

Extraction of Cellulose and Microcrystalline Cellulose from Kenaf

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ABSTRACT

Bast and core of kenaf which categorized as agriculture residues were used in the extraction of cellulose due to its lignocellulosic nature. In this study, cellulose was extracted from the raw kenaf by using 10% alkaline peroxide pre-treatment followed by extraction process at 85 °C using the combination of 20% (v/v) formic acid and 10% (v/v) hydrogen peroxide that formed peroxy acid. The extracted cellulose was further hydrolyzed by 1.5 M of hydrochloric acid at 80 °C to yield microcrystalline cellulose (MCC). Relatively high yield of 71.81% (w/w) and 94.8% (w/w) were achieved for extracted cellulose and MCC, respectively. Based on FESEM, the average diameter of kenaf cellulose and MCC were 12.43 μm and 11.64 μm, respectively with the separated fibrils and rod-like structural. FT-IR spectral peaks observed in the cellulose and MCC revealed that most hemicellulose and lignin were eliminated during the chemical treatments. XRD analysis results exhibited that kenaf MCC gives the sharpest and highest peak s compared to others. The results also showed that the crystallinity index of extracted cellulose and MCC were increased to 60.5% and 62.3%, respectively.

Keywords: Kenaf; Cellulose; Microcrystalline cellulose (MCC); Alkaline hydrogen peroxide, Peroxy acid

INTRODUCTION

The agricultural sector throughout the world is expending every year to meet the needs of an extreme growth of world's population that reached 7.4 billion on year 2016 (Worldometers 2016). Consequently, the production of agricultural residues will also be subsequently increased. These biomass have the potential to replace fossil fuels as a source of sustainable energy supply or fibres (Bentson, Felby & Thorsen 2014). Globally, around 41% of the total production of agricultural wastes destined as food for livestock, 29% is allocated as a source of energy (fuel) and 22% are not harvested (Wirsenius et al. 2003). Based on the data above, it shows that quite high percentage of agriculture residues is not being fully utilized. According to the study, about 72-86% of agricultural residues also known as lignocellulosic biomass, consisting of carbohydrates (cellulose and hemicellulose) and phenolic polymers (lignin) as the major components while extractives and ash as the minor components. Among all of them, cellulose is the most abundant natural polymer in the world which consisting thousands of β-(1,4) linked D-glucopyranosyl monomer units (George & Sabapathi 2015; Gladysenko 2011).

Cellulose microfibril consists of highly ordered, crystalline regions along with some disordered (amorphous) regions in varying proportions, depending on its source (George & Sabapathi, 2015). When appropriate treatment like chemical, mechanical or enzyme treatments was applied on the fibrils, cellulose which is in crystalline structure can be extracted resulting in the formation of microcrystalline cellulose (MCC) or nanocrystalline cellulose (NCC) (Haafiz et al.

2013). The size of the extracted crystalline cellulose depends on the time and process conditions (Collazo, Ortega, & Boix 2018; Ejikeme 2008). MCC is a cellulose derivatives that partially hydrolysed with 10-50 μm diameters and hundreds to thousands micron length. MCC can be utilized as the starting materials to be developed into nano-sized cellulose by further hydrolysis (Mishra et al. 2018). The NCC isolated is usually with the length of 100-500 nm and width of 5-10 nm (Kian et al. 2018). Generally, the applications of MCC are mainly on pharmaceutical, paint, chromatography and also explosive industries due to its unique compressibility and carrying capacity (Mishra et al. 2018; Kachrimanis & Malamataris 2004; Krogars et al. 2000; Limwong et al. 2004; Young et al. 2002). Other than that, MCC also applicable in food industry as a texturizing agent, naturally derived stabilizer or a fat replacer (Alexander 1992; Sakamoto 2008).

