

Preparation of Nanocellulose Directly from Kenaf Bast: The Change in Particle Size

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Producing nanocellulose from lignocellulosic plants is difficult but can be achieved with microwave-assisted treatment. However, the changes in dimensions during the process have not been investigated thoroughly. In this study, kenaf bast was used to produce cellulose nanofibers using microwave, chemical, and ultrasonic treatments. Fiber sizes were monitored throughout the experiment using an optical microscope and scanning electron microscopy (SEM). The kenaf single fiber cells were also isolated and measured. The results showed that the duration of microwave treatment notably influenced the destruction of kenaf fibers, and the concentration of NaOH in the chemical treatment had only a limited effect on the reduction of kenaf particle size. Both the microwave and chemical treatments were able to destruct the kenaf fibers longitudinally, and the ultrasonic treatment was able to reduce cellulose particles from micro-size to nano-size.

Keywords: Kenaf; Cellulose; Nanofiber; Microwave; Fiber cell

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INTRODUCTION

Nanocellulose products have received much attention due to their outstanding properties, which include a high tensile strength, a high Young's modulus, high flexibility, and a low coefficient of thermal expansion (Bhatnagar and Sain 2005; Ghaderi *et al.* 2014; Nagashima *et al.* 2014). There are a variety of nanocellulose production methods, such as chemical, mechanical, chemo-mechanical, and enzymatic treatments, that have been widely studied and used in research and industry environments (Henriksson *et al.* 2007; Saito *et al.* 2007). However, most of these methods require the use of cellulose-rich fibers and powders as raw materials (Bhatnagar and Sain 2005). Plants with high lignin contents are unsuitable for nanocellulose production (Jonoobi *et al.* 2012), which limits the output of nanocellulose and increases production cost. Therefore, a method that can effectively utilize plants with high lignin content to generate cellulose nanofibers is highly desirable.

The microwave-assisted liquefaction method converts lignocellulosic materials to nano-size cellulose fibers, and it extracts more than 90% of lignin using microwave treatment. It has the advantages of high speed and not contributing significantly to pollution. Next, the bleaching process easily removes the residual lignin and hemicellulose and generates pure cellulose fibers with small particle sizes. This process was successfully applied on sugarcane bagasse and soy (Li *et al.* 2012; Wang *et al.* 2013).

Xie *et al.* (2016a) studied the ability of microwave treatment coupled with sulfuric acid to produce cellulosic nanofibers from bamboo, obtaining fibers with diameters from 4 nm to 18 nm and lengths of 550 nm. The microwave method coupled with NaOH was also investigated (Huang *et al.* 2017). The reduction of biomass powders to nano-scale materials is a complicated mechanical and chemical process. Most research has focused on the properties of the final products (Xie *et al.* 2016b), but research on the changes that occur throughout the process is relatively sparse. Tracking the changes in the fibers throughout the production process would improve the understanding of process mechanisms and allow process optimization.

As one of the most traditional lignocellulosic fiber plants, the abundantly available kenaf is a potential source of nanocellulose because of its high cellulose content and high crystallization (Jiang *et al.* 2017a). In this study, nanocellulose was produced directly from kenaf bast using microwave treatment in conjunction with chemical and ultrasonic treatments. The main goals of the study were to monitor the changes in fiber size during the process and improve the understanding of the treatment mechanisms. The dimensions of kenaf single fibers were also measured.

EXPERIMENTAL

Kenaf Bast Preparation

Kenaf bast was harvested from Xinjiang Province, China. About 2 kg kenaf bast was stored under ambient conditions for 2 weeks. They were then separated into 2 groups. One group (group 1, 0.5 kg) was chipped to segments with lengths of approximately 2 cm. The other group (group 2, 1.5 kg) was cut and then ground to collect the 60 mesh powders using a micro plant grinding machine.

Kenaf Single Fiber Isolation

One g of kenaf segments from group 1 was placed into 80 mL 2% (w/w) NaOH solution in a 250 mL flask with condenser. The mixture was boiled for 40 min. After treatment, kenaf segments were washed with distilled water 3 to 4 times, and the fiber bundles were obtained. Single fibers were separated from the fiber bundles using a dissecting needle. The separated fibers were placed on glass slides for optical microscope observation.

