Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2019, 11(2): 1-5
(http://www.derpharmachemica.com/archive.html)

Spectroscopic Characterization of a Material of Natural Origin before and after Treatment with Different Solvents

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ABSTRACT

In this paper the beet pulp (BP) before and after of chemical treatment by three solvents was characterized. The examination of the Infra-Red (IR) spectrum of this material before treatment shows the existence of several characteristic peaks of several functional groups of cellulose, hemicellulose and pectin. After treatment of this material with the various solvents, the results obtained show that the treatment of BP by various solvents has a considerable effect on the chemical modification of the structure of this material. The X-ray Diffraction (XRD) results show that this material contains two zones, crystalline zone and amorphous zone. The analysis of the morphology obtained from this material by Scanning Electron Microscopy (SEM), shows that, this material contains compact and ordered zones, and disordered and porous zones, containing of fibers characteristic of hemicelluloses. After treatment by the three solvents, it can be concluded that the treatment with distilled water and ethanol has a considerable effect on the removal of some constituents of the original material. On the other hand, the treatment of the beet pulp with formaldehyde in an acid medium leads to a compact and ordered material.

Keywords: Spectroscopic characterization, IR, XRD, SEM, Beet pulp, Solvents, Chemical treatment.

INTRODUCTION

In Morocco, the sugar industry has known a remarkably developed in recent years, thanks to the important cultivation of sugar cane and sugar beet. The industry of these two plants has produced several by-products; each by-product is valued in several fields. The sugar cane wax is found among the constituents of sugar cane, which is used in the cosmetics and pharmaceutical industry, [1], it is also included in the composition of medicines that lowers cholesterol levels. Thus, the sugar beet molasses is used to produce alcohol, used as spirits or medicine, in the manufacture of perfumes [2,3].

The beet pulp is the second by-product of the sugar beet industry after molasses, and it is mainly used in the feeding cattle [4]. It is a food rich in digestible sugar and generally much appreciated by most animals. The beet pulp can be used as a fermentation substrate or of industrial methanation, as a primary fuel or as an absorbent for heavy metals and other pollutants in water treatment plants. It can also be used as an absorbent in disposable diapers for babies or in pet litters. The use of the pulp as an industrial fermentation substrate by bacteria or fungi allows the production of a wide variety of natural molecules: enzymes, proteins, sugars, natural vanilla flavors. The hydrolysis of the pulp provides many molecules for industrial use.

The galacturonic acid and his polymers derived from the pectin of the beet pulp are used for the manufacture of ecological detergents or surfactants. A derivative of his fermentation, lactic acid, can serve as a basis for producing fully biodegradable plastics [5]. Currently, researchers are also attempting to combine the dry beet pulp with polymers to obtain strong, lightweight building materials [6]. The beet fibers can also be used in the manufacture of insulating felts in the building. It provides the flexibility, elasticity and lightness. Also, other researchers have shown that it is possible to replace the fine sand in concrete or acoustic insulating panels (noise walls along the roads) by the beet pulp, the mixture is made cold with fresh pulp, Which allows a low-cost processing [7].

The production of beet pulp to find a new way of upgrading in the stationery industry [8-13]. It is used to improve the mechanical and optical properties of paper [7].

In this work, we are interested of characterizing the chemical modifications in the structure of this biomaterial before and after treatment, using the following spectroscopic techniques: Infrared (IR), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD).

MATERIALS AND METHODS

Preparation of the raw beet pulp (RBP)

The raw beet pulp was dried in the air by the action of sunlight and then ground and sieved to obtain homogeneous materials for the experimental designs and the fraction of granularity of very small diameter. The raw beet pulp is designated by the abbreviation RBP.

Preparation of beet pulp treated with the distilled water (BPTDW)

The treatment was carried out several times by contacting an amount of 5 g of the beet pulp crushed and sieved with a sufficient volume of the distilled water. The first treatment is done with hot distilled water under magnetic stirring for 2 hours. This operation involved both the removal of impurities and grinding residues and the evaluation of the soluble fraction, and the resulting material was filtered with filter paper and dried in an oven between 40 and 50°C, to constant mass. The beet pulp treated with the distilled water is referred to by the abbreviation BPTDW.

