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Preparation of cellulose nanoparticle from cinnamon

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ABSTRACT

The preparation of cellulose nanostructures is considered in this paper. Cellulose nanoparticles (nano cellulose) were extracted from cinnamon for the first time. The chemically-induced destruction strategy based on controlled strong acid hydrolysis treatment was used for dissolution of lignin and fragmentation of cellulose to nano sized structure. The products were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), UV-Vis and Mass spectroscopy. SEM images demonstrated the cellulose nanoparticles production. Size distribution histogram which was obtained from the SEM image showed that nanoparticles size were less than 100 nm with average size about 50 nm. XRD analysis showed amorphous structure of nanoparticles. Chemical structures and functional group of cellulose nanoparticles approved using FT-IR. UV-VIS spectrum of macro cellulose, micro cellulose and nano cellulose were done in water, acetone and acetic acid. These spectrums illustrate the same absorption for tree materials in agues, organic and acidic solvents approving the stability of structures and maintaining molecular structure during making nano cellulose. Mass spectroscopy peaks are in good agreement with the structure of the cellulose and its fragmentation during analysis.

Keywords: *Nano cellulose, Acid hydrolysis, Cinnamon.*

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INTRODUCTION

Cellulose is a bio-degradable, bio-renewable and the most abundant biopolymer in nature that exists in a variety of living species such as plants, animals, bacteria, algae and some amoebas [1]. The production of novel nano materials such as nano cellulose from various renewable bio sources is of considerable importance in the last decade due to less environmental problems. Nano cellulose properties such as good mechanical properties, thin layer properties and viscosity make it useful for many applications [2]. The main reasons for developing nano cellulose, are there reinforcing properties as well as low density and large specific area [3]. Nano cellulose is used in cardboard and paper industry due to the strong reinforcing effect on paper

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materials [4]. Food, medical, biomedical, cosmetic and pharmaceutical industries, manufacturing of composites, electronic equipment, wood and construction materials, oil recovery and automobile manufacturing are the other applications of nano cellulose [2, 5-8].

The basic properties of nano cellulose, such as morphology, crystallinity, dimension and surface chemistry affect significantly by changing the raw material source, extraction process and production method. There are various methods for generating nano cellulose such as enzyme [9], mechanical and chemical methods which are common. The mechanical methods include: high-pressure refiner treatment [10], ball-milled [11], Ultra- high pressure treatment [12] and high intensity ultra-sonication [13]. Varied particle size and consumption of intensive energy are mechanical methods disadvantage. The chemical method includes Ionic liquid [14], oxidation [15], alkali treatment [16] and strong acid hydrolysis [17] that removes the amorphous portion of cellulose fibers and produces nano size fibrils. Crystalline nano materials of cellulose are usually produced by strong acid hydrolysis [18]. Various acids such as sulfuric acid, hydrochloric acid, nitric acid or some acid mixture were also used in nano cellulose production [19]. Other acids such as formic acid and acetic acid were used to replace the mineral acids because they can be easily recovered and causes less equipment corrosion [20], but the less acidic power of these acids leads to incomplete removal of lignin and long reaction time. It seems that the two-step use of these organic and inorganic acids can reduce their disadvantages.

Nano cellulose was prepared from various kinds of bio material such as leaf fiber [21], oil palm residue [22], groundnut shell [23], pea stalks [24], coconut fiber [25], cotton stalks [26] and rice husk [27]. To the best of our knowledge, preparation from cinnamon has not been reported elsewhere. Cinnamon is a spice obtained from the inner bark of several tree species from the genus cinnamomum. It has many applications in the food, pharmaceutical, medical, cosmetic and health industries [28]. It has other beneficial properties such as antimicrobial activity, anti-diabetes, anti-inflammatory, anti hyperlipidemia and antioxidant activity [29-31], cholesterol-lowering, and preventing the proliferation of cancerous cells and is effective in treating flu. Different surveys have shown the antimicrobial and antifungal properties of cinnamon [32].

In this study, we extract cellulose nanoparticles from cinnamon for the first time by removing the lignin in the presence of acid hydrolysis and pH control using acetic acid and sulfuric acid. This product characterizes with a scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and UV-Vis and Mass spectroscopy.