Microwave Delignification

The microwave delignification of kenaf was carried out in a CEM laboratory microwave oven (MARS-6, CEM company, Matthews, NC, USA; 2000 W maximum microwave power, 350 °C maximum operating temperature, infrared temperature sensor) equipped with 50 mL sealed Teflon reaction vessels.

A mixture of glycerol and methanol (ratio: 2 to 1, w/w) were used as the solvent for delignification. To carry out the reaction, 32 g of kenaf particles, 256 g of the solvent, and 4.48 g of sulfuric acid (1.75% w/w) were well mixed and separated to 16 even portions. Each portion was added to a 50 mL Teflon vessel with a magnetic stirring bar, and a total of 16 Teflon vessels were prepared. During heating, the temperature of the mixture was increased from room temperature to 120 °C over 10 min and was then kept constant for 3 min, 6 min, 9 min, 12 min, and 15 min. The temperature was monitored and controlled by an infrared temperature control system.

During the heating process, the power of the microwave oven was automatically adjusted in the range of 0 W to 550 W based on the feedback from an infrared temperature sensor. After the reaction, the vessels were removed from the microwave oven and cooled for 15 min. The resultant reaction mixture was distributed in methanol and vacuum-filtered through No. 4 filter paper. The solid that remained on the filter paper was washed with methanol again and oven-dried at 105 °C.

Further Chemical Treatment

The residues from the microwave delignification process were further chemically purified to remove the residual lignin and hemicellulose. The residues were first bleached in an acidified NaClO₂ solution (0.1% w/v) at 75 °C for 1 h. The bleaching process was done to remove the lignin that remained in the residues after microwave delignification. The residue was filtered and washed with deionized water until its pH was neutral. Next, the bleached residues were treated with NaOH solutions with concentrations of 0.2%, 0.4%, and 1% at 75 °C for 30 min to remove hemicellulose. Finally, the residual was filtered and rinsed with deionized water until reaching a neutral pH.

Ultrasonic Nanofibrillation

Ultrasonic fibrillation was conducted in an ice bath. A total of 1 g of the chemically purified residues were soaked in 500 mL deionized water and treated with an ultrasonic generator equipped with a 1.5 cm cylindrical probe. The process was performed at a frequency of 25 kHz with an output power of 750 W for 30 min.

Optical Microscope Analysis

The diameters and lengths of kenaf fiber cells, kenaf fiber bundles, and kenaf particles were observed using optical microscopy (LEICA DM2700M, Solms, Germany) (Fig. 1). The diameter of the fiber cell was measured directly with the software. However, the length of the kenaf fiber cell exceeded the diameter of the view field of the microscope (1000 μm). To measure the length of the fiber cell, the glass slide was moved gradually, and several pictures were collected. The pictures were then combined to one picture using the software to show the whole fiber cell, and its length was measured. The lengths of the fiber bundles, which were mostly longer than 1 cm, were measured using a Vernier caliper. There were 200 kenaf fiber cells, and 50 microwave and chemical treatment residual particles were investigated to ensure data accuracy.

Scanning Electron Microscope Analysis

After chemical treatments, the kenaf particles and ultrasonic treatments were observed using scanning electron microscopy (SEM; JSM-6390LV, JEOL, Peabody, USA) with an operating voltage of 20 kV. Test samples were coated with gold using a vacuum sputter coater before being subjected to SEM analysis.

Transmission Electron Microscope Analysis

For the clear observation of separated nanocellulose, the TEM image of the final nanocellulose was obtained using a Hitachi—H7650 microscope. Before being observed and photographed, 1% of the nanocellulose suspension was dropped on the copper screen.

