

Microstructure characterization of the barks of eucalyptus "eucalyptus camaldulensis"

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Abstract— Lignocellulose residues can be valued in the treatment of wastewater as adsorbents clean, natural and low-cost. In this study, our approach is to develop the preparation and characterization by physical-chemical methods, of adsorbant material, made from the bark of eucalyptus "Eucalyptus camaldulensis". The preparation of adsorbent material includes the sieving of the barks, extraction of unwanted compounds, treatment with formaldehyde as an activating agent, and a chemical treatment with acrylic acid by reaction of grafting. The chemical modification, which aims the improvement of the ability of adsorption of the material, is verified by means of analysis: the Infrared to Transformed of Fourier (IRTF), the Diffraction of Rays X (DRX) (crystallinity index) and the method of Boehm. The chemical change of the lignocellulosic material induced a change in the microstructure of the material, particularly in the case of the grafting of acrylic acid and the Crosslinking with formaldehyde to increase his potential adsorption capacity.

Index Terms— Lignocellulosic Material, bark of eucalyptus, adsorption capacity, chemical treatment, characterization.

I INTRODUCTION

Wood, of vegetable origin, was the subject of numerous studies and continues to attract the attention of researchers because of its complexity and the many technological applications it offers. It would be necessary before any investigation, to provide a general description of this material.

Eucalyptus trees occupy 32% of the total area in Moroccan forest. They have been planted over the years fifty in places that do not meet the environmental skills of the Cork oak. After the eucalyptus plantations have been strengthened to supply mainly the Sidi Yahia pulp factory and produce incidentally for the wood industry (crates, formwork, Poles, pegs) and service. The main species of eucalyptus trees planted are: Eucalyptus camaldulensis, Eucalyptus grandis and Eucalyptus gomphocephala.

The bark of eucalyptus can also be valued in the treatment of wastewater as a natural biosorbants and low cost [1-4]. However, the valuation of these, the barks as adsorbents for the purification of wastewater contamination with micropollutants, requires knowledge of its structure and texture. The ability to bark of eucalyptus to fix pollutants, can be greatly improved by him undergoing a chemical treatment.

Among possible treatments, chemical modification of bark through acid grafting acrylic [5-8] or the Crosslinking with formaldehyde [9-11]. These treatments are especially aimed to decrease the water content of the wood and stabilize dimensionally.

effect of chemical modification on microstructure of the bark of eucalyptus "eucalyptus camaldulensis", in the context of the formulation of the lignocellulose adsorbent materials.

II. MATERIALS AND METHODS

1. Materials

The bark of eucalyptus has been collected from the region of Gharb-Kenitra-Morocco (near the Ibn Tofail University). They have been washed to remove impurities such as sand and dust and dried at 50 ° C to prevent a possible alteration of the physical and chemical properties of the material. Then, they have been crushed and sieved and varying between 112 and 250 µm diameter particles have been retained and used for analysis.

2 Methods

2.1 Conditioning of eucalyptus bark

Prior physical characterization, helped to determine the following parameters: pH (barks in aqueous solution), bulk density and moisture on the one hand. On the other hand, a quantification of the different proportions of the compounds of eucalyptus bark was made, according to the protocols developed by (Technical Association of the Pulp and Paper Industry) TAPPI standards.

2.2 Treatment of the material for adsorption

2.2.1 The Soxhlet extraction

Extractable that may inhibit the prehydrolyse of eucalyptus bark, are eliminated by extraction to the Soxhlet, a continuous flow process. Solvents solubilise extracts content in plant material, which are finally concentrated in the ball of recovery [12].

The extraction was performed in two stages: first with the help of a mixture of organic solvent: ethanol/toluene (report ½) for 16 hours, depending on the protocols presented in work earlier [13-16], then using acetone for 8 hours so as to remove the extractable substances. The solvent is chosen so as to extract the greatest amount of extract-

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In this context, and due to the economic and environmental importance of the valorization of the bark of eucalyptus in the treatment of wastewater, we are interested, first of all, to the question of the

able. Finally, the bark of eucalyptus has been dried in an oven at 100 ° C for 2 days. A mass of 50 g of bark of eucalyptus weighed in a cellulose cartridge and placed in the Soxhlet apparatus. The extraction was carried out at the rate of 1 to 4 cycles (soaking/leaching) per hour in 600 ml of organic solvent.

