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EXTRACTION AND THERMAL CHARACTERIZATION OF MICROCELLULOSE: FROM PISTACHIO SHELL

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ABSTRACT: *This study focuses on the extraction of micro-crystalline cellulose (MCC) from raw pistachio shell, one of the waste products in the pistachio industry. Using acid hydrolysis method, microcrystalline cellulose was produced from the raw pistachio shell. The particle size and thermal properties of obtained microcrystalline cellulose were performed using particle size and thermogravimetric (TGA) analyzer. Fourier Transform Infrared Spectroscopy (FTIR) was also used to study the effect of acid hydrolysis on the pistachio shell. Results indicated that the thermal stability of microcrystalline cellulose is higher compared to raw pistachio shell at all temperature region.*

KEYWORDS: Microcrystalline Cellulose, Thermogravimetric Analysis, Extraction, Pistachio Shell

INTRODUCTION

Tremendous increase in the agricultural waste resulted to attract the attention of the scientific world to convert these materials into value added products. Due to the pollution created by plastic materials tothe environment and the regulations imposed by each country has triggered the interest to produce more ecofriendly products. Many studies were performed to produce biodegradable composites to subsitiute the synthetic materials [1-3]. Natural fibers such as sisal, banana, hemp etc. are widely used to reinforce the polymer matrices to improve their thermal and mechanical porperties[4,5].

Cellulose is one of the most available, nontoxic biopolymer in the world. According to a statitics,the global cellulose market size was 219.53 billion USD in 2018 and will reach 305.08 billion USD in 2026 showing a CAGR of 4.2% during the forecast period[6]. Cellulose is a linear structured polymer consisting of thousands of glucose monomer joint together by β-1-4 linkages. Because of the presence of two hydroxyl groups they show strong hydrogen bonding which allow for it to achieve crystal structures [7]. This unique nature of cellulose resulted in the studies to extract micro cellulose from various renewable resources such as sisal, banana, bamboo, olive seeds etc. to use it as reinforcing agent in various polymers [8-10]. Pistachio is one of the crops widely cultivated in Middle East and Mediterranean countries. In 2018, around 1.4 million tons of pistachio were produced in the world, where United States and Iran acquired 72% of the total market [11]. Pistachio shells are agricultural waste and mainly used as food for animals and fuels. These can be also used as fillers in thermosetting polymers [12, 13]. Alsaadi et. al. [12] showed that addition of 10 wt.% of powdered pistachio shell can enhance the tensile strength of polyester matrix. Literature survey indicates fewer studies on the extraction of MCC from pistachio nutshell which can be useful to produce the composites which have good thermal and mechanical properties. Therefore, this study mainly aims on the extraction and thermal characterization of micro cellulose from raw pistachio nutshell.

METHODOLOGY

Materials

Raw pistachio shells were purchased from the local sources. Chemicals such as NaOH, HCl, hydrogen peroxide (H_2O_2), were procured from Sigma Aldrich Company.

Extraction of Microcrystalline Cellulose

Removal of wax

Initially the pistachio shells were washed, dried, and milled using a miller to have a powder with size less than 1000 µm. 50 g of powdered samples were transferred to soxhlet apparatus. 250 ml n-hexane was used in the 500 ml round bottom flask. Extraction was continued until all the color of liquid change from yellow to colorless.

Pretreatment of raw pistachio shell

The samples were treated with 17.5% conc. NaOH at 80˚C for 2 hours with continuous stirring. After the above process, the materials were immersed in a mixture of water and hypochlorite (ratio 1:1 vol%) at 80˚C for 30 minutes.

Acid hydrolysis

Followed the above treatment, samples were washed with distilled water, refluxed with 2.5M HCl for 30 minutes and taken out. The samples were then dried at 60˚C. After drying the samples were undergone whitening process using 166.66mL of 30% H_2O_2 repeatedly until the color changes to white. This helps to remove the unwanted non-cellulosic components and partial hydrolysis of amorphous cellulose. The scheme for the extraction of microcrystalline cellulose from pistachio shell is given in Figure 1.

