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Isolation of Cellulose from Sawdust of *Cedrus Deodara*: Effect of Preparation Conditions on their Morphological Behavior

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Abstract:
The Cedrus deodara was collected from Pakistan and was grounded and converts into powder. The powder was extracted through Soxhlet apparatus with various solvents to eliminate the soluble extractive and waxes. The raw cellulose was kept in autoclave to treat with alkaline solution to break the bond linkage. Most polar ingredients were removed through Ethylene diamine tetra acetate and hydrogen peroxide. The raw cellulose was further purified through acetic acid and nitric acid. The cellulose was neutralized by deionized water. The extracted cellulose was analyzed by analytical methods like X-ray Diffraction (XRD) to determine the crystallinity. Fourier Transfer Infrared Spectroscopy (FTIR) indicates different functional groups on the surface. Thermo gravimetric Analysis (TGA) specifies thermal degradation in which the mass loss is calculated with respect to time and temperature. Scanning Electron Microscopy (SEM) determined external morphology by scanning with a focused beam of electron which detected extremely observable holes with channels on the external surface. The extracted cellulose has highly crystalline, thermal constancy and good mechanical properties.

Keywords*: Cellulose, Soxhlet, Autoclave, Bleaching*

1. Introduction

Cedrus deodara species connected with cedar trees and its means wood of god in Sanskrit derived from devadaru. Cedrus deodara existed in northern region of Pakistan, western Himalayas, eastern Afghanistan, Kashmir, and central India. It is also called Pakistan national tree. It found 1500-3200 m above from sea level and increases up to 40-60m and remained evergreen.

Biopolymers of cellulose are abundantly present on the earth crust which contain straight chains of D-glucoselinked by ß-1, 4-glycosidic linkage by high quality of polymerization. The hydroxyl group is provided by D-anhydroglucopyranose at 2, 3, and 6, of carbon [1]. Through hydrogen bonding and Vander wall interaction the crystals of cellulose are closed to each other. The molecular structure of Cellulose shows the properties of degradability, hydrophylicity, chirality and wide chemical inconsistency. Cellulose is insoluble in water because of its molecular structure [2, 3]. From beginning it has been generally used as a source of paper. Cellulose and their derivatives have wide application in various fields. The current research work is on the production of bioethanol production from cellulose [4]. Recent research determined the significant practice of cellulose

achieved from biomass, particularly towards manufacturing of bioethanol which have greatly benefited for necessity of energy[5]. Usually it is used in the production of Bioethanol. 41 billion liters of bioethanol is produced internationally from cellulose in 2008.The major creator of bioethanol from cellulose in all over the world is, 37% in Brazil, 33% in United States, and 14% in Asia. In (2008) Bioethanol Manufacturing from sugarcane in Brazil is maximum than 17.1 billion liters to assist the economic statement for 18% of the country's fuel necessities [6].

Nowadays studies require extra attention of cellulose extraction from biomass because in green chemistry it has excessive application. Literature indicates that cellulose extracted from various sources contains straw of wheat, sugarcane, bagasse, rice straw, rice husk, soybean hulls, banana stem, pineapple leaf fiber and palm oil residue [7, 8].

The derivatives of cellulose contained Methyl, ethyl, and propyl cellulose. The extraction of biochemical is the most important objective to evaluate their applications on medical side. The human intestine cannot absorb, it can pass through digestive tract directly. Cellulose is also appropriate for the treatment of various diseases such as hemorrhoids, diverticulosis, diarrhea and irritable bowel syndrome [9, 10]. Methylcellulose is used as a lubricant and a major component as well as used for treatment of dry eyes[11].

On the construction sides Cellulose contain a large number of applications such as for additive performance and maximize the workability properties, water preservation, and adhesion. Industries like gypsum and cement used cellulose [12] furthermore it is applicable in Cement panels, tile adhesives, crack fillers, and tile grout [13]. For the fixation of delicate parts of art it is used as a glue and binder and as well as used to free the file, and wallpaper from ancient gum and pastes. In culture cell virology Methyl cellulose is useful particularly to detect virus-related replications. Generally cells are developed in those medium which are liquefied in the same nutrient. Methyl cellulose is used to prepare medium and then it was replaced by a common medium. Those cells which membranes are touched with one another the infected virus are capable to spread in them and those cells become dead [14, 15].