2.2.2 Chemical formaldehyde treatment

The Crosslinking of a biosorbant is a transformation of its chains of bio-polymer cross-section connections, creating three-dimensional polymer Intermolecular [17].

In contact with water, these barks replicating various components, resulting in a brownish coloration of the solution and a loss of groups complexation. To take into account these two aspects, the bark powder will be submitted to a treatment by the formaldehyde method by Randall et al. [18].

The experimental protocol adopted for the cross-linking of the support by formaldehyde in acid environment is the following:

5 mL of an aqueous solution of formaldehyde (about 35% HCHO) is added to 100 mL of a solution of sulfuric acid 0.1 M. The mixture is heated up to 50 ° C. This mixture is added 10 g of bark of eucalyptus crushed and under stirring for 2 h at 50 ° C. The mixture is filtered and washed with deionized water excess. The resulting bark powder is then dried at 50 ° C for 24 h.

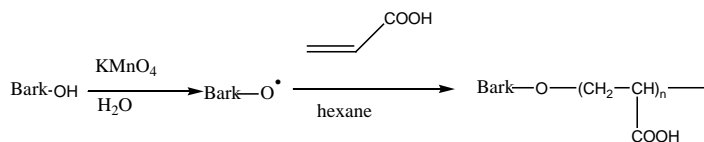
2.2.3 Chemical acrylic acid treatment

Copolymerization with acrylic acid reaction is carried out in two stages: preliminary oxidation of wood leading to the formation of macro-radicaux and copolymerization with acrylic acid.

- First step: pretreatment by KMnO₄: 0.5 g of bark are agitated with 25 ml of an aqueous solution of 0.016 M of KMnO₄ for 30 min at room temperature. The bark is then filtered and rinsed to eliminate the rest of permanganate.
- Second step: grafting of the monomer on the bark of eucalyptus

Still wet pretreated Barks are introduced in a ball of 100 ml equipped of a refrigerant and mixed with 0.5 g of acrylic acid in 30 ml of hexane. The reaction is continued for two hours at reflux, then barks filtered on Büchner after cooling of the reaction medium. These are then washed with a solution of the hydrochloride of hydroxylamine at 10% in H₂SO₄ (1 M), then rinsed with distilled water, the mixture is filtered. Wet powder is end extract to the Soxhlet with the dioxane 6 hours, before be dried in an oven at 100 ° C overnight.

The reaction scheme adopted for the grafting of acrylic acid on the bark of eucalyptus is the following:



2.2.4 Determination of density in bulk

The apparent density has been measured using a test tube of 10 cm³. The dry powder of eucalyptus bark (PEB) has been added to the test tube by tapping gently to ensure the deposit of particles at the bottom and that all of the air spaces are filled.

$$\text{Apparent density} = (\text{masse of PEB occupying the volume of } 10 \text{ cm}^3) / 10 \text{ cm}^3$$

2.3 Physical-chemical characterization of the samples of the bark of eucalyptus "eucalyptus camaldulensis" raw and treated

2.3.1 Analysis of the functions of surface by the method of Boehm

The dosage of surface features was made according to the method of Boehm [19-20], which corresponds to the acid-base titration of surface functional groups. Samples of material (1 g) have been in contact with 50 ml of basic solutions of normalcy 0.1N of different forces and HCl, respectively for the determination of acid and base of surface features. The excess base or acid was tilted back on 10 ml of filtrate through a solution of HCl or NaOH normality 0.1N. This method also lets you calculate the acidity and total alkalinity of a material adsorbent, the respective sum of functional groups acid and base. The result is expressed as mmol/g or meq/g of material.

2.3.2 Analysis by spectroscopy Infrared to transformed of Fourier (IRTF)

The Infrared Spectra to Transformed of Fourier (IRSTF) was carried out using a device of type VERTEX 70 in the range of wavelengths of 400 to 4000 cm⁻¹. The spectral resolution is 4.0 cm⁻¹. The pellets were conducted from an intimate mixture of sifted sample (1 mg) and potassium bromide (100 mg) under a pressure of 4.5 108 Pa.