To extract MCC, the most common method is through acid hydrolysis. During the hydrolysis process, the amorphous region will be dissolved and the crystalline region will be left over. MCC can be separated through dialysis. Conventionally, the chemical used in the bleaching or delignification process to extract cellulose is sodium chlorate (NaClO₃) which was banned under the Montreal Protocol on Substances that Deplete the Ozone Layer as a pesticide/fumigant on year 2005. This means that sodium chlorate is not an environmental friendly chemical. Prior research have emphasized on few alternatives method with the use formic acid, phosphoric acid, hydrochloric acid and sulphuric acid in hydrolysis (Aprialia). Studies have also relied on the use of nitric acid and sodium sulphite, followed by sodium hydroxide extraction (Azubuike

& Okhamafe 2012). A number of authors have suggested an alternative method with the use of acetic acid or formic acid as a solvent combined with oxidizing agents such as hydrogen peroxide (H_2O_2) to form peroxy acid, which can be an effective bleaching agent to delignify biomass (Lam et al. 2001; Kham et al. 2005; Jahan et al. 2007; Jahan 2009; Jahan et al. 2014).

The majority of prior research has applied the utilization of wood pulp, cotton, hemp, flax and jute for cellulose extraction for paper, textile and building industry (George & Sabapathi 2015). Several studies suggested that kenaf can also be used as biodegradable and natural alternative source of cellulose and MCC (Azubuike & Okhamafe 2012; Aprilia et al. 2016; Wang et al. 2010). Kenaf is one of the potential fibre crops with high cellulose content and reported to captures greenhouse gas at a significantly high rate owing to high photosynthesis rate compared to some other conventional trees, making it beneficial in global sustainable development (Shah et al. 2019).

In this study, the aim was to investigate and develop agriculture residues as the nonconventional source of cellulose through acid hydrolysis. The scope of this study will be focus on the extraction of MCC from kenaf. To our knowledge, no prior studies have been examined in details the properties and behavior of MCC extracted from kenaf fibers as a source of cellulose using hydrogen peroxide and formic acid. The yield of cellulose and MCC was the

crucial part of this study. The morphology and structural characteristic of native biomass, extracted cellulose and MCC was investigated by Field Emission Scanning Electron Microscopy (FESEM). The chemical functional group was identified by Fourier Transmission Infra-red spectroscopy (FTIR). The crystalline properties were studied by X-ray diffractometry (XRD).

METHODOLOGY

Materials

Biomass bast and core kenaf that purchased from Everise Crimson Company was originated from Bachok in Kelantan, Malaysia. The chemicals, sodium hydroxide (pellet, Macron), formic acid (85.0%, PC Laboratory Reagent), 30% hydrogen peroxide (Bendosen) and hydrochloric acid (36.5-38%, Bendosen) of ACS grade were used as purchased.

Compositional Analysis

A series of compositional analysis were done based on laboratory analytical procedure that developed by National Renewable Energy Laboratory (NREL) and Technical Association of the Pulp and Paper Industry (TAPPI). The type of analysis and the respective methodology was shown in Table 1.

TABLE 1 Type of analysis and the respective methodology

Analysis	Methodology
Moisture content	NREL/TP-510-42620 (Sluiter 2008)
Ash	NREL/TP-510-42622 (Sluiter 2005)
Structural carbohydrates	NREL/TP-510-42618 (Sluiter 2011)
Acid-insoluble and acid-soluble lignin	NREL/TP-510-42618 (Sluiter 2011) & TAPPI T 222 om-11 (TAPPI 2011)

Pre-Treatment

Biomasses were milled until the average size is equal to 0.2 mm by using centrifugal mill (ZM200, Retsch). After that, 30 g of biomass were soaked in 10% of 100 ml NaOH, followed by 10% of 100 ml H_2O_2 . It was then covered with aluminium foil and put into oil bath at 121 °C and 1 bar for one hour. After 1 hour, kenaf fibers were collected from the solution by using filter bag, followed by several rounds of washing until clear water was observed.

Extraction of Cellulose

After pre-treatment process, the filtered fibres were added into the mixtures that contain 10% hydrogen peroxide and 20% formic acid at 1:1 ratio (v/v). The mixture were then put into a water bath with temperature equal to 85 °C and last for 2 h. After 2 h, delignified fibres were filter up from the mixture by using filter bag. During the filtration process, the

solid residues were washed several times with distilled water.