Mostly ethyl cellulose is used as thin-film covering. Ethyl cellulose is used for the food preservation as an emulsifier [16]. Acetyl cellulose is derived by examining wood into purified white cellulose and also a main source in the production of cigarette and playing cards. Mostly it is soluble in numerous solvents holding acetone and organic solvents which can be improved to soluble in water. In textile applications, it delivers comfort and permeability, but its strength is fail in wet condition. Its fibers are used for the treatment of allergic. It is destabilized by strong basic solutions and strong oxidizing agents [17].

Cellulose is used as absorbing agent in paper, paper board and textile industries to prevent oil and water. It is used as buffer additive in capillary electrophoresis to decrease electro osmotic flow for improved separation [18-19]. Furthermore it is also used in house hold, such as for manufacturing of glasses, switches, clothes, coatings, fabrics, marriage gathering attire, toothpaste, laxatives, drugs, shampoos, and aquatic based dyes. In nonvolatile eye drops it is also used as a lubricant [20-21].

2. Material and Methods

2.1. Material

N-hexane and Ethanol (96%) were purchased from SCHARLAU. NaOH, H_2O_2, Ethylene diamine tetra-acetate, CH_3COOH (99%) and HNO_3 (65%) were purchased from SIGMA-ALDRICH and an autoclave (model Stermax 20EHD).Without any purification the chemicals were used.

2.2. Cellulose Isolation

The saw dust of *Cedrus deodar* was collected from the mountains of Khyber pukhtoonkhwa Province Pakistan. The sample was converted into smaller particles with hammer and mills. The acquired particles were washed in Soxhlet apparatus with various solvents such as n-hexane, Ethanol, and deionized water for 3 hours to remove the polar, extractives and waxy materials. For drying the sample was retained in oven at 80^{o}C. Saw dust which is free from extractive was treated in autoclave at 121 ^{o}C and 2 atm of pressure, in a 1:100 for 30 min with an aqueous solution of sodium hydroxide 5 % (w/v) for the separation of fiber and bond breaking [22].

Most polar materials such as hemicelluloses, lignin and pectin were eliminated by bleaching process which was described previously for the straw of wheat [23]. The biomass was reacted with in the solution of hydrogen peroxide 2 % (v/v) and ethylene diamine tetra-acetate 0.2 % (w/v) in a 1:25 (g /ml) with stirring for 12 hours, at 48 ^{o}C. The pulp was filtrated and neutralize with deionized water. The step is known as bleaching I. The raw cellulose was purified in bleaching-II, treated with acetic acid 80 % (v/v) with 1:33 (g/ml), and $HNO_3$65 % (v/v) solution with 1:4 (g /ml) at 120 ^{o}C for 30 minutes, under mechanical stirring. Finally cellulose was filtered and washed with ethyl alcohol and deionized water to obtain pH 7.