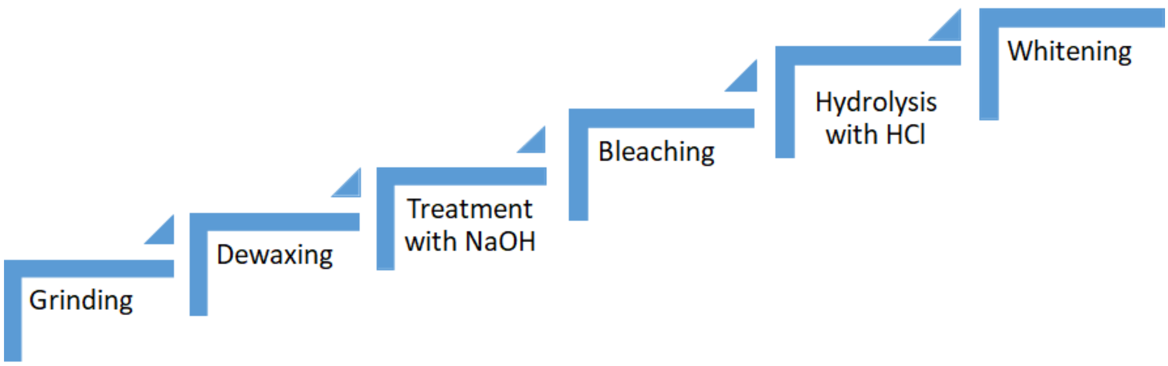

Figure 1: Preparation of MCC from Pistachio Shell

Characterization

Particle size

Particle size of MCC was performed using Microtrac Turbo trac dry powder dispersion system equipped with particle size analyzer (S3550 Series). One gram of microcrystalline cellulose was loaded for each measurement.

FTIR analysis

FTIR analysis using attenuated total reflectance was conducted by Thermo NICOLET 6700 FT-IR Spectrometer at scan rate of 32 scans, resolution of 4 cm^{-1} from wavelength region 600 to 4000 cm^{-1}.

TGA analysis

Thermal stability of prepared MCC was conducted using thermogravimetric analyser, Pyris-6 (Perkin Elmer). Around 5 mg of samples were heated from 30 to 800°C in an inert (nitrogen) atmosphere at a scanning rate of 10°C/min.

RESULTS

Particle Size Analysis

Particle size analysis helps to identify the particle size distribution of prepared microcrystalline cellulose. The particle size distribution of MCC synthesized from pistachio shell is given in Figure 2. From the figure it's clear that the particle size differs from 25 to 574 µm, with an average size of 194 µm.

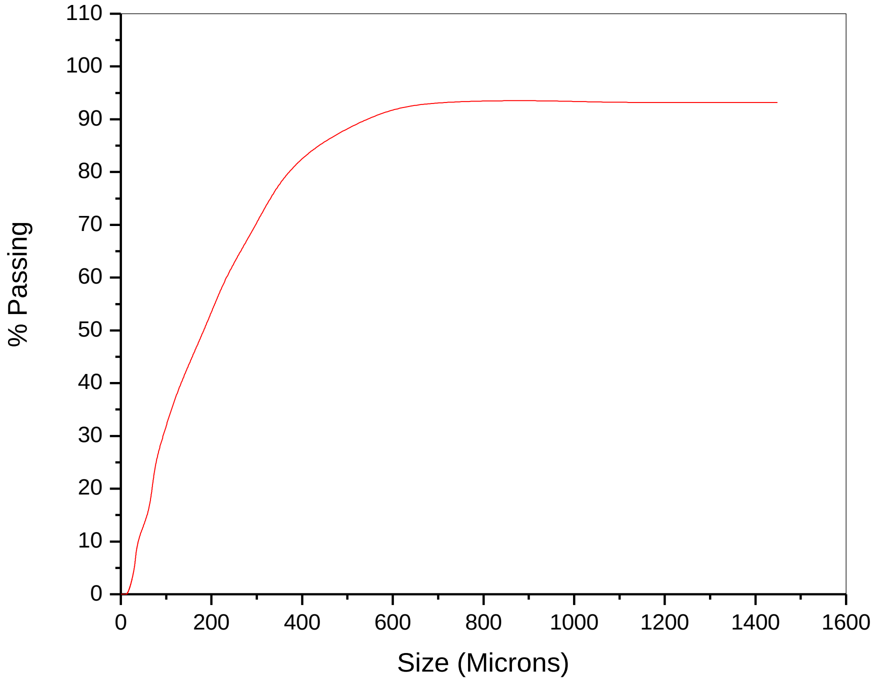

Figure 2: Particle Size Distribution of MCC Extracted from Pistachio Shell.

FTIR

Figure 3 displays the FTIR of pistachio shell and extracted microcrystalline cellulose.