The pre-treatment process and extraction of cellulose was repeated until the kenaf fibres become purely white in colour. Any yellowish colour left indicates that there are still lignin residues in the samples. After that, white suspension on the mixture was being filtered and washed several times by distilled water. This filtered white fibre is the cellulose fibres and its yield was calculated. Percentage of lignin content existed in the kenaf fibres was determined according to the standard TAPPI T 222 om-11 (TAPPI 2011) for every cycle repeated.

Extraction of Microcrystalline Cellulose (MCC)

1 g of extracted cellulose fibres was soaked in the solution that contained 1.5 M HCl at 80 °C for 1 h at a ratio of acid to fibre that equal to 20:1. The hydrolysis process was carried out in a water bath. After 1 h, the fibres were collected through vacuum

pump filtration that using glass microfiber membrane (0.22 μm) followed by washing several times with distilled water. The extracted MCC were then dried in oven at 60 °C for 24 h. After that, the MCC were stored in desiccator. The yields of MCC were calculated and sent for further analysis.

CHARACTERIZATION

Morphology

Morphological study on native biomass, extracted cellulose and MCC were undergoes by using Field Emission Scanning Electron Microscope (FESEM, Zeiss Supra 55VP). Samples were suspended in alcohol ethanol. A drop of sample was placed on carbon tape and dried for 24 h under room temperature. Afterwards, the sample was coated by gold by using sputtering method to avoid charges and the voltage was accelerated up to 2 kV level. Morphology on those samples were observed and the mean diameter was calculated based on the 10 fibres that randomly chosen from the image. When an electron beam penetrated the sample, the X-ray produced was collected, and detected by Silicon drift detectors (SDD) and the X-ray map was recorded (Nazir et al. 2013).

Functional Group Analysis

Chemical investigations of functional groups that existed in the native biomass, extracted cellulose and microcrystalline cellulose (MCC) was conducted by using Fourier Transmission Infra-Red spectroscopy (FT-IR, Thermo Fisher Scientific Nicolet 6700) with the sampling technique of Attenuated Total Reflectance (ATR). FT-IR spectra was produced after 50 times scanned at a resolution of 4cm^{-1} transmission in the wavelength range between $4000 - 450\text{cm}^{-1}$ (Nazir et al. 2013).

Crystal Size and Crystallinity Justification

X-ray diffraction (XRD, D8-Advance Bruker-AXS) was used to define crystal size and crystallinity.

Wavelength (CuK α radiation) of 1.540\AA , scan speed of $2^\circ/\text{s}$ and a 2θ range of $2-80^\circ$ were set during the analysis. The crystallinity index, C_{lr} , was calculated by using formula (Azubuike & Okhamafe 2012; Luthfi 2016):

$$C_{lr} = [(I_{200} - I_{am}/I_{002})] \times 100$$

where, I_{200} = highest peak intensity of the crystalline fractions;
 I_{am} = low intensity peak of the amorphous region.

The crystallite size was using Scherrer's equation to determine (Patterson 1939):

$$D = K\lambda/\beta\cos\theta$$

where, K = constant 0.91;
 θ = Bragg's angle;
 β = intensity of the full width at half of the maximum (FWHM) corresponding to a high intensity peak of the diffraction plane 200.

RESULTS AND DISCUSSION

Compositional Analysis

Compositional analysis on kenaf was determined by using NREL's procedures and the results were shown in the Figure 1. Based on the figure below, kenaf is dominated by lignin followed by glucan that mainly come from cellulose. Other than that, other structural carbohydrates like xylan, mannan and acetyl that build up hemicellulose were giving total percentage of 12% and became the third dominated group in kenaf. The existence of acetyl indicates that hemicellulose in kenaf is a xylan backbone structure hemicellulose. For the lignin content analysis that using TAPPI's procedures, the result gained was 29.36%.