EXPERIMENTAL

Materials and characterization

All chemicals were purchased from Merck Chemicals co. (Germany). Reagents were used without further purification. In addition, deionized water was used as solvent. The obtained products characterized using SEM, XRD, FT-IR, UV-Vis and Mass spectroscopy. SEM image was observed using SEM (Philips XL 30 and S-4160) with gold coating. Powder XRD spectrum was recorded at room temperature by a Philips X'pert 1710 diffractometer using Cu Kα (α = 1.54056 Å) in Bragg-Brentano geometry (θ-2θ). FT-IR spectra were obtained over the region 400-4000 cm-1 with NICOLET IR100 FT-IR with spectroscopic grade KBr. UV-Vis spectroscopy was done by X Pert MPD Philips. Mass spectra were recorded on a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 20 eV. The Microstructure Measurement software was used to measure the particle size. The Origin and Microsoft excel software were used for determining the size distribution and average particle size.

Preparation of micro cellulose

50 g of cinnamon was soaked for 5 days and washed with deionized water and dried in an oven at 80°C for 24 hours. Then the cinnamon was poured into pieces of 5-10 mm using a mortar followed by sieving. The crushed cinnamon boiled with a solution of toluene and ethanol at a ratio of 2 to 1 for 6 hours. The fibers were filtered and washed with ethanol for 30 minutes and were dried. At the end, the fibers were boiled with sodium chloride 7% at a ratio of 1 to 50 for 2 hours and its pH was reduced to fewer than 4 with acetic acid which leads to remove lignin and stabilize hemicelluloses. The obtained hemicelluloses was mixed with sodium hydroxide 17.5% and then washed with deionized water and dried in an oven at 60°C to maintain a constant weight. The gained sediment is micro cellulose.

Preparation of nano cellulose

The obtained micro celluloses were mixed with sulfuric acid 64% and placed on a magnetic stirrer in medium range of 45 °C for 30 minutes. Then, the solution was centrifuged for separating sulfuric acid from the sediment. Washing with sodium hydroxide solution (1%, 2.5 mole/lit) and water, followed by centrifuging were done several times in order to eliminate acidic environment. The residual sediment at the end of the tube was extracted and dried in oven, which were cinnamon nano celluloses.

RESULTS AND DISCUSSION

Electron microscopy

The SEM images in Figure 1(a-c) show the morphology of the ordinary cinnamon, cinnamon micro cellulose and cinnamon nano cellulose respectively. The images illustrated the surface morphology and size of the materials. It is clear that the structure of cinnamon shrinking due to preparation. First pollution and impurities were deleted with soaking in water and ethanol. Then refluxing in NaCl followed by controlling pH with acetic acid led to remove lignin and stabilize hemicelluloses. At the end the base hydrolysis cause to fracturing the structure, crushing the macro to micro structure and forming of pores that can be seen obviously in Fig 1.b. In the next steps the acid hydrolysis with refluxing by Sulfuric acid cause in preparation of nano cellulose. Controlling the size and the amount of crushing were done by refluxing time and pH controlling with Sodium hydroxide. As shown in Fig.1.c the cellulose materials are in the particle forms and size distribution under 100 nm that related to Zero- Dimenthional (ZD) nanostructures like nanoparticles and nano powders. It was also observed that after the acid hydrolysis, we can obtain nano cellulose. Fig 2 shows the size distribution histogram gained using Origin and Microsoft excel software. The obtained histograms confirm the narrow diameter distribution for 50 observed nanoparticles. The average diameter of nano cellulose is 50±3 nm.