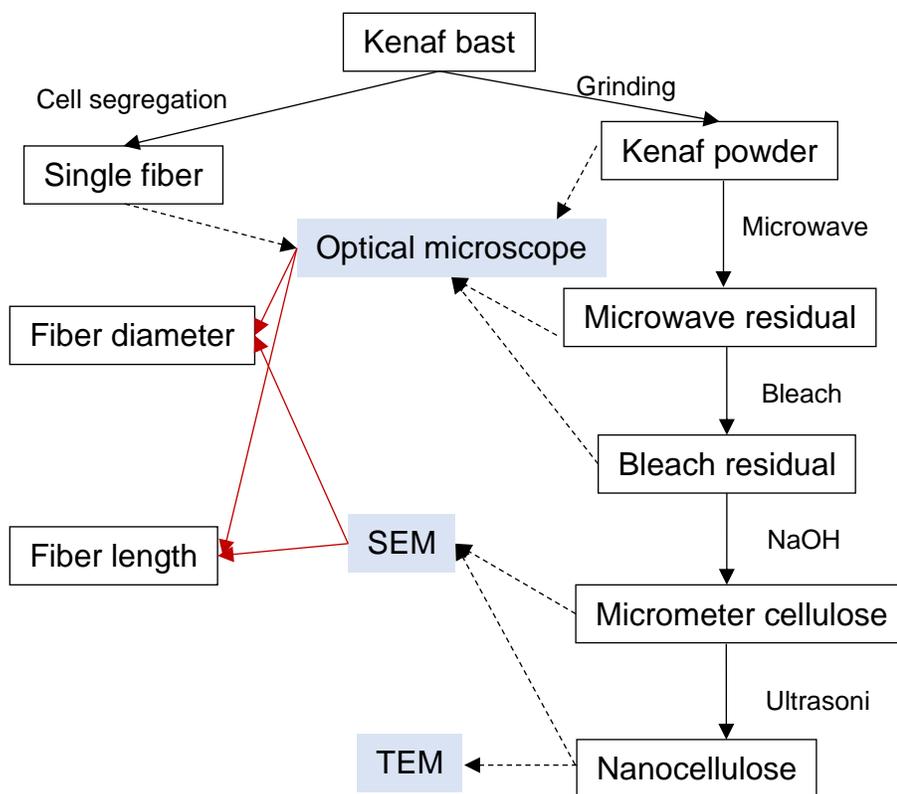


Fig. 1. Schematic diagram for the degumming and characterization process

RESULTS AND DISCUSSION

Size Distribution of Kenaf Single Fiber

The diameter and length of the fiber cell were measured and shown in Fig. 2A and Fig. 2B, respectively. The average diameter of the 200 kenaf fiber cells measured in this work was $10.6 \mu\text{m}$, and the average fiber length was 2.16 mm . As a natural fiber, the fiber diameter and length variation were relatively high. The standard deviations of the diameter and length were $2.02 \mu\text{m}$ and 0.57 mm , respectively, as listed in Table 1.

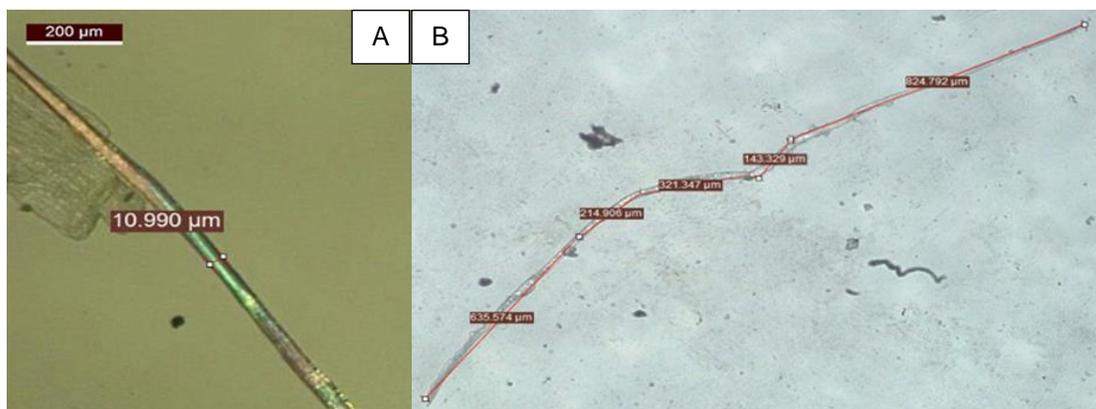


Fig. 2. The measurement of diameter (A) and length (B) of kenaf fiber cells

The small diameter of the fiber suggests it could be a good raw material for nanofiber production, but the length of kenaf fiber cells is short and not suitable for use as a textile fiber. Fortunately, its fiber bundle had an average diameter of 95.6 μm and an average length of 25.4 mm (Table 1), which are acceptable for both textile processing and other fiber reinforced composites (Jiang *et al.* 2017b; Song *et al.* 2017).

