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Extraction of Microcrystalline Cellulose from Two Different Agriculture Waste via Chemical Treatment

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Abstract. Microcrystalline cellulose (MCC) was successfully extracted from coconut husk fibre (CHF) and pineapple leaf fibres (PLF) using alkali and bleaching treatments. The extracted cellulose from the chemical treatments were characterized using X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). XRD analysis revealed that the extracted microcellulose from CHF and PLF using chemical treatments have high crystallinity. The thermal stability analysis of the extracted microcrystalline celluloses was investigated revealed that the CHF and PLF lose their lignin and hemicellulose during chemical treatments. Morphological investigation using SEM shows that chemical treatment could remove the layer of extractives from surface of CHF and PLF.

1. Introduction

Agricultural waste is known as one of the rich resources in Malaysia. Most of these agricultural wastes have high quantities of organic and inorganic materials which could produce various useful products. Utilizing these agricultural wastes as resource materials in different application not only provide us cheap and sustainable resource materials but also could tackle the waste disposal issue which making big pollution for environment [1]. In last few decades, more research is focusing on the use of cellulosic waste as filler and this study field has grown rapidly. Many researchers studied production of crystalline cellulose from agriculture waste such as coconut husk fibres, soy hulls, pineapple leaves, sugarcane bagasse, cornstalks, banana rachis, mulberry bark, straw, soybean pods [2]. Due to its biodegradability, availability, renewability, and environmental friendliness, natural fibres or lignocellulose fibres has attracted much attention which are being used as reinforcing components for thermoplastic and thermoset matrices. Coconut coir or coconut husk fibre is the natural fibres that has good thermal and low specific weight while benefit from its low cost and friendly processing [3]. However, its application affected by its limitation for high temperature process conditions and its degradability towards humidity [4]. pineapple leaf fibre contains natural fibres that displays high specific strength and rigidity. Pineapple leaf fibre is abundantly available, low cost, and very hygroscopic. The mechanical properties of pineapple leaf fibres can be associated with high cellulose content and low microfibrillar angle [5].

Natural fibres mainly contain of cellulose, hemicellulose and lignin as their main content. The most dominant reinforcing phase in plant structures called cellulose. cellulose is one of the most abundant biopolymers on earth available in plant-based materials such as wood, cotton and any other plants. It is relatively non-toxic, biodegradable and renewable materials which consider one of the most popular materials for polymer reinforcement in new research fields [6]. It can be processed into whisker-like microfibrils, microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC) and many more. Extraction of cellulose commonly involve chemical treatment which include alkali treatment and bleaching, mechanical treatment and chemo-mechanical treatment [7].

To improve the compatibility of natural fibres, various methods have been studied. To modify the fibre surface, both physically and chemically methods were used. Most of the methods have been used for improving the properties of natural fibres such as surface geometry, dirt removal, fibre strength, and the interaction between the fibre and the matrix are chemical treatments [8]. Alkali treatment is the common chemical treatment method which used to extract most of hemicellulose, lignin, waxes and oils and make fibre surface more rough to reduce fibre aggregation [9]. Studies on alkali treatment of the agricultural waste to extract microcrystalline cellulose from natural fibres has been done by many researches using different agriculture wastes [10–12]. However, there isn't enough research on comparing the extraction of microcrystalline cellulose from different agriculture waste using the same treatment methods. Hence, the main objective of this study was to study the extracted microcrystalline celluloses from the coconut husk fibre (CHF) and pineapple leaf fibre (PLF) using the alkali treatment and bleaching method for both wastes.

2. Materials and methods

2.1. Materials

The CHF and PLF were collected from local agriculture farm, Sabak Bernam, Malaysia. Both wastes were washed and cut into small pieces before dring in an oven at temperature 35°C. The dried samples then were grind using grinder machine until become powder. Samples then washed again repeatedly with distilled water and dried in a temperature-controlled oven at 60°C for 18 h. The dried samples were kept in a desiccator before analysis.

Toluene, ethanol, potassium hydroxide acetic acid and sodium chlorite were purchased from R & M Chemicals Ltd., United Kingdom (reagent grade) and were used directly without any purification.