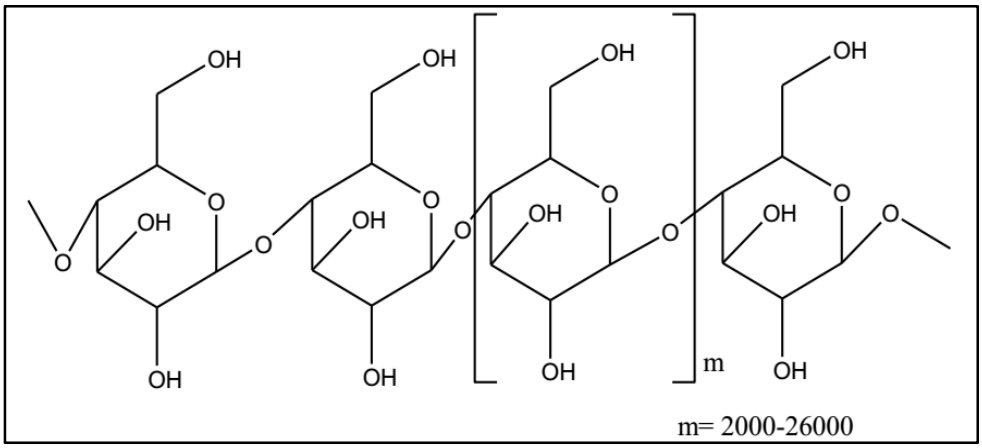

Figure 1: Structure of Cellulose

2.3. Parameters for Analysis

Cellulose was analyzed with advance technique such as; Scanning Electron Microscopy (SEM) was used to examine surface morphology of the extracted cellulose, *(JSM 5910, JEOL, JAPAN).* The XRD is significant analytical technique to indicate the crystallinity of sample. X-rays are used to accumulate material about properties of the sample *(X-ray diffractometer Rigaku D/Max-II, Cu Tube, JAPAN).*Thermo gravimetric analysis (TGA) is a procedure in which mass of the sample is detected as a function of temperature or time (*TA Instruments model TGA Q5000 IR)*. Fourier Transfer Infrared Spectroscopy (FTIR), characterization was performed to identify altered functional groups existing on the surface of raw sample and pure cellulose together from each step of the extraction (*FTCOM-1,8201PC Shimadzu Fourier)*.

3. Result and Discussion

3.1. FT-IR Investigation

FTIR study was performed to know about several functional groups on the surface of cellulose extracted from every stage. The FTIR bands of the cellulose were verified through Fourier Transform Infrared Spectrophotometer bypotassium bromide pallet technique. The sample was evacuated when the bands of the sample are recorded before manufacture the pallet and it was capture below atmospheric pressure at25^{o}C. The bands were examined in the series of 800-2000 per cm [24]. The constituent which are present in *Cedrus deodara* is lignin, hemicellulose, and cellulose [25]. By various steps the bands were identified like raw *Cedrus deodara* during washing, treatment with sodium hydroxide, and decolorized of cellulose with certain infrared rangeswere taken in table- 1.

Fig- 2indicates FTIR bands achieved from *Cedrus deodara* at every periods of reaction. The bands situated in 1265 percm recognized C-O-C (aryl-alkyl ether). This spectrum is exposed when it was bleached with acetic acid while disappears after bleaching-II with the treatment of HNO_3. The adsorption bands displayed at 1029 per cm in the sample without treatment, at 1027 cm^{-1}indicates CH_3COOHtreatment and 1018 cm^{-1} is determined the treatment of alkaline, moreover strong spectraseems at 1032 cm^{-1} specified the C-O stretching bond in the final cellulose when reacted with acetic acid and nitric acid [26-27].

C-0	C-1	C-2	C-3	C-4	Assignment
1029	1027	1018	1029	1032	C–O stretching
1128	1145	1149	1144	1128	C–O symmetric stretching of primary alcohol
1266	1260	1265	1265	-	C–O stretching of ether linkage
1525	1520	1520	1520	1527	C=C stretching of aromatic ring

Table 1: Infrared adsorption spectra of the cellulose isolated from the wood of Cedrus deodara as designated in table wave length (cm^{-1})