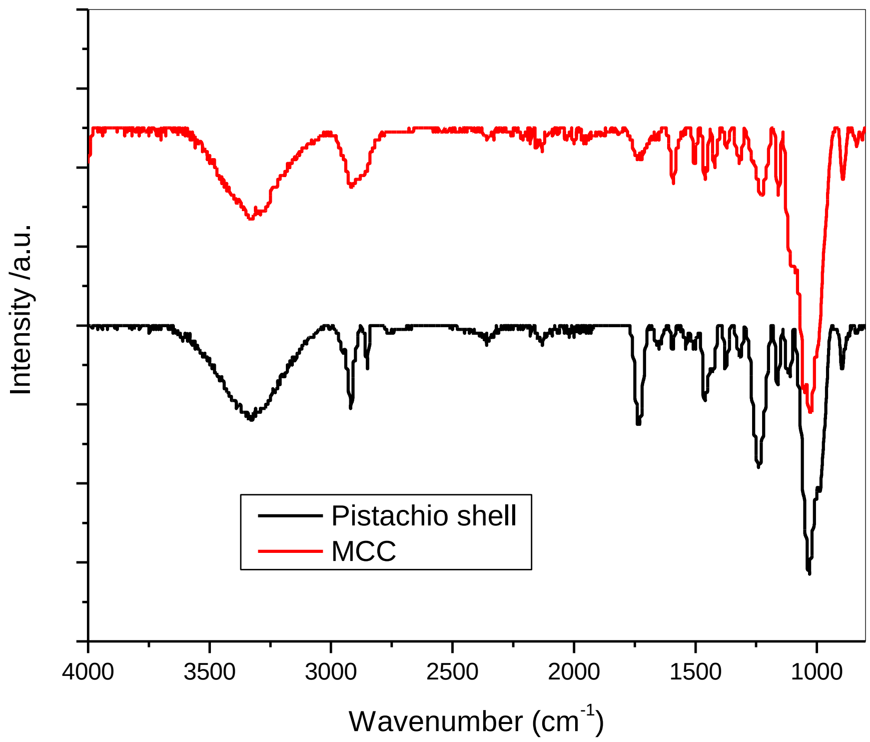

Figure 3: FTIR Spectra for of the Raw Pistachio Shell and the MCC

It can be seen that both, pistachio shell and extracted microcrystalline cellulose exhibits two important region of absorbance. Initial one varies in the range of 700-1800 cm^{-1} and the latter at 2700 to 3500 cm^{-1} approximately. The stretching vibrations of O-H which are present in the pistachio shell and MCC causes a broad band in the region of 3600–3000 cm^{-1}. Stretching of C-H causes a peak in the region of 2900-2800 cm^{-1} indicating cellulose in the pistachio shell and MCC. The carbonyl groups (C=O) associated with the presence of acetyl ester and carbonyl aldehyde groups of hemicelluloses and lignin results a band at 1735 cm^{-1}[14]. Even after drying process, due to the interaction between cellulose and water, the adsorbed water cannot be extracted completely. Hence a peak at 1648 cm^{-1} can be seen in FTIR spectra of all samples which corresponds to O-H bending vibrations of adsorbed water [15]. This confirms the presence of cellulose even after the chemical treatment of pistachio shell. Peaks at 1500 cm^{-1} and 1238 cm^{-1} were related to C-C bonds in aromatic rings in lignin and the C-O-C stretching. The peaks at 1033, 1160, 1032cm^{-1} and 895 cm^{-1} were related to C–O stretching and C–H rock vibrations of cellulose. It's noticeable that when compared to the raw pistachio shell, the intensity of the peak at 1739 cm^{-1} and 1229 cm^{-1} for the MCC decreased which can be due to the reduction in the amount of hemicellulose and lignin after acid hydrolysis.

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Thermal Stability

In order to know the effective usage of a material for high temperature application, the studies of thermal properties are essential. For that thermal stability analysis of the pistachio shell and MCC thermogravimetric analysis was performed. Figures 4 a and b represent the TG and DTG curves of the pistachio shell and the MCC obtained from it.