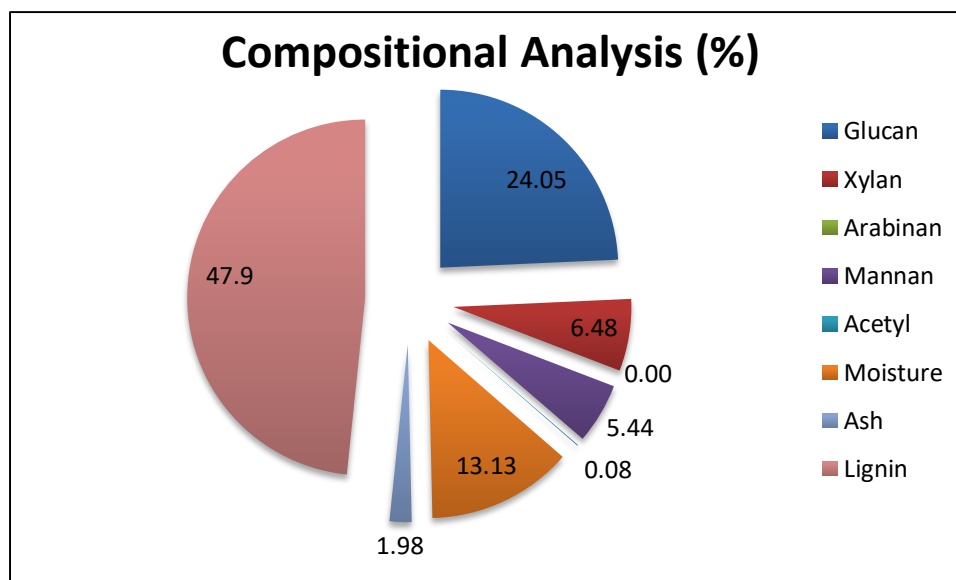


FIGURE 1 Compositional analysis on kenaf

Yield of Cellulose and Microcrystalline Cellulose

In this study, cellulose was successfully extracted from kenaf after undergoes three cycles of treatment. Each treatment consists of two steps which are pre-treatment that using alkaline hydrogen peroxide and extraction of cellulose that

using peroxy acid method. The obtained yield of cellulose from kenaf was 71.81% (w/w) on a dry weight basis which was lower than the previously reported yield at 96.41% that using kenaf bast as raw material (Karimi et al. 2014). The percentage of remaining Klason lignin in kenaf for each cycle was determined and the results are tabulated in Figure 2.