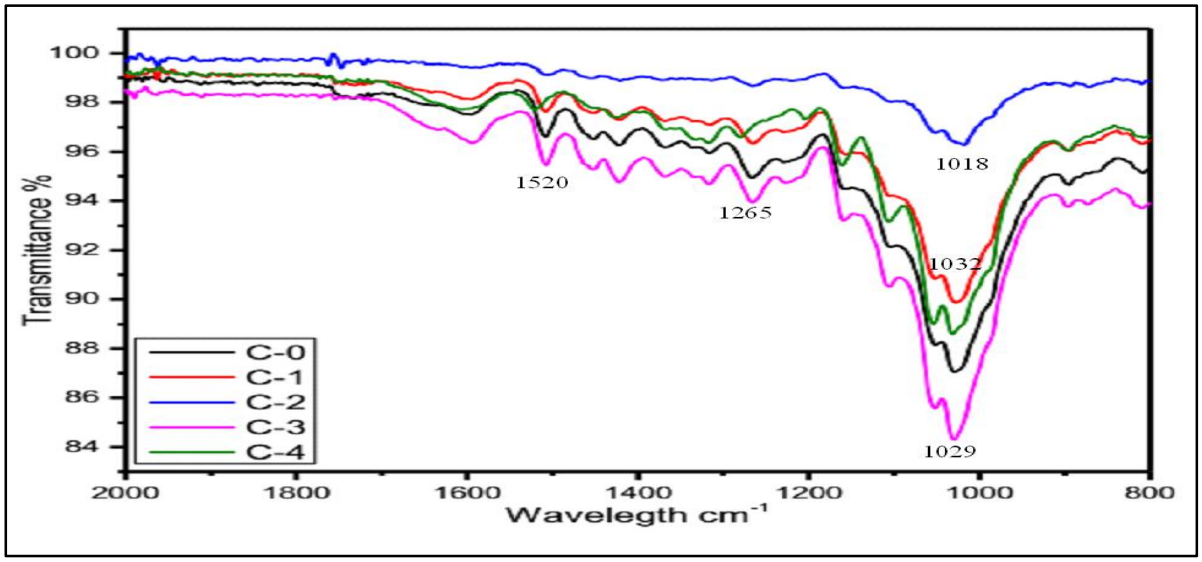

Figure 2: FTIR spectra at various stages of cellulose isolated from the wood of Cedrus deodara

3.2. X-Ray Diffractometery

XRD is significant characterization procedure to indicate the crystallinity of sample. X-rays are used to accumulate information about the properties of sample. X-rays are scattered once the X-rays focus on the surface of sample. In scattering there is an opportunity of positive or negative interference in crystalline surface. Crystallinity of cellulose is examined through X-rays diffraction. Literature survey explained, Segal's equation is the greatest way to known about the cellulose crystallinity because it gives highest curve and do not required background [28-29]. Segal's equation is:

$$X_C = 100(I_{200} - I_{AM})/I_{200} \quad (1)$$

I_{200} indicate supper most curve which specifies the sample crystallinity. Whereas I_{am} shows the amorphous portion which is amongst 200 and 110. The pure cellulose which is extracted from *Cedrus deodara* is 70% crystallinity. The maximum peak value is 1021 and minimum peak value is 322 as presented in the figure- 3 which is near to the commercial cellulose obtain from rice straw which crystallinity is 69% [30].

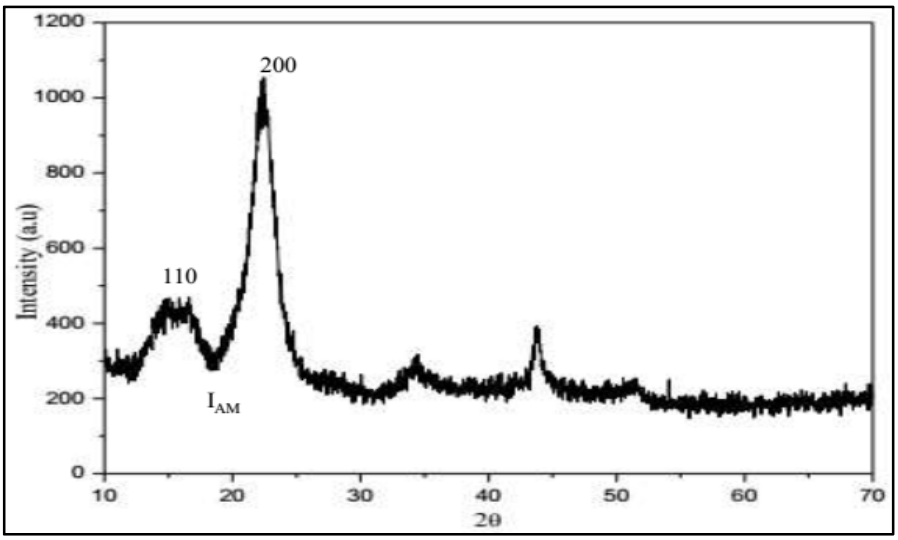

Figure 3: XRD spectra of cellulose isolated from the wood of Cedrus deodara

3.3. Thermo Gravimetric Analysis

TGA investigation is a method in which the sample mass is identified on the base of temperature/ time. At 100°C mass yield is reached to 90% due to the loss of water. Waxes materials started to degrade at 300 °C and the mass yield is 75%. Moreover at temperature 370°C the loss of mass is equal to 30% and at 460°C the mass yield is reached to 17% because the removal of lignin and hemicellulose take place. This means that components were degrading below 600 °C which is mainly composed by soluble compounds is shown in figure- 4 [31-32].