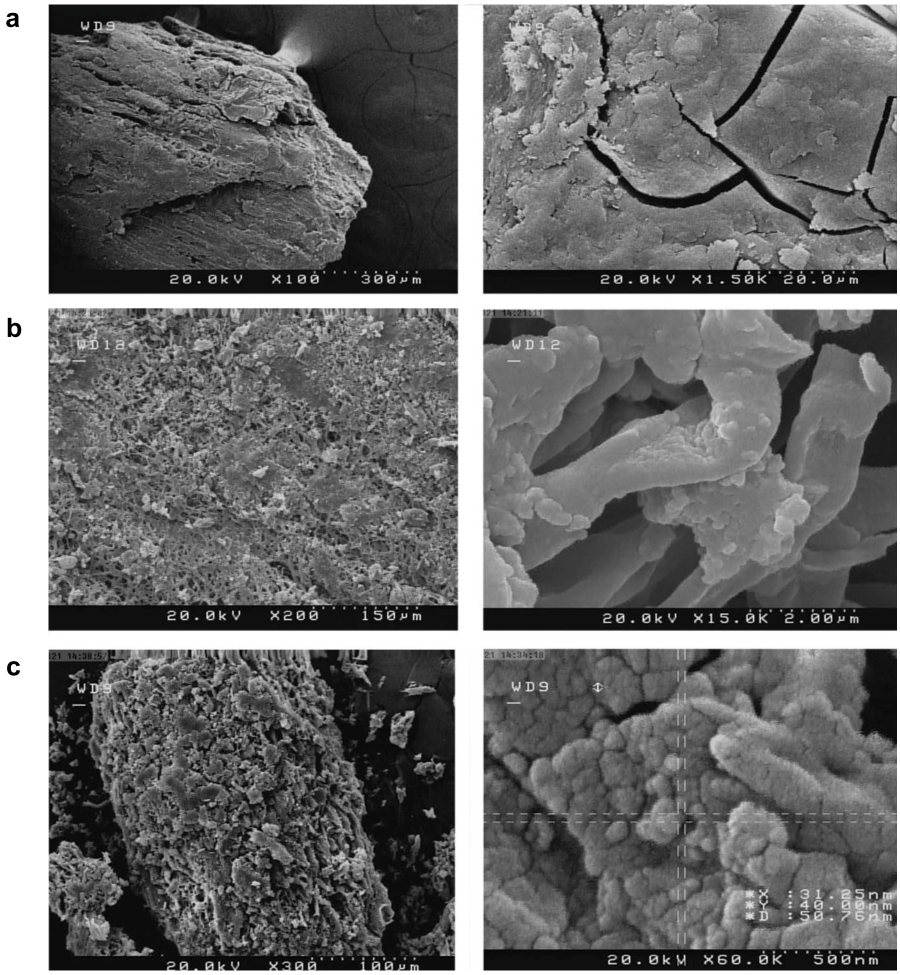

Fig. 1. SEM amage of a) ordinary cinnamon, b) microcellulose, c) nanocellulose.

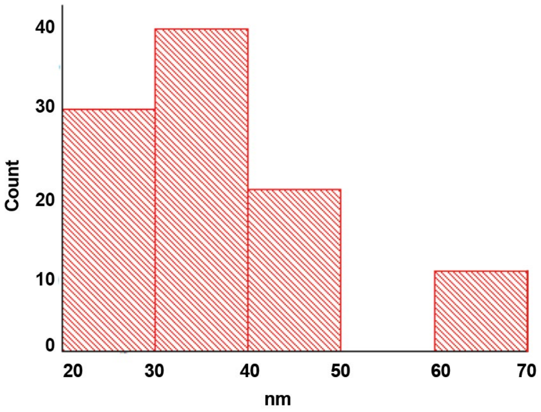

Fig. 2. Nanoparticle diameter distribution.

Infrared spectra

Figure 3 provides the FT-IR spectra of Cinnamon nano cellulose. As observed in Fig. 3 the peaks at about 3200-3600 cm^{-1} corresponds to –OH stretch and hydrogen bonds in callouses structures. And the peaks about 2923 nm, 1100 and 1640 nm, corresponding to *v* C–H, *v* C––O, *v* C—O-C respectively. This figure approves the chemical structure of cellulose and non-degradation of structure during the nanoparticle preparation.

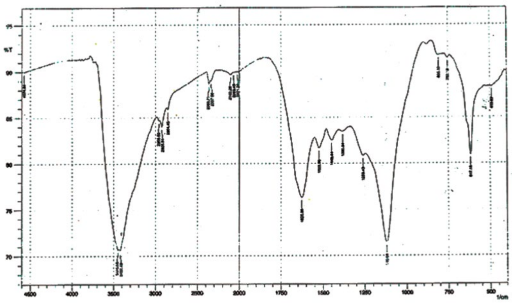

Fig. 3. FT-IR spectra of Cinnamon Nano cellulose.