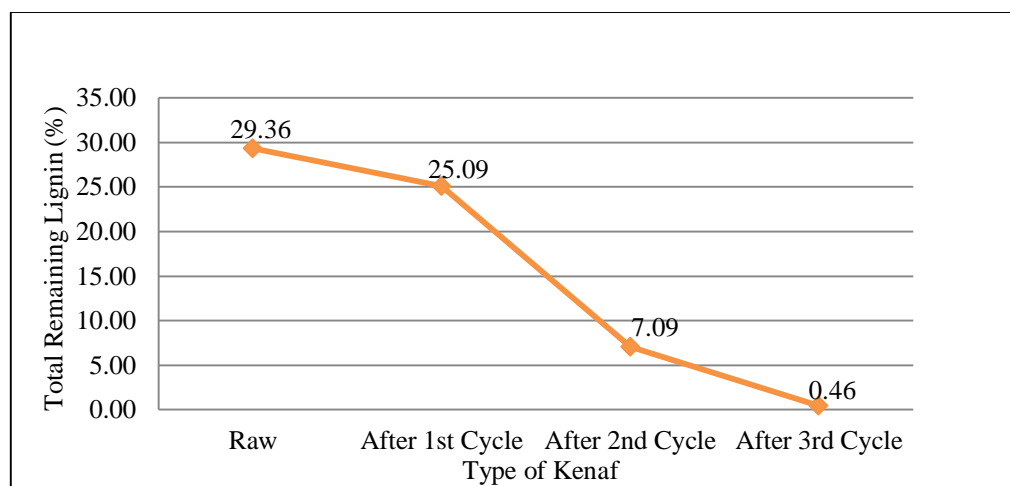


FIGURE 2 Lignin content in kenaf after each cycle of treatment

The total percentage of reduction for the Klason lignin content after first cycle of treatment was reported as 14.53% followed by 75.85% after second cycle and finally achieved 98.43% after third cycle. The percentage of removed lignin at the first cycle was least compared to the second and third cycle due to rigid structure of kenaf at first cycle. After the first cycle of chemical treatment, the rigid structure of kenaf was being destroyed and lead to the high efficiency of delignification process. Sodium hydroxide that used in pre-treatment hydrolysed lignin by releasing hydroxide ion that attacked the carbon of ester bond connecting lignin and carbohydrate (Modenbach 2013). For the hydrogen peroxide which also included in pre-treatment, it is unstable under alkaline condition that yield super reactive hydroxyl radical ($\text{HO}\cdot$) and attacked lignin structure cause cleavage of carbon-carbon chain and carbohydrate degradation (Gray 2013). Thus, lignin was oxidised to aliphatic carboxylic acid that soluble in water. Other than that, kenaf was bleached by hydrogen peroxide through the reaction of hydroperoxide anion (HOO^-) which is a strong nucleophile with the ethylenic and carbonyl groups present in lignin leaving behind the non-chromophoric species (Sun et al. 2000).

Formic acid was responsible for the solubilisation of hemicellulose through hydrolysis. The combination of formic acid and hydrogen peroxide produced performic acid that can formed hydroxonium ion OH^+ (Kham et al. 2005). This ion is a strong electrophile that reacted with lignin and cause oxidative depolymerisation of lignin, thus increased its solubility (Kham et al. 2005). Hydrogen peroxide under acidic medium act as delignifying and activating agents and not as bleaching agent (Kham et al. 2005). The decomposition products of peroxy acid are CO_2 ,

H_2O , and O_2 which are less hazardous than the chloro-organic compounds generated with the use of chlorite (Nazir et al. 2013).

Microcrystalline cellulose (MCC) was produced from cellulose of kenaf and giving the yield of 94.8% which considered quite high if compared to the result of Aprilia et al. (2016). The cellulose are not completely converted to MCC may be due to the insufficient time to react or the concentration of acid used is not high enough for most of the amorphous part of cellulose to be hydrolysed. According to previous study, the temperature and reaction time will have a significant effect on the yield (Aprilia et al. 2016). Longer hydrolysis time increase contact time of the cellulose with the acid, therefore increase the yield of MCC. However, they also reported that increasing in hydrolysis time causing the yield of MMC to decrease.

Morphological Investigation

The morphological structure of raw kenaf, extracted cellulose, kenaf MCC and commercial MCC was studied using FESEM, as shown Figure 3. Raw kenaf having a rough surface indicates that it was deposited by wax, inorganic compounds, hemicellulose and lignin. The extracted cellulose show an isolated fibril that having smooth and flat surface elucidate the successfully removed of wax, hemicellulose and lignin. While for the kenaf MCC, it has an isolated rod-like structure and look a bit difference from the commercial MCC. Commercial MCC look like agglomerated fibres pieces rather than rod-like structure (Haafiz et al. 2013). Average diameter for raw kenaf gives the value of $72.64 \mu\text{m}$, while for the extracted cellulose it has an average diameter of $12.43 \mu\text{m}$. This indicates that the hemicellulose and lignin that bonded on the surface

of cellulose was successfully removed. Diameter of extracted cellulose was dropped to 11.64 μm after undergoing hydrolysis process to obtain MCC. The difference between the average diameter of

extracted cellulose and MCC was little suggesting the severity of hydrolysis is not adequate. Average diameter of commercial MCC is slightly higher than the extracted MCC which is 12.60 μm .