2.3.3 Estimate of the index of crystallinity by Diffraction for X rays (DRX)

To determine the effect of chemical treatment on the crystallinity of cellulose, we opted for the determination of the index of crystallinity by the empirical method of the height of the peak of DRX, developed by Segal L et al (1959) [21] and Safou-Tchiama S (2005) [22], which is to consider the changes in the Spectra DRX, after chemical treatment. The cry crystallinity index was calculated from the ratio of the area of the crystalline phase and the total area (crystalline phase and amorphous phase), using the formula below [23]:

$$\text{CrI} = \text{Crystalline surface} / (\text{Crystalline surface} + \text{Amourphous surface})$$

This method is useful to compare the differences between the samples before and after chemical treatment.

The sampling technique used is that of a diffuse reflectivity. Powder samples were swept for the wave 0-4000 cm⁻¹ and degree 2θ number (0-50 °). The diffractometer of x-ray used is of the type "Diffractometer system = XPERT-3", using monochromatic radiation Kα₁ of copper (CuKα radiation) (λ = 0,154 nm) to 35 kV and 30 modes of mine and continuous sweep.

2.4 Mining of heavy metals tests

Lead is chosen as an ion representative heavy metal due to their high toxicity and their use in plating factories and industry. We made synthetic solutions containing Pb by dissolution of lead nitrate salt in distilled water.

Extraction of Pb²⁺ ions has been achieved in a beaker of 250 ml under the effect of agitation with a mass of 0.1 g of each support in

contact with a solution of Pb^{2+} concentration of 20 ppm and a volume of 100 ml for 3 hours. After each test mining, the solution has been filtered using the filter under vacuum, then the filtrate was analyzed by type nov AA350 Analytik jena spectrometer atomic absorption spectroscopy.

Yield of extraction was calculated by the following relationship:

$$R\% = (C_0 - C_e) 100/C_0$$

With C_0 : Initial concentration of the metal in solution in mg/l, C_f : Final concentration of the metal in solution in mg/l and R: % Extraction performance.

III. Results and Discussions

1. Adsorbent material characterization

1.1 Physical and chemical material analysis

The macromorphologies of eucalyptus barks "eucalyptus camaldulensis" before and after chemical treatment, are illustrated in the figure 1:



Figure 1 : surface morphology of barks of eucalyptus "eucalyptus camaldulensis" untreated (a) and treated chemically (b, c, and d)

The results of the physical-chemical analysis of the bark of eucalyptus raw and processed are summarized in table (1):

Table 1: Physicochemical results of barks of eucalyptus before and after chemical treatment

Support	BR	BS	BF	BAA
Moisture (%)	5,19	5,63	4,98	4,81
Mineral matter (%)	14,92	6,96	8,09	1,51
pH	4,25	4,56	3,18	3,28
Bulk density (g/cm3)	0,75	0,61	0,81	0,77
Cellulose (%)	37	-	-	-
Hémicellulose (%)	20	-	-	-
Lignine of klason (%)	26	-	-	-
Matter extractable (%)	4,03	-	-	-

The gross chemical composition of eucalyptus bark has been determined according to TAPPI standards [24-27].

1.2 Analysis of surface functions

The results of dosage surface functional of the materials by the method of Boehm are illustrated in table (2):

Table 2: Functions of surfaces of materials in various states

Material	Functions carboxyls (mmol/g)	Functions lactones (mmol/g)	Functions phenols (mmol/g)	Total of functions acids	Functions basic (mmol/g)
BR	0,09	0,12	0,45	0,66	0
BS	0,08	0,02	0,6	0,7	0
BF	0,1	0,09	0,47	0,66	0
BAA	0,57	0,14	0,55	1,26	0

At first sight we see that the chemistry of surfaces of various materials is slightly affected by the chemical treatments.

Generally bark of eucalyptus (brute and treated) are acidic in nature ($pH < 5$), which, if explained by the presence of the acid functions at the surface of all materials on one hand and on the other hand by the lack basic functions.

The treatment of the bark of eucalyptus with acrylic acid, caused a marked increase in surface functions carboxyl (0.57 mmol/g). For other materials (ARE and EF) found values are almost identical to those of rough bark (EB). However the bark extracted by Soxhlet present a low content functions lactones (0.02 mmol/g), which is due to the loss of extractable material (resinous compounds and tannins) [28].

