwen W., Hu J., Liu Q., Shen D. and Xiao R., *Polym. Degrad. Stab.* 108 (2014) 133-138.
7. Sharma R.K., Wooten J.B., Baliga V.L., Lin X., Chan W.G. and Hajaligol M.R., *Fuel* 83(11/12) (2004) 1469-1482.
8. Hu J., Shen D., Wu S., Zhang H. and Xiao R., *J. Anal. Appl. Pyrol.* 106 (2014) 118-124.
9. Bouchelta C., Medjram M.S., Bertrand O. and Bellat J.-P., *J. Anal. Appl. Pyrol.* 82 (2008) 70-77.
10. Yang T. and Lua A.C., *J. Colloid Interf. Sci.* 267 (2003) 408-417.
11. Guo J. and Lua A.C., *Mater. Lett.* 55 (2002) 334-339.
12. Matos J., Nahas C., Rojas L., Rosales M., *J. Hazard. Mater.* 196 (2011) 360- 369.
13. Zhang J., Fu H., Lv X., Tang J. and Xu X., *Biomass Bioenergy* 35 (2011) 464-472.
14. Li W.-H., Yue Q.-Y., Gao B.-Y., Wang X.-J., Qi Y.-F., Zhao Y.-Q., Li Y.-J., *Desalination* 278 (2011) 179-185.
15. Kriaa A., Hamdi N. and Srasra E., *Desalination* 250 (2010) 179-187.
16. Nabais J.M.V., Nunes P., Carrott P.J.M., Carrott M.M.L.R., García A.M., Díaz-Díez M.A., *Fuel Process. Technol.* 89 (2008) 262-268.
17. Atul V. Maldhure and J.D. Ekhe, *J. Environ. Chem. Eng.* 1 (2013) 844-849.
18. Savy D. and Piccolo A., *Biomass Bioenergy* 62 (2014) 58-67.

19. Sun Y.-C., Xu J.-K., Xu F. and Sun R.-C., *Ind. Crops Prod.* 47 (2013) 277-285.
20. Boeriu C.G., Bravo D., Gosselink R.J.A. and van Dam J.E.G., *Ind. Crops Prod.* 20(2) (2004) 205–218.
21. Carrott Suhas P.J.M. and Ribeiro Carrott M.M.L., *Bioresource Technol.* 98 (2007) 2301-2312.
22. Umesh P. Agarwaj and Rajai H. Atalla, '4 Vibrational Spectroscopy', in *Lignin and Lignans: Advances in Chemistry*, Edited by C. Heitner, D.R. Dimmel and J.A. Schmidt, (2010) 103-136.
23. Tiwari D. and Lee S.M., *Wat. Environ. Res.* 83(9) (2011) 874-881.
24. Markovic J.P., Radovic J.B., Strbanovic R.T., Bajic D.S. and Vrvic M.M., *J. Serbian Chem. Soc.* 74(8–9) (2009) 885–892.
25. Bykov I., Master Thesis, Division of Chemical Technology Department of Chemical Engineering and Geosciences Lulea University of Technology S-971 87 Lulea (2008).
26. Bai Y.-Y., Xiao L.-P., Shi Z.-J. and Sun R.-C., *Inter. J. Mol. Sci.* 14(11) (2013) 21394-21413.
27. Karmanov A.P. and Derkacheva O.Yu., *Russ. J. Bioorg. Chem.* 39(7) (2013) 677-685.
28. Fitigau I.F., Peter F. and Boeriu C.G., *Inter. Scholarly Scientific res. Innovation* 7(4) (2013) 167-172.
29. Esam Mohammed Sheet, Sheet Mohammed Saleh and Ali Younis Hamed, *Mesopotamia J. Agric.* 35 (1) 2007.
30. Tchakala I., Bawa L.M., Djaneye-Boundjou G., Doni K.S. et Nambo P., *Inter. J. Biological Chem. Sci.* 6(1) (2012) 461-478.
31. Saha S.C., Das B.K., Ray P.K., Pandey S.N. and Goswami K., *J. Appl. Polym. Sci.* 43 (1991) 1885-1890.
32. Silverstein, Webster and Kiemle, 'Identification spectrométrique de composés organiques', 2^{ème} édition, De Boeck (2007).
33. Sebbahi S., El Fakir L., Rghioui L., El Hajji A., Brik Y., Kifani-Sahban F. and El Hajjaji S., *J. Mater. Environ. Sci. JMES* 6(9) (2015) 2461-2468.
34. Sun R., Tomkinson J., Zhu W. and Wang S.Q., *J. Agric. Food Chem.* 48 (2000) 1253-1262.
35. Pandey K.K., *J. Appl. Polym. Sci.* 71 (1999) 1969.
36. Faix O. and Beinhoff O., *J. Wood Chem. Technol.* 8 (1988) 505-522.
37. Faix O., *Holzforschung* 45 (1991) 21-27.
38. Stevanovic T. and Perrin D., La lignine, in: *Chimie du Bois*. Lausanne, Presses Poly. et Univers. Romandes (2009) 145-177.
39. Doherty W.O.S., Mousavioun P. and Fellows C.M., *Ind. Crops Prod.* 33 (2011) 259-276.
40. Kifani-Sahban F., Kifani A., Belkbir L., Zoulalian A., Arauso J. and Cordero T., *Thermochim. Acta* 298 (1997) 199-204.
41. Sebbahi S., Yaouiss M., Rahho R., Kifani-Sahban F., Boukallouch M. and Kifani A., *Sci. Lett.* 5(2) (2003) 1-6.
42. Pastor-Villegas J., Meneses Rodríguez J.M., Pastor-Valle J.F., Rouquerol J., Denoyel R. and García García M., *J. Anal. Appl. Pyrol.* 88 (2010) 124-133.
43. Gomez-Serrano V., Piriz-Almeida F., Duran-Valle C.J. and Pastor-Villegas J., *Carbon* 37(10) (1999) 1517-1528.
44. Yang T. and Lua A.C., *J. Colloid Interf. Sci.* 267 (2003) 408-417.
45. Guo J. and Lua A.C., *Mater. lett.* 55 (2002) 334-339.
46. Perezdrienko I.V., Molodozhenyuk T.B., Shermatov B.E. and Yunusov M.P., *Russ. J. Appl. Chem.* 74 (2001) 1650-1652.
47. Sebbahi S., Kifani-Sahban F., El Hajjaji S. and Zoulalian A., *Bull. Soc. Roy. Sci. Liège* 84 (2015) 194-206.

(2017) ; <http://www.jmaterenvironsci.com>