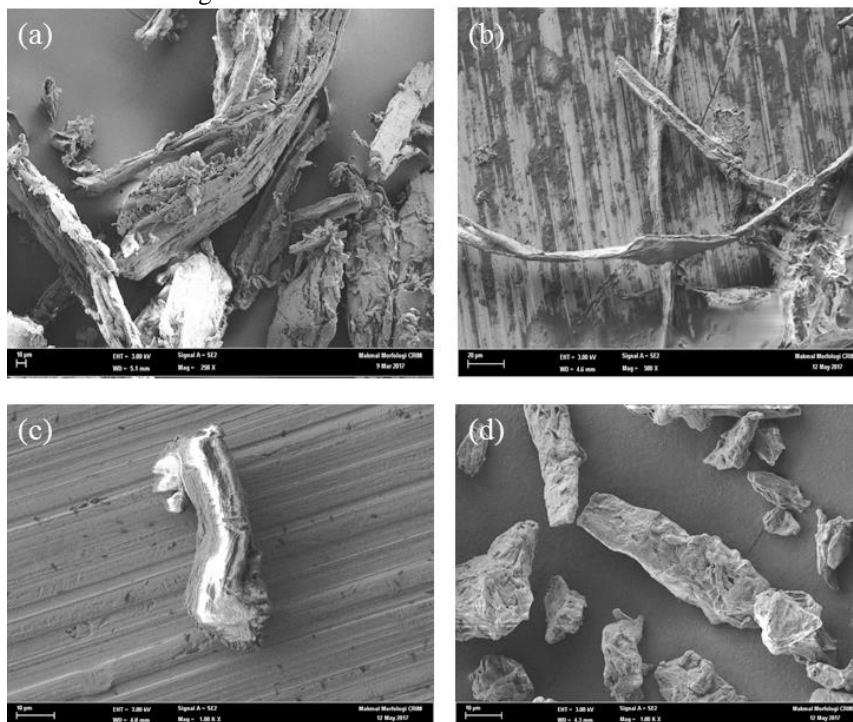


FIGURE 3 FESEM micrographs, (a) raw kenaf; (b) extracted kenaf cellulose; (c) extracted kenaf MCC; (d) commercial MCC

Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra in Figure 4(a), (b), (c) and (d) show the transmittance peaks at 3500-3300 cm^{-1} which were attributable to the hydrogen bond ($-\text{OH}$) with increasing intensity from (a) to (c) and shifted to lower wavenumbers. This indicates that the degradation of the amorphous part, which enhanced the crystallinity of cellulose and MCC (Aprilia et al. 2016). The peaks appeared at 1737, 1595.9, 1504.4, 1462.8 and 1242.9 cm^{-1} which can be attributed to lignin and hemicellulose that only shown or very prominent at the spectra of raw kenaf confirmed the elimination of most of these two components (Azubuike & Okhamafe 2012). Bands at 1162-1158, 1109-1107, 1059-1052 and 1033-1032 cm^{-1} indicate the vibration of asymmetric C-O-C bridge stretching, anhydroglucose ring asymmetric

stretching, C-O stretching and in-plane C-H deformation respectively were more prominent in spectra 4(b), (c) and (d) (Kian et al 2018). These spectral changes are characteristics of cellulose, which further demonstrates the removal of hemicelluloses and lignin (Nazir et al. 2013). The FT-IR peaks of commercial MCC were similar to the MCC extracted from kenaf spectra. In comparison with the cellulose extracted, no alteration in the chemical compositions of the acid-hydrolyzed MCC was observed. Although the acid hydrolysis had an effect on the crystallinity and morphology of the fibers, it did not influence the chemical components of the fibers (Aprilia et al. 2016). The assignment of the IR bands on each samples and their respective functional groups were clearly showed in Table 2.