Table 1. Diameters and Lengths of Kenaf Fiber Cell

	Total Number	Average (μm)	Max (μm)	Min (μm)	SD
Fiber diameter	200	10.56	16.78	5.49	2.02
Bundle fiber diameter		95.61	185.93	29.05	34.68
Fiber length		2160	3060	989	569
Bundle fiber length		25400	57000	8500	11150

Evolution of Kenaf Fiber through the Microwave and Chemical Treatments

Microwave and the following chemical treatments have different effects on the kenaf fiber. The initial kenaf powders passed through 60 mesh (which the average size approx. length *ca.* 1000 μm , diameter *ca.* 140 μm). Both the length and diameter decreased dramatically with the increasing duration of microwave treatment. The average lengths were 490 μm , 380 μm , 250 μm , 200 μm , and 70 μm after microwave treatments of 3 min, 6 min, 9 min, 12 min, and 15 min, respectively, and the average diameter were 72 μm , 67 μm , 38 μm , 31 μm , and 16 μm after microwave treatments of 3 min, 6 min, 9 min, 12 min, and 15 min, respectively. After 3 min of microwave treatment, the bleach treatment reduced the average length from 490 μm to 170 μm and the average diameter from 72 μm to 18 μm . In addition, the 0.2% NaOH treatment further decreased the average length and diameter to 57 μm and 10 μm , respectively. With increasing duration of microwave treatment, the effect of the bleach and NaOH treatments decreased. In particular, when the duration increased to 15 min, the length and diameter of the kenaf powder decreased to 68.0 μm and 13.4 μm , respectively, by the microwave treatment, and no evident change in size was observed after the bleach and NaOH treatments. It was also observed that the average length and diameter of the fibers changed minimally with increases in the concentration of NaOH, as shown in Table 2.

Table 2. Diameters and Lengths of Kenaf Microfiber after NaOH Treatment with Different Concentrations

Kenaf Microfiber	Total Number	NaOH Concentration (%)		
		0.2	0.4	1
Fiber diameter (μm)	50	13.36 \pm 4.17	13.04 \pm 4.38	13.75 \pm 4.42
Fiber length (μm)		67.99 \pm 25.21	62.63 \pm 24.65	64.61 \pm 22.13

As illustrated in Fig. 3, the initial kenaf powder was identified as kenaf fiber bundles. The average length and diameter of the particles were about 1000 μm and 140 μm , respectively, which are comparable with the fiber bundle's length of 989 μm to 3060 μm and diameter of 29.0 μm to 185.9 μm . The microwave and chemical treatments were able to break down the fiber bundles to single fiber cells, which resulted in noticeable reductions in the length and diameter of the samples. The minimum diameter of the fibers treated with a microwave treatment of 3 min and a 1.0% NaOH solution was 10.31 μm ,

which is similar to the fiber cell's average diameter of 10.56 μm . However, both the microwave and chemical treatments were unable to further break down the sample to nanofibers.