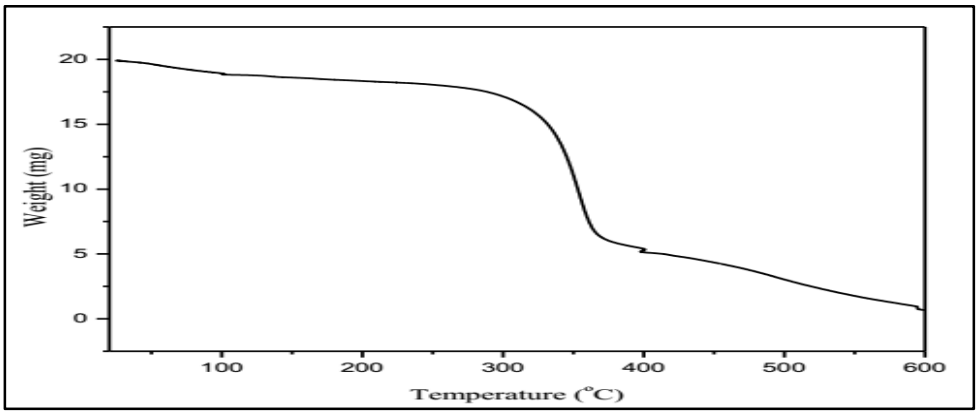

Figure 4: TGA spectra of cellulose isolated from the wood of Cedrus deodara

3.4. Scanning Electron Microscopy

Through SEM it is probable to identify various properties on the sample surface according to the stages of pre-extraction and pulping. The variations in the external epidermis display the chemical occurrence suffered by the material at altered periods. Scanning electron microscopy determined surface morphology of the pure cellulose isolated from *Cedrus deodara*.SEM micrographs at various magnifications expose the elimination of pectin, lignin, and hemicellulose particles from surface of the sample[33]. Thorough SEM it is indicated that the pores possess on the sample surface of dissimilar shapes and size is shown in figure- 5.Maheswari *et al*[34] cellulose extracted from agricultural residue. The sample was analyzed through SEM. The micrographs exposed the structure, morphology and size of cellulose. Rubio *et al* [35] worked on the isolation of cellulose and was confirmed through different analytical techniques through FTIR, XRD, TGA, and the surface morphology was studied by SEM.

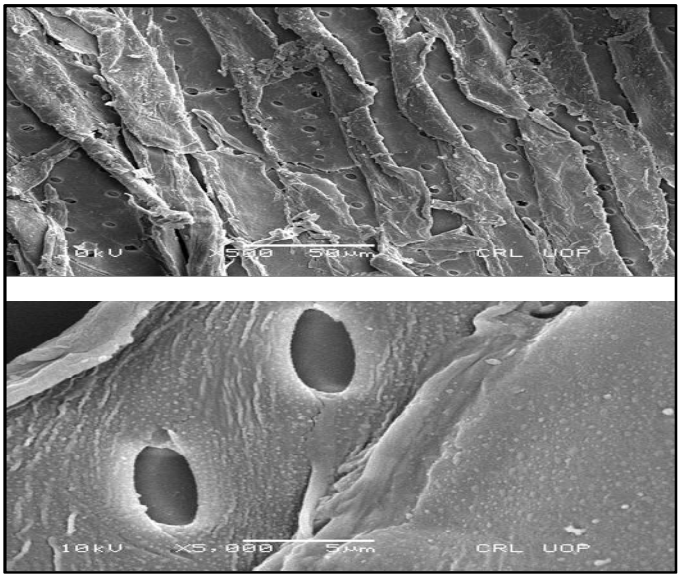

Figure 5: SEM micrograph of cellulose isolated from the wood of Cedrus deodara (X500, X5000 resolution)

4. Conclusion

The saw dust is low-cost, supportable, and renewable and the process of cellulose isolation is environmental friendly. The purified cellulose was examined by modern analytical techniques such as FTIR, XRD, TGA, and SEM and shows its different aspect and properties. Thermo gravimetric (TGA) analysis determines that at 100^{o}C the water is evaporate from the surface. The soluble extracted are eliminated at 300^{o}C and lignin/hemicellulose are decomposed at 370-400^{o}C. FTIR determines removal of different functional groups from cellulose which are lignin, pectin and hemicellulose. XRD data represent that the cellulose have high value of crystallinity which is 70%. The extracted Cellulose was examined by SEM for shape and surface morphology. Extremely observable pores were identified on the pure cellulose. The data collected have strong correlation with the literature review.

5. Acknowledgment

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