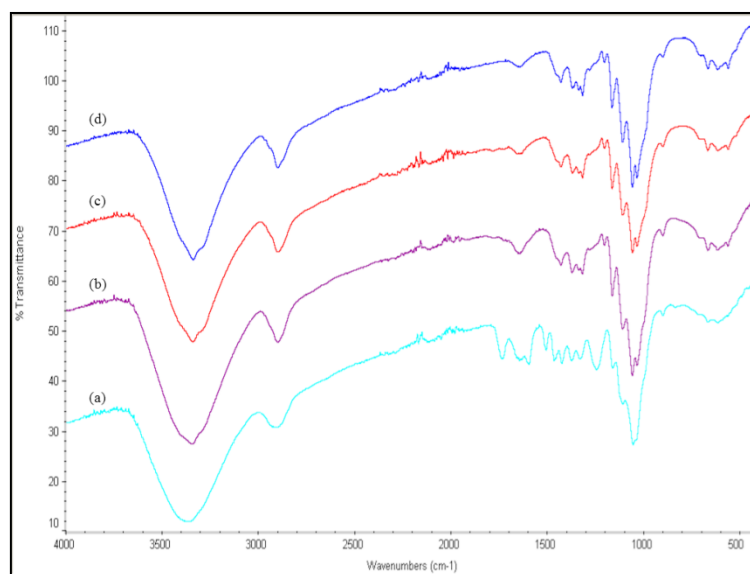


FIGURE 4 FT-IR spectra, (a) raw kenaf; (b) extracted kenaf cellulose; (c) extracted kenaf MCC; (d) commercial MCC

TABLE 2 Assignment of the IR bands on samples and their respective functional groups

Functional Groups	Wavenumber (cm ⁻¹)	Raw Kenaf	Kenaf Cellulose	Kenaf MCC	Commercial MCC
O-H (stretching)	3500-3300	/	/	/	/
C-H (symmetry stretching)	2900-2800	/	/	/	/
C=O (stretching)	1737	/	×	×	×
O-H (water absorption)	1643-1642	/	/	/	/
Lignin	1595.9, 1504.4 & 1462.8	/	×	×	×
-CH ₂ (bending-“crystalline band”) & C=C (stretching)	1430-1423	/	/	/	/
C-H (bending-aromatic ring of cellulose)	1373-1369	/	/	/	/
C-O (aromatic ring of cellulose)	1330-1315	/	/	/	/
C-O-C (aryl-akyl ether lignin)	1243-1200	/	/	/	/
C-O-C Bridge (asymmetric stretching)	1162-1158	/	/	/	/
Anhydroglucose Ring (asymmetric stretching)	1109-1107	/	/	/	/
C-O (stretching)	1059-1052	/	/	/	/
In-plane C-H deformation	1033-1032	×	/	/	/
C-O-C (stretching-“amorphous band”)	900-898	/	/	/	/
Deformation of Anhydroglucopyranose Unit	1800-559	/	/	/	/

X-ray diffraction (XRD)

The X-ray diffractogram of the fibers are shown in Fig. 5 while the crystallinity index, C_r and crystallite size for each of the samples are shown in Table 3. Basically, all of the diffraction patterns showed peaks at planes (110), (110), (200) and (004) that located around $2\theta = 14^\circ$, 16° , 22.5° and 35° respectively indicating the typical cellulose I structure. The only difference concerns were the intensity change in the peaks, representing changes occurred towards the fibres' crystallinity (Luthfi et al. 2016). For fibres with high cellulose content, two peaks around 16° were observed; however, for the raw kenaf, only one broad peak was observed due to

the presence of amorphous material which covered the two peaks (Subramanian et al. 2005; Tserki et al. 2005). Plane (004) having a broad peak for both raw kenaf and extracted cellulose were indicating the great existence of amorphous cellulose region. Raw kenaf fibres are composites of amorphous (hemicellulose, lignin & cellulose) and crystalline (cellulose) structures, hence the smallest peak intensity was shown compared to the others samples (Figure 4a) as the cellulose fibres may still be entrapped in amorphous hemicellulose and lignin. The peaks intensity was increased gradually from raw kenaf, kenaf cellulose, commercial MCC to kenaf MCC based on Figure 5. Cellulose extracted from kenaf giving a high intensity peak (Figure 4b)

compared to raw kenaf suggests that the removing of hemicellulose and delignification had been successfully achieved (Wang et al 2010; Shah et al. 2019). While for the kenaf MCC, it performed the highest and sharpest peaks (Figure 4d) among those samples indicates that it has the highest crystallinity

degree and the relative amounts of amorphous regions within the cellulose were greatly diminished. The sharp high intensity peak describes the crystalline nature of the material, and the intensity value shows the amount of crystalline structure (Nazir et al. 2013).