Preparation of the beet pulp treated by the ethanol (BPTET)

5 g of the beet pulp crushed and sieved and the fraction of granularity very small diameter was treated 5 times with 65% ethanol to remove the residual sugars (sucrose, arabinose, fucose). The first treated was carried out hot until it boiled, it eliminates any trace of enzymatic activity. Subsequently, the material obtained was filtered with a filter paper, and then dried in an oven at 40°C. The beet pulp treated with ethanol is designated by the abbreviation BPTET.

Preparation of beet pulp treated by formaldehyde (BPTFA)

A mass of 5 g of beet pulp crushed and sieved was placed in the mixture of 100 ml of H_2SO_4 at a concentration of 0.1 mol/l and the formaldehyde (36.5%). The mixture obtained was brought to reflux under mild magnetic stirring at 50°C. After 4 h the material obtained was cooled and washed with distilled water to pH=4, filtered with filter paper and dried in an oven at 40°C-50°C, until A constant weight. The beet pulp treated with formaldehyde is referred to as BPTFA.

The treatment of raw beet pulp by formaldehyde in an acid medium consists of crosslinking the biopolymers of the side chains contained in the beet pulp into three-dimensional polymers by creating intermolecular cross-links (formation of bridges).

Analytical techniques

For the characterization of the materials, we used Infrared Spectroscopy (IR) of Bruker type and Tensor 27 model, and X-ray diffraction (XRD) of the Panalytical X Pert^3 Powder type, which is carried out at the research center of The Faculty of Science of Kenitra.

RESULTS AND DISCUSSION

Analysis of RBP, BPTDW, BPTET and BPTFA by IR

The Figure 1 shows the superposition of the infrared spectra of the raw beet pulp (RBP), the beet pulp treated with distilled water (BPTDW), the beet pulp treated by ethanol (BPTET) and the beet pulp treated by the formaldehyde in acid medium (PBTFA).

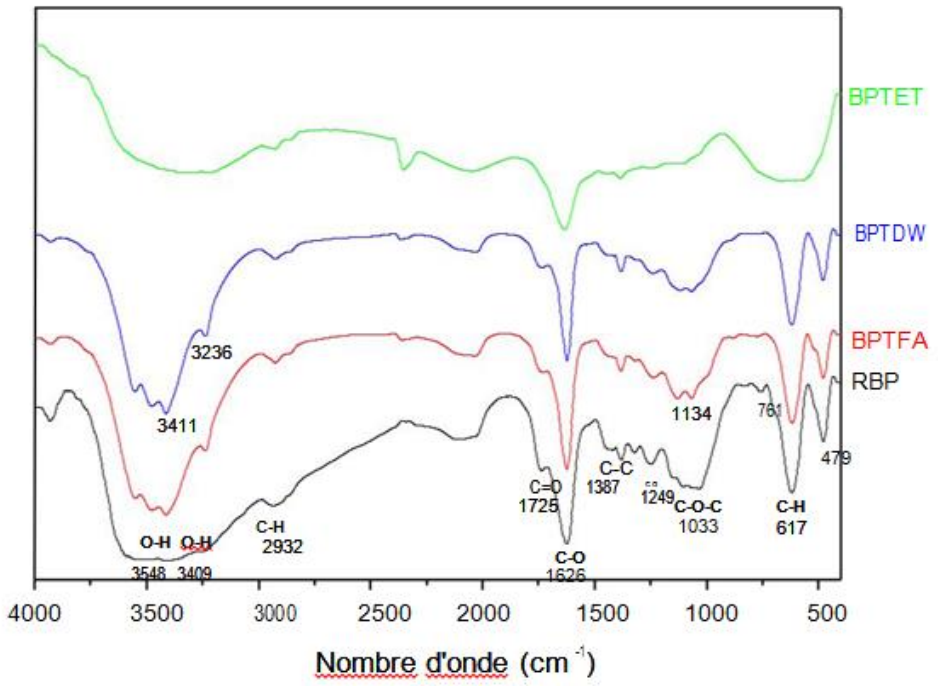

Figure 1: IR spectra of materials RBP, BPTDW, BPTFA and BPTET

The examination of the IR spectrum of PBB shows the existence of several peaks characteristic of several functional groups. The vibration at 3548 cm^{-1} is characteristic of the intramolecular hydrogen bond of the cellulose, and the band around 3409 cm^{-1} is attributed to the elongation vibration of the cellulose OH bond, hemicelluloses and Pectin. The peak at 2932 cm^{-1} corresponds to the asymmetric elongation vibration of the C-H bond. The band around 1626 cm^{-1} is attributed to the vibration of the C-O group of hemicelluloses and galacturonic acid. The peak at about 1725 cm^{-1} is characteristic of the C = O valence vibration of galacturonic acid. The bands which

appear at the frequency between 1419 -1323 cm^{-1} correspond to the vibrations of elongations of the group C-C. The peaks between 761-479 cm^{-1} are attributed to the out of plane deformation of the C-H group. The band 1249 cm^{-1} corresponds to the symmetrical elongation vibration of the C-O bond, and the peak at 1033 cm^{-1} is characteristic of the vibration of the C-O-C group.