X-ray diffraction study

Cellulose is a high molecular weight linear polymer with the repeating unit of cellulose. Various ordered crystalline arrangements of cellulose result from different intra- and intermolecular hydrogen bonds of hydroxyl groups. Four different crystalline allomorphs have been identified by their characteristic X-ray diffraction: celluloses I, II, III and IV. Cellulose I is the most abundant form found in nature. Another form of cellulose can be prepared during alkali treatment, ammonia treatment, heating, solublization and recrystallization.The study of the crystalline structure of cellulose has been ongoing since 1990. Thorough reviews of cellulose crystalline allomorphs can be found in literature [33-35]. Its structure is still not fully understood because of its complexity. The diffraction peak location and intensities are influenced by the cellulose form, the forms mixing ratio, crystallinity index, the sample orientation and percent of amorphous fraction. S. Nam et al showed the diffraction patterns calculated from the cellulose I and cellulose II crystal models as well as the ball-milled cotton cellulose as fully amorphous structure [36]. Their calculation has indicated that celluloses I and II had two distinct groups of peaks in 2θ around 10-20 and 20-30. As compared with the patterns of crystalline celluloses with distinct peak, peaks of cellulose were merged together and become wider with increasing of FWHM values and percentage of amorphous fraction, Insofar as, very broad peak has been seen in 2θ around 10-30 for ball-milled cotton cellulose.

Here in prepared nano cellulose crystalline structure was examined by X-ray diffraction. Typical XRD patterns of the sample, prepared by the present method, are shown in Fig. 4. Diffraction peaks are a set of peaks at 2θ around 10° and 20° without obvious mono peaks. As shown in Fig. 4., the observed diffraction peaks agree well with the amorphous structure of cellulose.

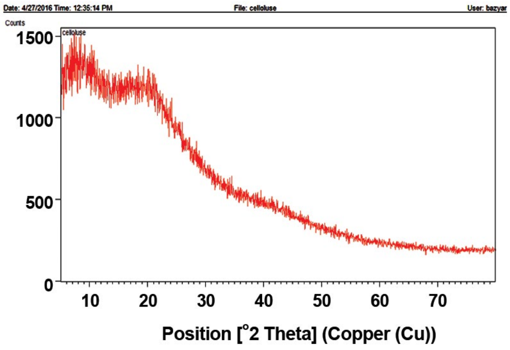

Fig. 4. X-ray diffraction spectrum of cinnamon cellulose nanoparticles.

UV-Vis spectroscopy

UV-Vis spectroscopy was used to approve maintaining cellulosic molecular structure during the preparation of nano cellulose. For this purpose, the spectrum of macro cellulose, micro cellulose and nano cellulose was performed in distilled water, acetone and acetic acid solvents. First UV-Vis spectroscopy was done with dispersing the substances in distilled water. As shown in Fig 5. The absorption spectrum is observed at 192 nm for macro cellulose, micro cellulose and nano cellulose. It shows that the molecular structure has not been manipulated during making nano cellulose. Then substances were dissolved in acetone as organic solvent by stirring for 10 minutes, then they were dispersed in ultrasound bath condition in 10 minutes.

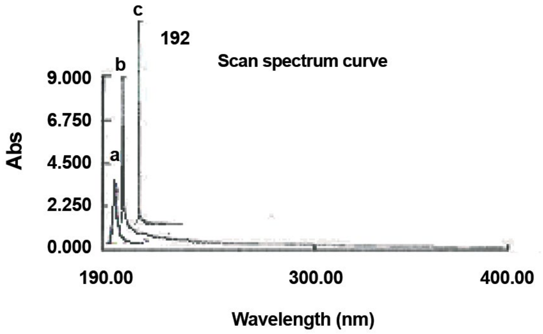

Fig. 5. UV-Vis spectroscopy of a) macro cellulose, b) micro cellulose, c) nano cellulose in distilled water solvent.

Figure 6 shows the absorption spectra in 329 nm for all three materials which indicates the same absorption spectra and no change in the molecular structure of substances in acetone solvent. Finally, UV-VIS spectrum of micro cellulose cinnamon and nano cellulose was obtained by dispersing it in acetic acid solvent to consideration of the stability of nanostructure in acidic condition. Figure 7, shows the absorption spectra in 212 nm and 215 nm which indicate the same absorption spectra and good stability of nano cellulose in acetic acid solvent too. UV spectrums show that the width of peak affected by size of the compounds in All of figures. It can be seen that width of peak decrease with decreasing the cellulose size from macro to nano.