1.3 Analysis by infrared (IRTF) the bark of eucalyptus raw and processed

The spectra obtained by analysis, infrared (IRTF) eucalyptus bark samples of raw and treated (EB, ES, EF, and EAA), are shown in figure (3). Characteristic vibration bands have been attributed to different chemical functions (figure 3), in agreement with the literature data. At first sight, raw and treated eucalyptus bark IR spectra have almost the same pace, but with increasing intensity for bark treated with formaldehyde (EF) and acrylic acid (EAA).

The all Infrared Spectra reveal the presence of a broadband to 3400 cm^{-1} , which corresponds to the vibrations of the O - H of aromatic structures, binding elongation and aliphatic phenol (Group of the lignin and cellulose) except for the bark treated with acrylic acid (EAA) there is a net increase in the intensity of this band of the fact of grafting of acrylic on the pool acid OH different structures contained in the bark. The Strip to 2930 cm^{-1} is an asymmetric elongation of the C - H of the cellulose binding. As for the Strip to 2850 cm^{-1} corresponds to the vibration of symmetrical elongation of the lignin methoxy groups C - H bond.

The peak to 1720 cm^{-1} is characteristic of the vibration of Valencia (C = O) of carboxylic acids and/or esters of the xylenes, present in the hemicelluloses [29-31]. For the compound treated with acrylic acid this same pic appears with a marked increase in intensity due to the appearance of the link C = O of the carboxylic acids of acrylic acid grafted on the bark.

In addition, observed to 1630 cm^{-1} band corresponds to the $\text{C} = \text{C}$ aromatic cycles of lignins deformation. The bands observed 1380 cm^{-1} and 1230 cm^{-1} are attributed to vibration $\nu(\text{C} - \text{O})$ of lignin methoxy groups and the link formed during the action of formaldehyde on cellulose (C-O-C). The Strip in 1159 cm^{-1} in the spectrum of bark treated by acrylic acid corresponds to the elongation of the link $\text{C} - \text{O}$ of the acid group due to the grafting of the acid functions on the bark of eucalyptus.

The peak at 1030 cm^{-1} corresponds to the vibrations of $\text{C} - \text{O}$ and $\text{C} - \text{O} - \text{C}$ links Valencia, cellulose [32], the peak becomes more intense in the case of bark treated with formaldehyde (EF), due to the action of formaldehyde on the groups OH the cellulose and the $\text{C} - \text{O} - \text{C}$ bond formation according to the reactions following [33] :

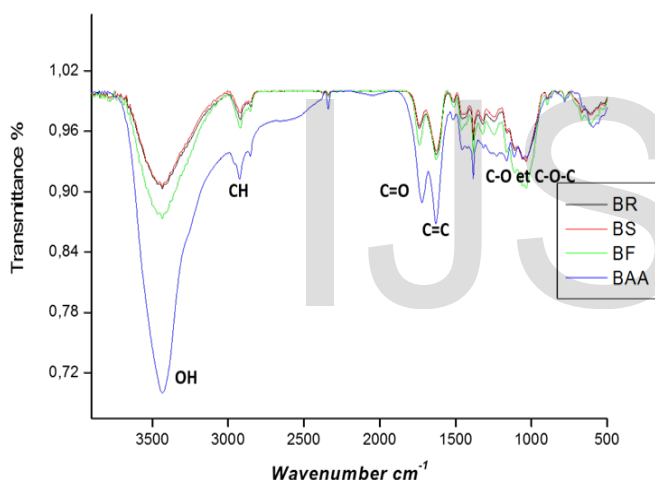
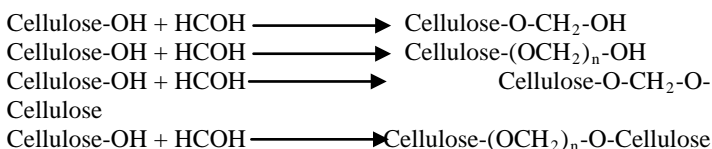


Figure 2: Spectra infrared of the barks of eucalyptus rough (BR) and treated (BS, BF and BAA).