After treatment of the PBB with the distilled water (PBTED), we notice a shift in the number of waves of the OH group (hydrogen bond) to 3411 cm^{-1}, thus a displacement of the wave number from 3409 to 3236 cm^{-1} of the elongation vibration of the OH bond with a decrease in its intensity. These results are probably due to the elimination of some O-H groups during the treatment with the distilled water.

The treatment of the beet pulp with the formaldehyde in an acid medium (PBLFA), leads to the appearance of a peak of the wave number at about 1134 cm^{-1}, characteristic of the C-O-C group.

After treatment of the beet pulp with the ethanol (PBLET), we note the disappearance of some peaks characteristic of some groups (O-H), and vibrations of deformation outside plane C-H and vibrations of the groups C-O.

Thus, it can be concluded that the treatment of PBB by these different solvents has a considerable effect on the chemical modification of the structure of this material and especially the washing with formaldehyde and ethanol.

Analysis of materials by X-ray diffraction (XRD)

The plant material generally has highly ordered regions called s, and disordered regions called amorphous zones. In the case of beet pulp, the crystalline regions are constituted by well-ordered cellulose and pectin (polygalacturonic acid) and the hemicelluloses which contain the amorphous zones.

In the Figure 2 we have presented the superposition of the XRD spectra of raw beet pulp (RBP), beet pulp treated with distilled water (BPTDW), beet pulp treated by ethanol (BPTET) and beet pulp treated with formaldehyde in acid medium (BPTFA).