2.2. Preparation of microcrystalline cellulose from CHF and PLF

2.2.1. Dewaxing. The ground samples were dewaxed under reflux using toluene and ethanol with the ratio 2:1 for 6 hours. The solid was then filtered and washed several times using distilled water.

2.2.2. Bleaching process. The dewaxed fibres were sequentially delignified with acidified sodium chlorite (acetic acid was used to reach pH 4) at 70°C for 1 hour and this treatment were repeated thrice until the treated samples became white. Then it was filtered to remove water-soluble components and washed with distilled water until the pH was neutral.

2.2.3 Alkaline Treatment. The alkali treatment was performed to extract the cellulose by removing lignin and hemicellulose from the coconut husk fibre (CHF) and pineapple leaf fibre (PLF). The residue from bleaching process was then treated using potassium hydroxide (6 wt. %) overnight at room temperature. After filtration, the treated samples were washed carefully with distilled water until the pH was neutral and dried in an oven for 16 h at 40 °C. The dried cellulose was stored for further use.

3. Results and Discussion

The prepared samples were characterized by X-ray Diffraction (XRD) analysis, Thermogravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM). Figure 1. present the raw coconut husk fibre (CHF) and pineapple leaf fibre (PLF) powder and the extracted microcrystalline cellulose from them.

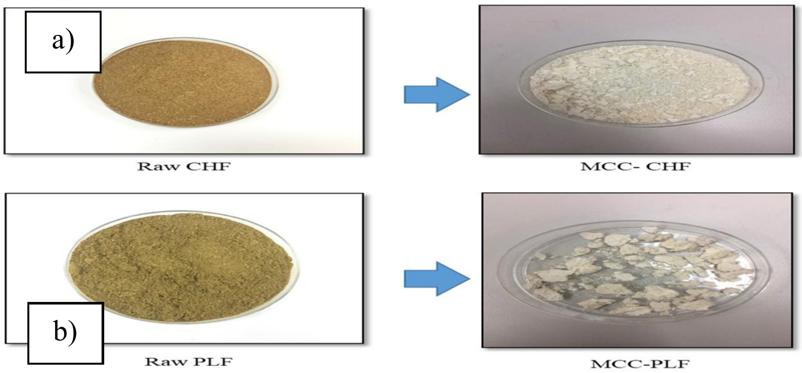

Figure 1. (a) coconut husk fibre powder and its extracted Microcrystalline cellulose (b) pineapple leaf fibre powder and its extracted Microcrystalline cellulose.

3.1. X-ray Diffraction (XRD) Analysis

X-ray diffraction analysis was conducted to analyze the crystallinity of prepared samples. The crystallinity index of the prepared samples were calculated based on Segal *et al.*, (1959) [13] method using equation 1:

$$C_I\ (\%) = I_{cry} - I_{ams} / I_{cry} \times 100 \quad (1)$$

Where, C_I is the crystallinity index (%), I_{cry} is the maximum intensity at a 2θ, and I_{ams} is the intensity of the amorphous material at an angle in the valley between the peaks. The Scherrer formula was used to calculate the crystallite size (table 1.). Figure 2 depicted the X-Ray diffractograms of prepared samples. Cellulose has a crystalline structure due to its hydrogen bonding interactions and Van der Waals forces between their adjacent molecules[14]. From the XRD of MCC-CHF and MCC-PLF, a sharp peak is set which is indicate that crystalline in nature at $2\theta = 22.80°$ and $2\theta = 22.76°$ respectively and both peaks are broad which conclude that as amorphous nature.

Table 1. The crystallinity index and crystallite size of MCC-CHF and MCC-PLF.