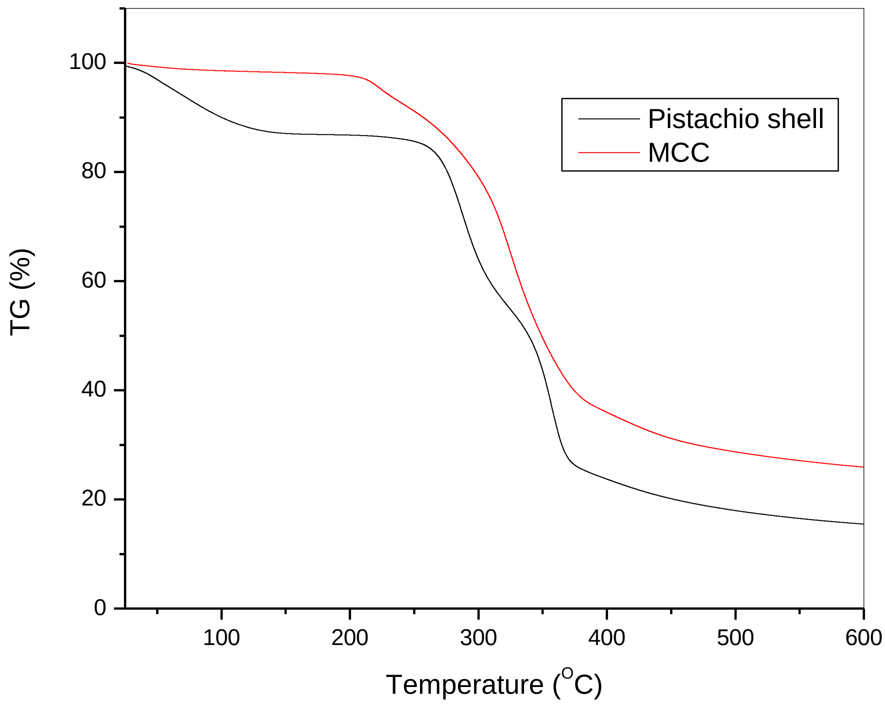

Figure 4 a: TG Curves of the Raw Pistachio Shell and the MCC

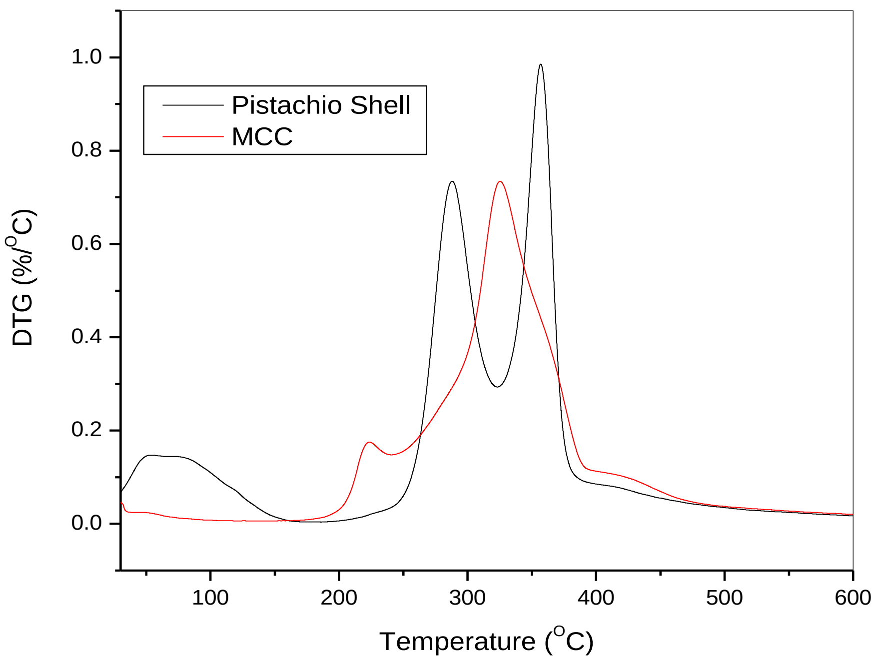

Figure 4 b: DTG Curves of the Raw Pistachio Shell and the MCC

From TG curves, it's clear that all the samples undergo two stage thermal degradation processes. When temperature of process increases the weight, loss increases and the weight loss is higher after 200˚C. At all temperature regions, the weight loss is higher for the pistachio shell compared to the MCC. Initially a small weight loss occurred between 30-150˚C in both which is due to the evaporation of absorbed moisture and other volatile compounds which remains after the extraction process [16].For raw pistachio shell distinct two degradation peaks can be seen in the DTG curves between 200-325˚C and 325-400˚C with peak maxima value of 287˚C and 356˚C.The first degradation peak is attributed by the degradation of hemicellulose and pectin which have less thermal stability. This low thermal stability can be due to the presence of acetyl group in hemicellulose. The second degradation is due to the degradation of cellulose which is present in the pistachio shell. The degradation temperature is higher than the earlier because of its high crystalline nature. A residue of 13.74% was observed at 800˚C.

For the MCC, the mass loss below 150˚C was very less compared to raw pistachio shell. Followed that mass loss started to occur from a temperature of 200˚ and ends at 400˚C with peak maxima of 323˚C. A small shoulder was seen in the DTG curve after the main degradation peak which is attributed by the lignin and other non-cellulosic components. However, when compared to the DTG curve of the raw pistachio shell the intensity of this peak is lower since the acid hydrolysis removed wholly or partly most of the hemi-cellulose and lignin in the pistachio shell which can be corroborated with the FTIR results. The TG curves indicate that the thermal stability of raw pistachio shell is lower than MCC. This can be explained as follows: in the raw pistachio shell, the cellulose is surrounded by lignin, hemicellulose and lignin. The presence of hemicellulose which is located between the cellulose fibrils decreases the crystallinity of the raw pistachio shell. These may initiate more active sites and accelerate the beginning of thermal degradation [17].

CONCLUSIONS

The present study revealed that MCC can be extracted from raw pistachio shell by combined treatment of bleaching, alkaline and acid hydrolysis. FTIR spectra indicate the chemical structure of cellulosic components had not been changed only acid hydrolysis removed the hemicellulose and lignin. Based on TGA, it was found that MCC exhibit high thermal stability compared to raw pistachio shell.

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