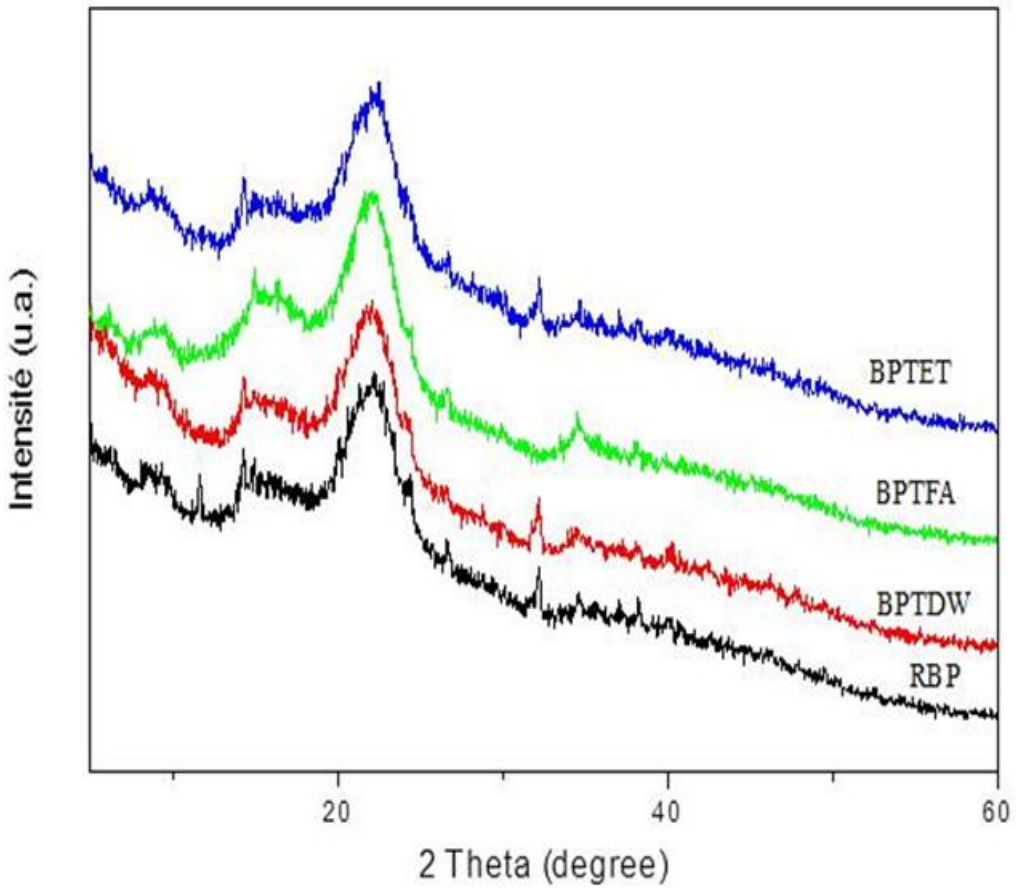

Figure 2: XRD spectra of RBP, BPTDW, BPTET and BPTFA

The examination of the XRD spectra of RBP, BPTDW, BPTET and BPTFA clearly shows that their surfaces are different, and to better understand, the crystallinity rate (CR) can be calculated by the following formula:

$$CR\ (\%) = \frac{TotalArea - AmorphousArea}{TotalArea}$$

With, Total Area- amorphous Area = Crystalline Area.
The surfaces of the XRD spectra are computed by X-ray diffraction software.
The spectrum of the RBP (Figure 3) is obtained as an example of calculation of the crystallinity rate.

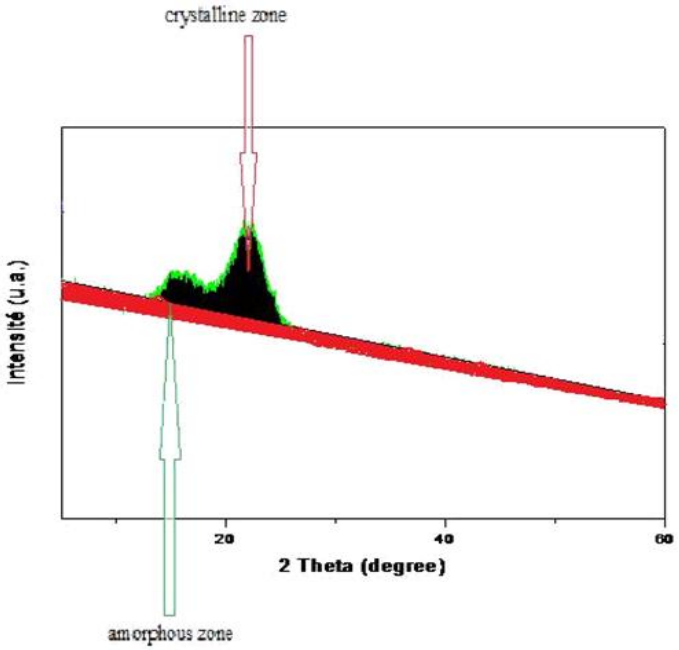

Figure 3: Amorphous and crystalline surface of XRD spectrum of the RBP

Thus, the crystallinity rate of the RBP is 18%. In the same way, the following crystallinity rates are obtained: CR (BPTDW) = 21%, CR (BPTET) = 12%, CR (BPTFA) =28%.

Thus, the crystallinity rate of these materials follows the following order:

CR (BPTFA)>CR (BPTDW)>CR (RBP)>CR (BPTET)

According to the obtained values of the crystallinity rate of RBP, BPTDW, BPTET and BPTFA, we observe that the crystallinity rate increases after treatment with formaldehyde and distilled water. It goes from 18% to 28% for BPTFA and from 18% to 21% for PBTED. This translates into an increase in the crystalline zone and a decrease in the amorphous zone and thus elimination of some constituents of the beet pulp. The crystallinity rate obtained after treatment with formaldehyde is explained by the crosslinking of the side chains of the beet pulp with formaldehyde in an acid medium. On the other hand, the treatment of the pulp with ethanol leads to a decrease in the crystallinity rate. It rose from 18% to 12%. This phenomenon can be explained by the removal of constituents of the crystalline part by ethanol.

Analysis of materials by SEM

Our samples were analyzed by scanning electron microscopy (SEM), this characterization method will allow us to look at the surface morphologies of the RBP, BPTDW, BPTET and BPTFA. The Figure 4 shows the morphologies of RBP, BPTDW, BPTET and BPTFA.