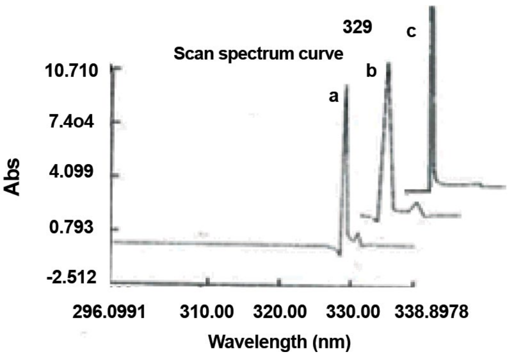

Fig. 6. UV-Vis spectroscopy of a) macro cellulose, b) micro cellulose, c) nano cellulose in acetone solvent.

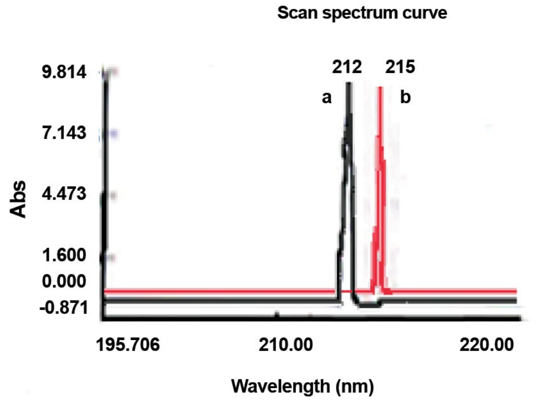

Fig. 7. UV-Vis spectroscopy of a) micro cellulose, b) nano cellulose in acetic acid solvent.

Mass spectroscopy

Mass spectroscopy analysis was used to determine the structure and mass distribution of the different species present in the sample. A mass spectrum of producing cinnamon nano cellulose has been shown in figure 8. As it can be seen in the figure, the main peaks appear in m/z: 504, 403, 341, 279, 240, 167, 162, 149, 128, 107, 81and 58. These peaks agree well with the structure of the cellulose and its fragmentation during analysis. The mother molecular ion appears in m/z (504), exploiting the fact that when celluloses are hydrolyzed in acids at high temperatures the degree of polymerization (DP) of the isolated cello oligosaccharides does not exceed a value of 7 [37]. This DP behavior is thought to be related to reaction parameters (especially time and temperature), methods of hydrolysis and neutralization after hydrolysis, the size of the crystalline zones along the cellulose fiber and is therefore dependent on the species and tissue from which the cellulose originates [38].

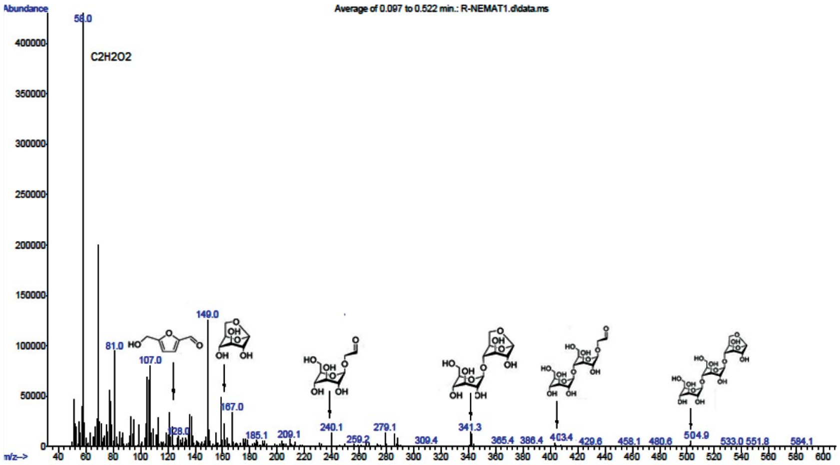

Fig. 8. Mass spectroscopy of nano cellulose

CONCLUSION

In this study, we have demonstrated for the first time the preparation of Cinnamon nano cellulose from cinnamon by acidic hydrolysis method. The products were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) , Fourier transform infrared (FT-IR), UV-Vis and Mass spectroscopy. The SEM images of materials showed that final structure is in zero dimensional nanostructure in the nanoparticle forms with size distribution less than 100 nanometers. The obtained histograms confirm the narrow diameter distribution with the average diameter of nano cellulose about 50±3 nm. Observed diffraction peaks for XRD agree well with the amorphous structure of cellulose. UV-VIS spectrum of macro cellulose, micro cellulose and nano cellulose were done in water, acetone and acetic acid. These spectrums illustrate the same absorption for tree materials in agues, organic and acidic solvents approving the stability of structures and maintaining molecular structure during making nano cellulose.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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