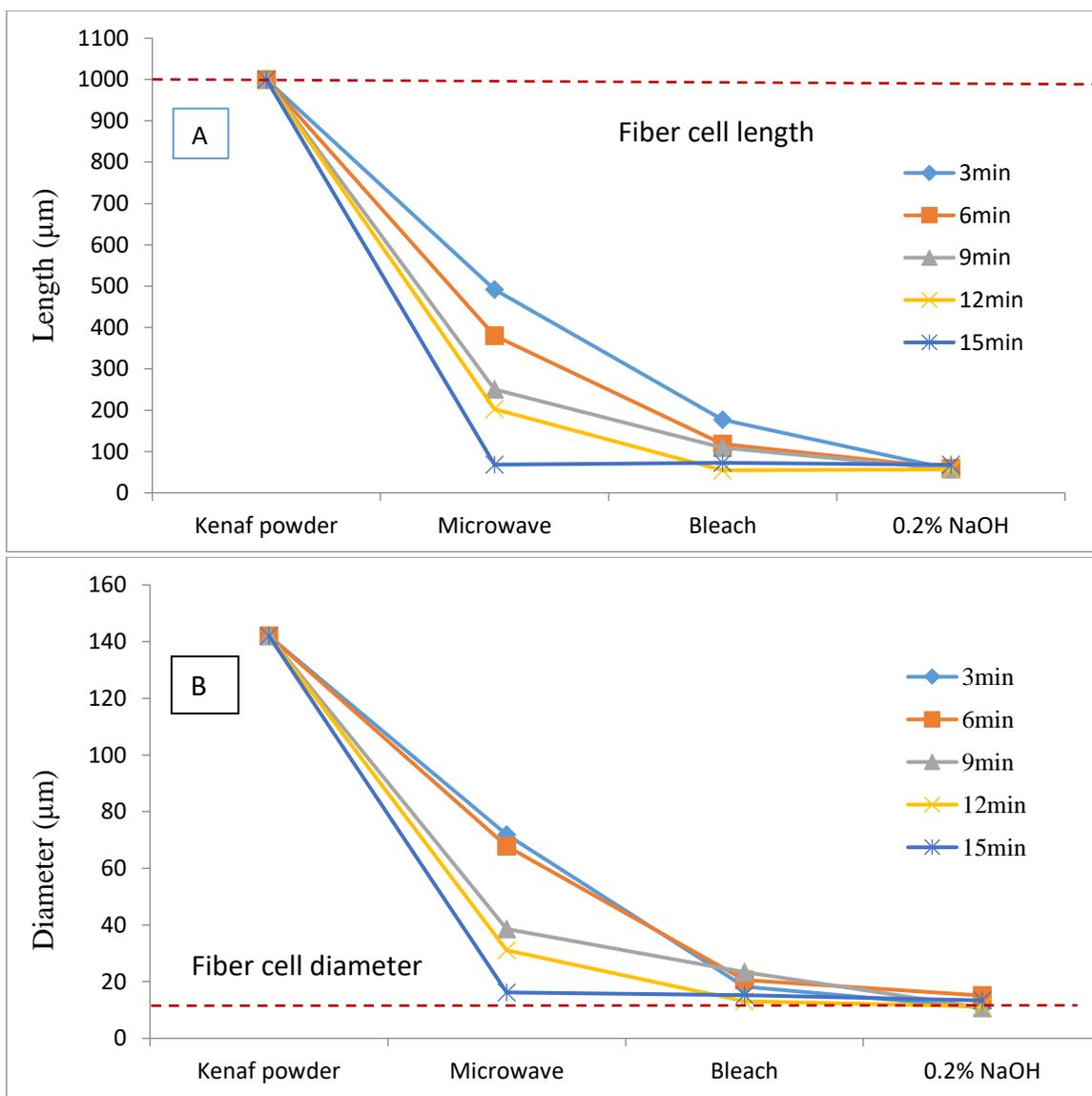


Fig. 3. The changes in length (A) and diameter (B) of the kenaf particles

SEM Analysis of Kenaf Cellulose Microfiber and Nanofiber

SEM images of kenaf cellulose microfiber were captured after the 0.2% NaOH treatment (Fig. 4A). The cellulose microfibrils had a diameter range of about 8 μm to 13 μm and a length range of 30 μm to 100 μm . Some longer and shorter fibers were also observed, but the variation in diameter was relatively small. Again, the observed diameter was comparable with the average diameter of a single kenaf fiber cell (10.6 μm , Table 1), confirming that the kenaf microfibrils obtained after the microwave-chemical treatment were single fiber cells. Figure 4B illustrates a cross section of a cellulose microfiber. The

microfiber was composed of cell walls and a cell lumen, which is the same structure as that of a fiber cell. The results verified the above conclusion.

Nanocellulose images were collected after the ultrasonic treatment (Fig. 5). The nanofibers had a length range of 400 nm to 1500 nm and a diameter range of 33 nm to 100 nm. The results demonstrate that the ultrasonic treatment was able to further destruct the microfibrils obtained by the microwave-chemical treatment and successfully produce nanocellulose. The nanocellulose was also confirmed by the TEM image shown in Fig. 6. The microwave treatment coupled with chemical treatment was able to reduce kenaf samples to micro-scale size, and the ultrasonic treatment could reduce micro-size samples to nano-size.