Samples	Crystallinity Index (%)	Crystallite size (nm)
MCC-CHF	71.8	4.47
MCC-PLF	68.2	4.14

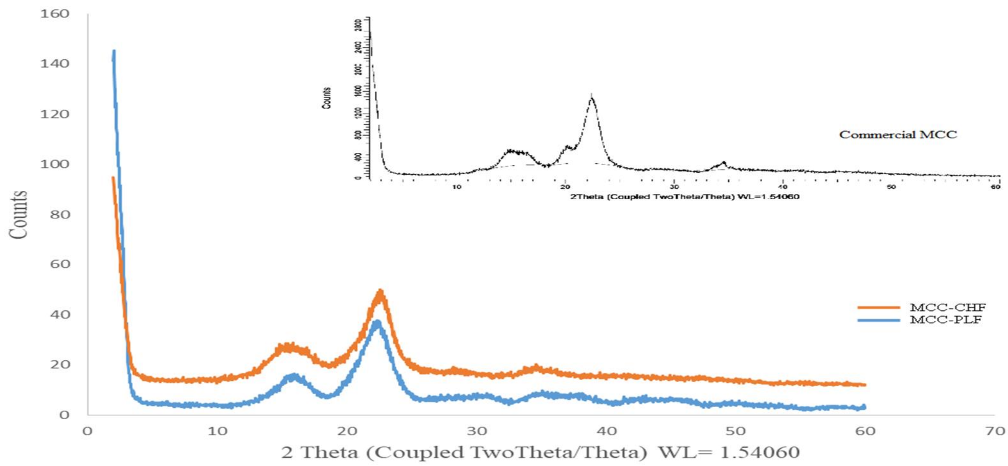

Figure 2. X- ray diffractograms of MCC-CHF, MCC-PLF and commercial MCC.

As shown in table 1, both MCC-CHF and MCC-PLF show a partial crystalline and amorphous nature. The crystallinity index of MCC-CHF (71.8%) is higher than MCC-PLF (68.2%). It is known that the crystallinity of cellulose on natural fibres can be affected by using chemical treatment.

3.2. Thermogravimetric Analysis (TGA)

TGA was performed by using Perkin Elmer Thermal Analyser (Waltham, MA, USA). This analysis was performed to evaluate the thermal stability of both fibres, MCC-CHF and MCC-PLF. The thermo-stability property of the sample prepared was analyzed by using about 6 mg of sample that were used from room temperature to 600°C with a heating rate of 10°C/min under nitrogen (30 ml/min). Figure 3 shows the TGA and derivative thermogravimetry (DTG) curves for prepared samples. According to figure 3 there is significant weight loss for both MCC-CHF and MCC-PLF within temperature 60 ºC to 100ºC due to the removal of bound water in the cellulose [15].The graphs also show the removal of lignin and hemicellulose within 210ºC - 500ºC for both samples. The fastest weight change was observed within 220ºC- 340 ºC.