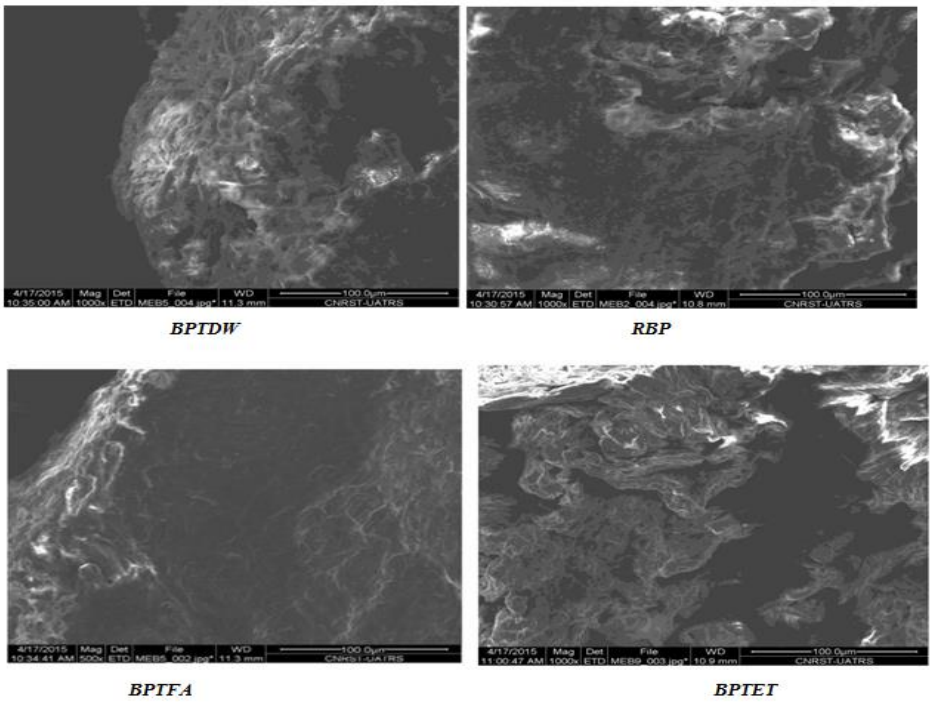

Figure 4: SEM Micrography of RBP, BPTDW, BPTET, BPTFA

The morphology obtained from the raw beet pulp (RBP) shows that this material contains compact and ordered zones, and disordered and porous zones containing fibers characteristic of hemicelluloses.

In compared to the morphology of raw beet pulp (RBP) and beet pulp treated with distilled water (RBPTDW), beet pulp treated by ethanol (BPTET) and beet pulp treated by formaldehyde in acid medium (BPTFA), we find that the morphologies of these materials are different.
Indeed, the treatment of the beet pulp with distilled water and ethanol, leads to less compact materials. Thus, it can be concluded that treatment with these solvents has a considerable effect on the removal of some constituents of the original material. On the other hand, the treatment of the beet pulp with formaldehyde in an acid medium leads to a compact and ordered material. This is explained by the crosslinking of the side chains of the beet pulp with formaldehyde in an acid medium.

CONCLUSION

The spectroscopic characterization of the beet pulp before, and after chemical treatment with different solvents (distilled water, ethanol and formaldehyde in an acid medium) has been studied. The results obtained give the following conclusions:
The examination of the IR spectrum of this material before treatment shows the existence of several characteristic peaks of several functional groups of cellulose, hemicellulose and pectin. After treatment of this material with the various solvents, the results obtained show that the treatment of BP by these various solvents has a considerable effect on the chemical modification of the structure of this material and especially the treatment with formaldehyde and ethanol.

In the case of the analysis of this material by XRD before and after treatment by the solvents, the results obtained show that this material contains two zones, crystalline zone and amorphous zone. The calculation of Crystallinity Rate (CR) which is at a significant relationship by the surface of the XRD spectra clearly shows that the surfaces of the spectra obtained before and after treatment are different.

The analysis of the morphology obtained from this material by scanning electron microscopy (SEM), shows that, this material contains compact and ordered zones, and disordered and porous zones, containing of fibers characteristic of hemicelluloses. After treatment by the three solvents, it can be concluded that the treatment with distilled water and ethanol has a considerable effect on the removal of some constituents of the original material. On the other hand, treatment of the beet pulp with formaldehyde in an acid medium leads to a compact and ordered material. This is explained by the crosslinking of the side chains of the beet pulp with formaldehyde.

Thus, it can be concluded that the chemical treatment of the beet pulp by the solvents has a considerable effect on the chemical and morphological modification of this material.

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