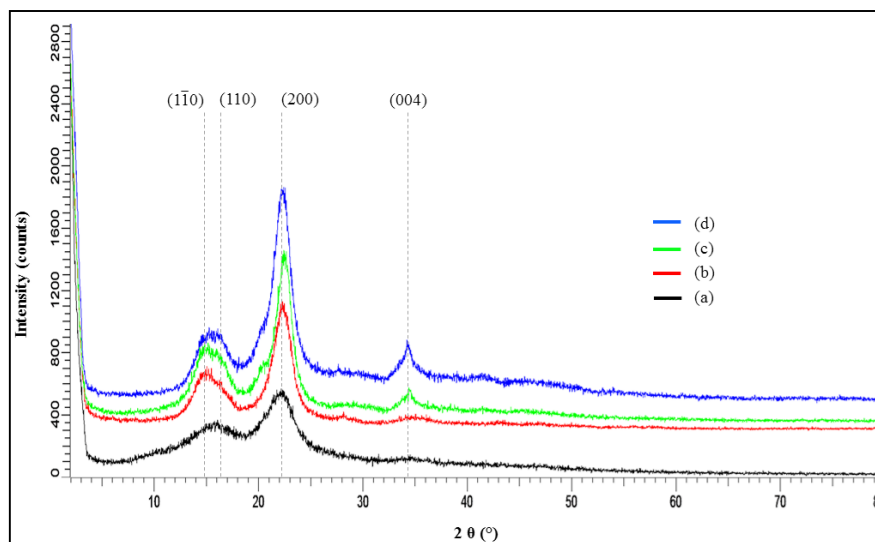


FIGURE 5 X-ray diffractogram, (a) raw kenaf; (b) extracted kenaf cellulose; (c) commercial MCC; (d) extracted kenaf MCC

Based on Table 3, crystallinity index, C_r was increased gradually from raw kenaf, extracted cellulose kenaf MCC due to the removed of hemicellulose, lignin and also the amorphous region of cellulose. The increase of C_r for kenaf MCC was not prominent if compared to extracted. This might be due to C_r only can reflect the percentage of crystalline material in the total cellulose (Luthfi 2016). The total amount of the crystalline region in the cellulose may not experience a rapid increased, but an increased in the degree of crystallinity of the

crystalline cellulose was very prominent and can be proven based on the X-ray diffractogram (Figure 5). Crystallite size of kenaf cellulose are larger than raw kenaf due to the lateral coalescence of microfibrils and their co-crystallization, leading to increased apparent crystal size (Aprilia et al. 2016). Crystallite size of kenaf MCC are similar to commercial MCC but smaller than kenaf cellulose which might due to the cleavage and peeling of cellulose chain under acid hydrolysis.

TABLE 3 Crystallinity index and crystallite size at plane (200)

Samples	Crystallinity Index, C_r (%)	Crystallite Size at Plane (200), (nm)
Raw Kenaf	52.11	4.39
Kenaf Cellulose	60.50	5.68
Commercial MCC	63.69	4.57
Kenaf MCC	62.34	4.24

CONCLUSIONS

1. Composition of kenaf was dominated by lignin, followed by cellulose and the third is hemicellulose.
2. The yields of cellulose extracted from kenaf under the combination of alkaline hydrogen peroxide and peroxy acid treatment was giving the value of 71.81%. While for the HCl-hydrolyzed kenaf cellulose yielded 94.8% of MCC.
3. Observation based on FESEM, FT-IR and XRD revealed that cellulose and MCC was successfully isolated from kenaf fibre, which is the third world fiber crop that planted in Malaysia

4. This research is a pioneering work that demonstrates the applicability of kenaf fibre in the production of cellulose and microcrystalline cellulose.
5. Future research should focus on the use of kenaf MCC to produce NCC and the effect of acid concentration, hydrolysis time and temperature on the yield.

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