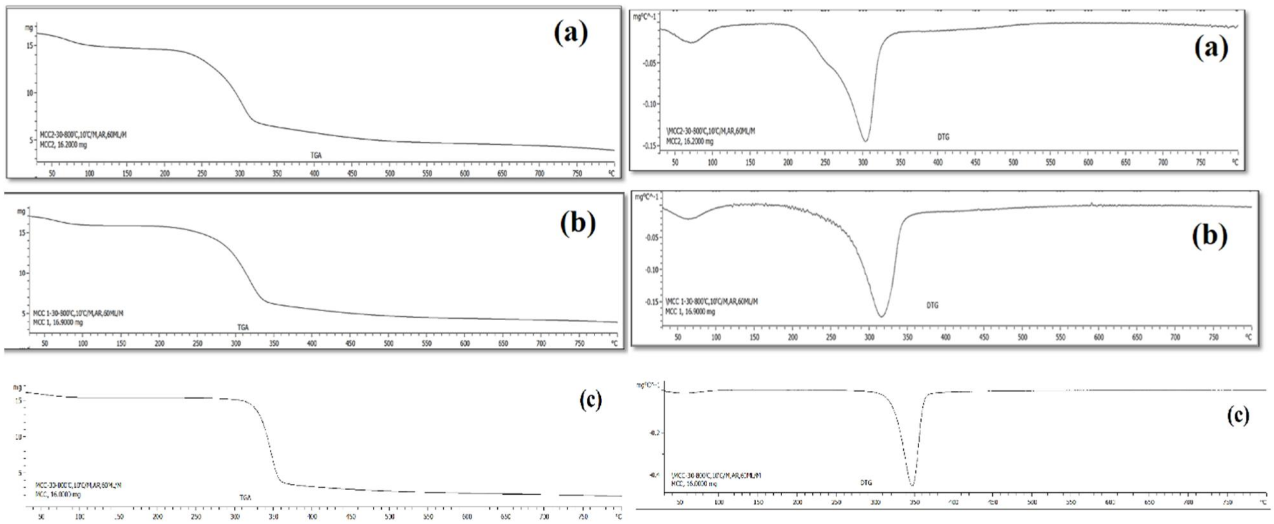

Figure 3. TGA and DTG of (a) the MCC-CHF, (b) the MCC-PLF and (c) commercial MCC.

3.3. Scanning Electron Microscopy (SEM)

Surface morphology of the fibres was studied by JEOL 175 Model JSM-6390 LV scanning electron microscope. The samples were coated with gold in a plasma sputtering apparatus. Figure 4 shows the SEM micrographs of extracted MCC-CHF and MCC-PLF respectively.

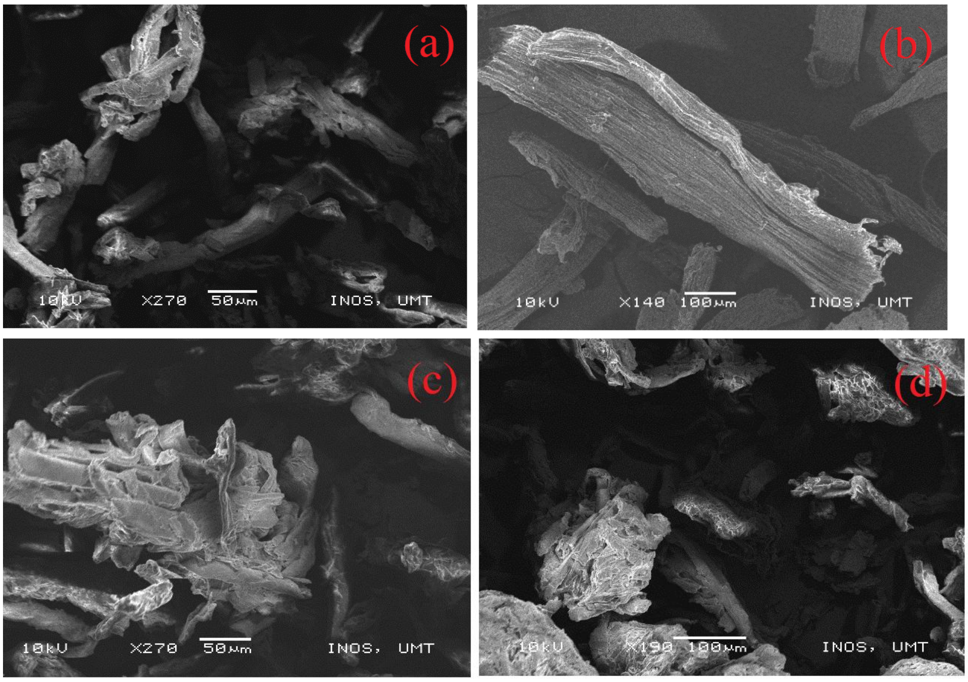

Figure 4. SEM images from MCC-CHF (a) and (b); MCC-PLF (c) and (d).

The agglomeration of fibrse could attribute to the incomplete removal of water in extracted samples. Meanwhile, the roughness of the surface is resulted from partially removal of hemicellulose, lignin, pectin, wax from the samples surfaces by chemical treatments [16].

4. Conclusion

In this study, microcrystalline cellulose successfully extracted from coconut husk fibre (CHF) and pineapple leaf fibres (PLF) using same chemical treatment methods which include alkali and bleaching treatment. The extracted microcrystalline celluloses exhibit rough surface because of partially removal of hemicellulose, lignin, pectin, wax from the sample's surfaces. The extracted microcellulose from coconut husk fibre (MCC-CHF) showed higher crystallinity index compared to extracted microcellulose from pineapple leaf fibres (MCC-PLF) which attributed to the various effect of chemical treatment on the fibers with different composition and microstructures.

Acknowledgement

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