1.4 Analysis by X-Ray Diffraction (XRD) of raw and processed eucalyptus barks

The bark of eucalyptus consists of amorphous polymers (hemicelluloses and lignin) and organized polymers, by location, in the crystalline areas (cellulose). It has been shown that amorphous areas from cellulose, are more sensitive to chemical and enzymatic attack than the crystalline areas [34-35].

The curves of X-Ray Diffraction of eucalyptus bark samples "eucalyptus camaldulensis" gross and modified are represented in the figure 3.

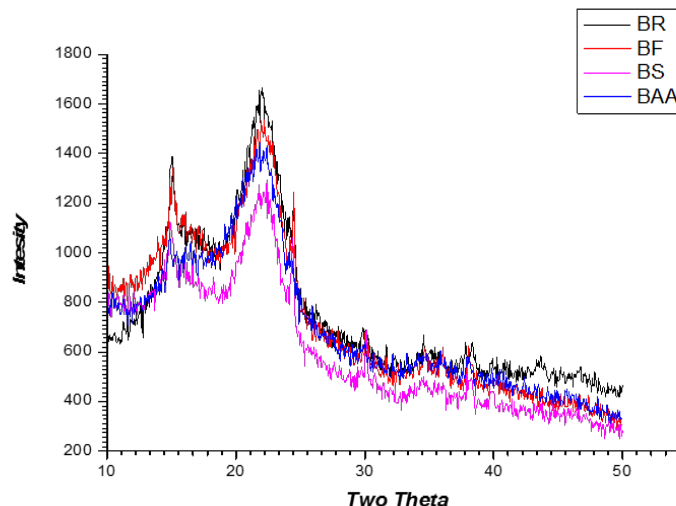


Figure 3: curves of diffraction to the X-rays of barks of eucalyptus rough and treated.

It appears that all samples show the characteristic shape of the native cellulose materials lignocellulosic, with a net dominance in the amorphous form [36].

The analysis of these curves to infer overall crystallinity of raw and treated eucalyptus bark.

The data in the table (3), show that, the barks have been affected by the treatments used, where the index of crystallinity of the bark of eucalyptus treated with formaldehyde has decreased under the effect of the cross-linking of cellulose from 46,57% for raw bark (EB) 45.50% for bark treated by formaldehyde and 41,44% for bark treated by acrylic acid (EAA). This decrease is due to the reaction of groups OH the cellulose with acrylic acid. Therefore, their hydrogens are no longer available to form intermolecular hydrogen bonds, cellulose thereby loses its crystalline form. In addition, there is a slight increase in the index of crystallinity for the bark extracted by solvent (ES) (48.44%), this increase is due to the loss of extracts (amorphous) bark during extraction with organic solvents.

Table 3: index of crystallinity of bark of eucalyptus rough and treated measured by diffraction with the X-rays.

Biomass	Index of crystallinity CrI (%)
Rough bark (BR)	46,57
Bark reticulated by formaldehyde (BF)	45,50
Bark extracts by Solvent (BS)	48,44
Bark copolymerized by acrylic acid (BAA)	41,44

2 Mining of heavy metals tests

According to the results shown in table 4, we noted that all materials

studied previously have the best performance of extraction opposite the Pb^{2+} ion which confirms the ability to apply these different materials to the treatment of waters loaded with heavy metals. Except the raw material despite his good ability to extract remaining unusable because of the problems it causes to the contact of the water, where it releases various components, resulting in a brownish coloration of the solution and a loss of complexation groups

Table 4 : The yields of extraction of the Pb^{2+} ions by different supports

Matériau	EB	ES	EF	EAA
R (%)	90	91	83	94

IV. Conclusion

This study permits the characterization of the microstructure of materials made from the bark of eucalyptus Virgin and having undergone chemical treatment. The chemical modification of the bark of eucalyptus, helped influence the microstructure of the lignocellulosic material, resulting in a change in the properties of the functions of the surfaces of the material (grafting of COOH, supported by formaldehyde cross-linking and functions the removal of extracts by Soxhlet). These results have been verified by TFRI, the method of Bohemia and the DRX. These results show that the bark of eucalyptus changed can be valued and used the field of pollution in wastewater.

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