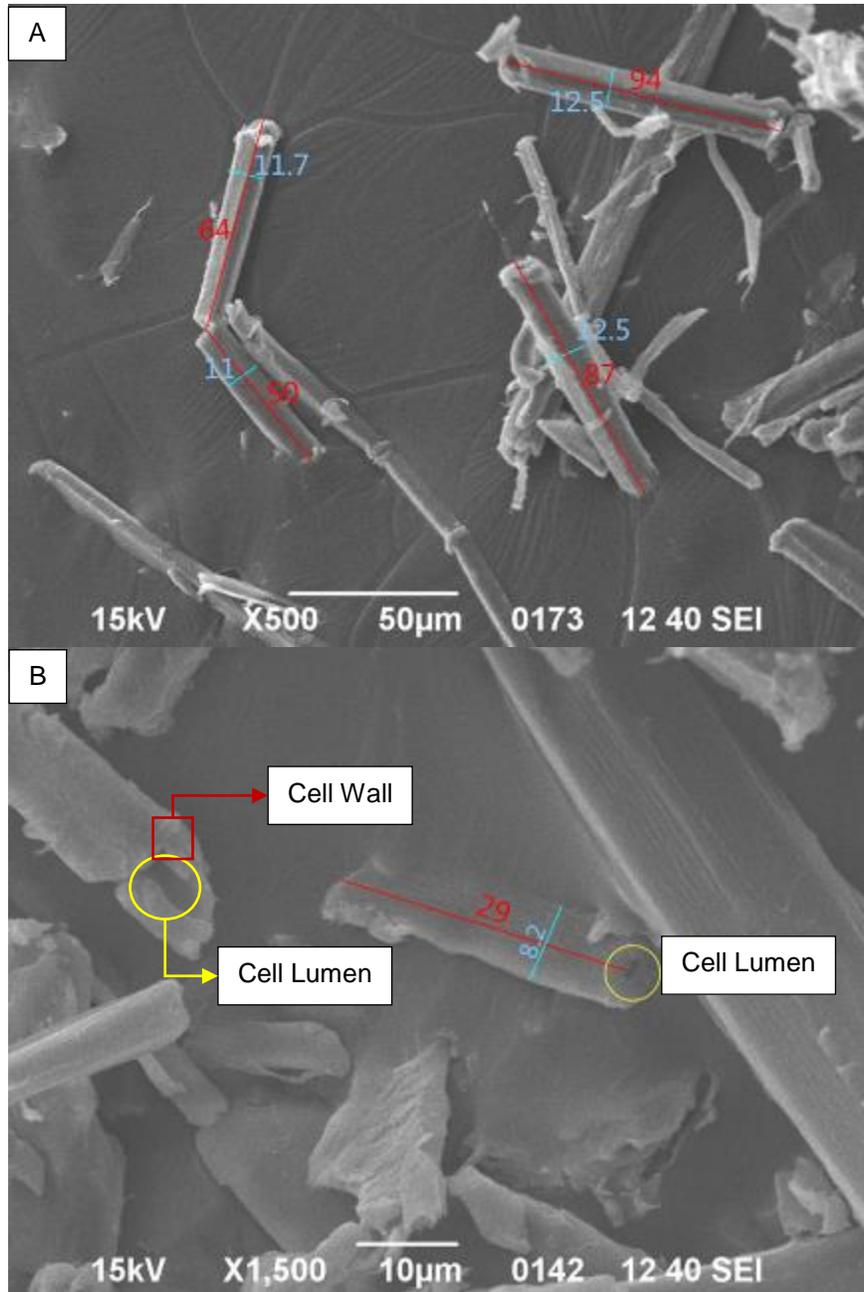


Fig. 4. SEM images of cellulose microfibril after 0.2% NaOH treatment

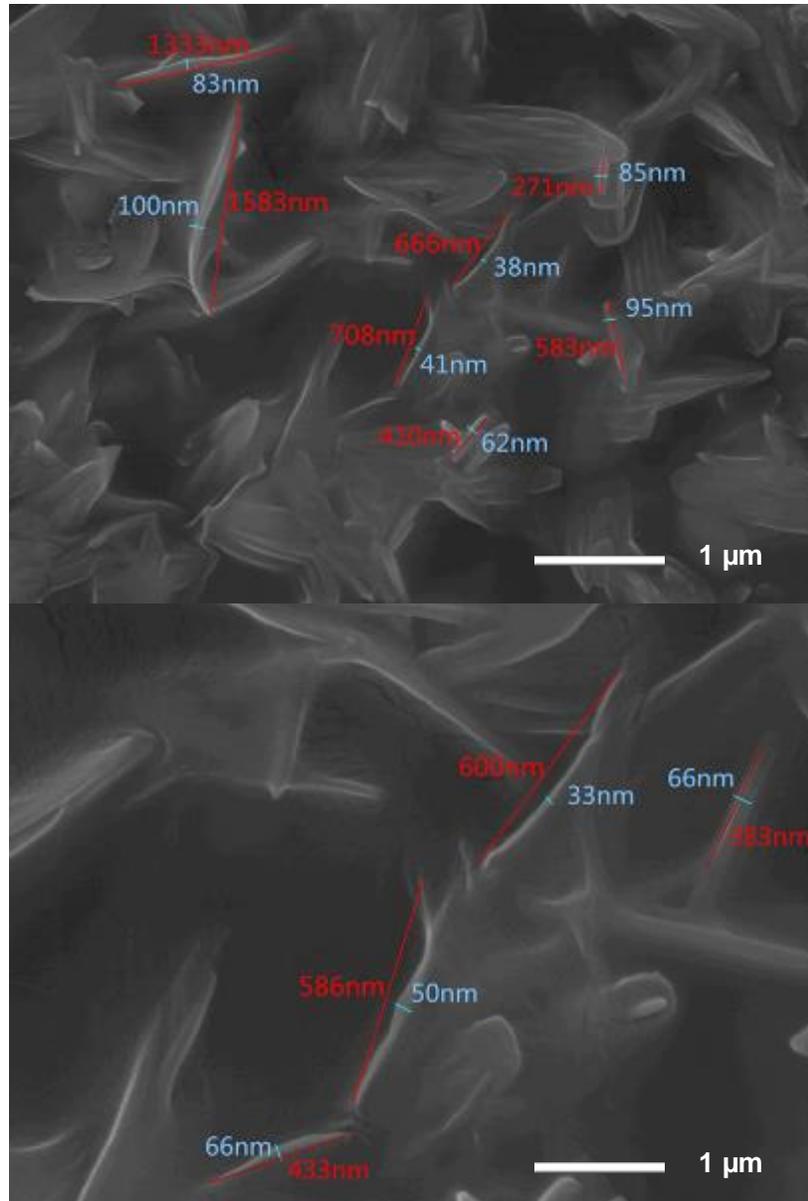


Fig. 5. SEM images of nanocellulose after the ultrasonic treatment

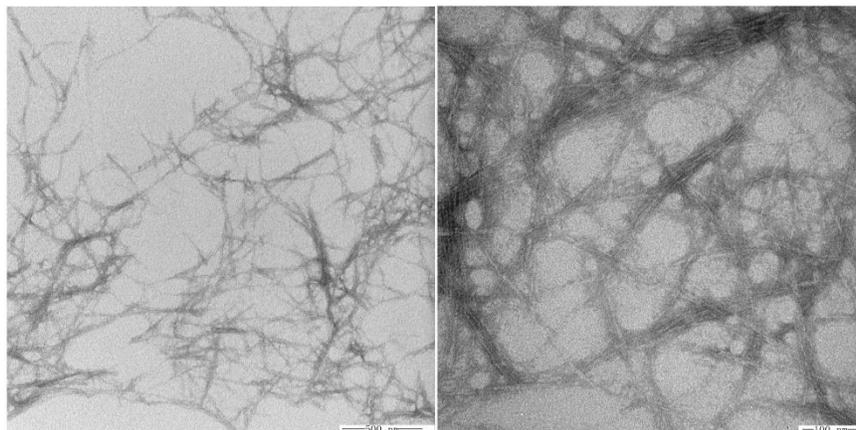


Fig. 6. TEM images of nanocellulose after the ultrasonic treatment

There are several types of nanocellulose, which can be obtained by different production methods and which have different dimensional size of the final product. These types include nano-fibrillated cellulose (NFC), nanocrystalline cellulose (NCC), nano-fibrils (NF); micro-fibrils (MF), *etc.* The prepared nanocellulose in this study showed a nano-size in diameter (<100 nm), but this is too big to be regarded as nanocrystalline cellulose. Based on the electron micrographic images (TEM, SEM) the product that was obtained in this work by using microwave following by the alkaline hydrolysis and ultrasonic treatment can be regarded as nanofibrillated cellulose.

CONCLUSIONS

1. Nanofibrillated cellulose was obtained from kenaf with a combination of microwave, chemical, and ultrasonic treatments.
2. Change in fiber size was monitored throughout the study. The microwave treatment noticeably reduced the particle size of kenaf samples. After 15 min of microwave treatment, the kenaf powder was directly broken down to micro-scale size. The concentration of NaOH had little effect on the reduction of the size of kenaf particles.
3. The combined microwave and chemical treatment was able to break down the kenaf fibers to micro-scale particles, and nano-size fibers were obtained by final ultrasonic treatment.

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