



Extraction, characterization, and improvement of banana stem and water hyacinth cellulose fibers as reinforcement in cementitious composites

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Abstract

A sequential treatment for cellulose isolation from the banana stalk (BNSF) and water hyacinth (WHCF) based on the simultaneous fractionation of hemicelluloses and lignin by alkaline peroxide extraction has been studied. The crude cellulose was then purified by using an acetic acid-nitric acid mixture and further bleached with acidified sodium chlorite. The isolated cellulose was subject to analyses of associated hemicelluloses and lignin content. The structural changes between crude and purified celluloses were revealed by using FT-IR, TGA, and XRD analyses. The successive alkaline and bleaching treatments led to a significant loss in hemicelluloses and lignin, enrichment of the cellulose fraction, and increase in cellulose crystallinity but led to 3.1% to 5.4% degradation of the original cellulose. The crystallinity index of isolated cellulose was found to be increased from 38% to 90% for WHCF and 62% to 95% for BNSF. The cement composite with purified WHCF and BNSF exhibited comparable flexural strength to pure cement. The results showed that the flexural strength of the composites with 2.33 wt% of α -WHCF, 2.33 wt% of α -BNSF, and without fibers was 13.89 10.65 and 8.65 MPa, respectively. In other words, the flexural strength of the composite with α -WHCF was improved by 125%.

1. Introduction

The recent growing environmental awareness has triggered the research attitude of researchers toward developing bio-degradable products [1]. Natural fibers are eco-friendly and little energy is needed for the production of fibers. Nowadays, the level of production of cellulosic fibers does not fulfill the growing industrial demands. That is why, during the past few decades, there has been increasing interest in the use of natural fibers as reinforcements in cementitious materials that are used in construction [2-17]. This has been due largely to its high availability at a relatively low cost when compared to other synthetic fibers, encouraging its use in several applications. They can be easily found in nature and agricultural wastes that currently have limited economic value [18].

One of the solutions found for the valorization of natural fibers is its use in Portland cement composites. Several papers reported the benefits of using natural fibers such as interesting mechanical and physical properties [19], reduction in the thermoacoustic transfer [20], low specific weight, and reduction in the cost of production [21,22]. However, the alkaline cement attacks the lignin in the natural fibers. This causes significant degradation in the composite strength [23]. The other main problem is fiber mineralization due to the migration of hydrated products of Portland cement to the central cavities, walls, and voids of the fibers due to their high water absorption thus causing their weakening [24].

To diminish these problems, recently much work has been done on pretreatment to extract cellulose. The majority of cellulosic pulps used to reinforce cement-based materials are provided from crop plant resources and are obtained chemically. For instance, experienced researchers in cement composites, such as Savastano and co-workers have successfully used banana pulps [25-28] obtained from chemical and thermo-mechanical treatment with percentages in the range of 4 wt% to 8 wt% to reinforced Portland cement matrices. Another important source of pulp fibers used to reinforce composites is water hyacinth [29-31]. Water hyacinth is very abundant and cheap source of fibers. Sisal [28,32] pinus pulp [25,33,34] cotton linters [35] and agricultural waste [36] have been also successfully used to prepare cement-based composites. Nevertheless, little has been done about the sequential extraction to produce high quality cellulose fiber. These may increase the accessibility of cellulose using mild treatment. Furthermore, banana and water hyacinth fibers were used for the production of cellulose fibrils, which at present is an agricultural waste and has a higher economic value compared to the existing use. Although it has often been suggested in the scientific literature that natural fibers provide poor reinforcement for building products compared to glass, steel, and synthetic organic fibers, this is not always the case. Therefore, in this study, banana stalk and water hyacinth were treated with sequential extraction treatment and followed by bleaching treatment to maximize the removal of hemicelluloses and lignin with less degradation of cellulose. The developed technique

can be employed also for the preparation of high quality cellulose fibers of other natural fibers based on fruit, seed, and leaf. The novelty of the proposed technique is that we can produce high quality cellulose fibers by applying simple laboratory techniques.

2. Experimental

2.1 Materials

Banana stalk and Water hyacinth from Ayuttaya province (Thailand) were used in this work. Analytical grades of acetic acid, toluene, and sulfuric acid (Merck Chemicals), sodium hydroxide pellets, sodium chlorite, and sodium bicarbonate (Sigma Aldrich Chemicals) were used.

2.2 Method

2.2.1 Banana stalk and water hyacinth fiber extraction

Banana and water hyacinth fibers were extracted from stems and trunks by a mechanical retting machine. The separated fiber strands were washed thoroughly using water and then sun dried for one week to ensure maximum moisture removal. Finally, the fibers were then kept in a hot air oven for 24 h at 80°C to remove moisture. The dried fiber was milled in a grinding machine and screened to obtain a fiber dimension of about 3 mm to 5 mm in size.

2.2.2 Cellulose isolation

The following experimental procedure was based on the work of Sun and Sun [37] and Sun *et al* [38].

Procedure 1

Sequential treatment was performed to reduce the content of non-cellulosic compounds that cement the fiber aggregates. The method adopted includes preconditioning, alkaline treatment, bleaching, and acidic treatment. The preconditioning process was used before cellulose extraction with a 2:1 (v/v) mixture of toluene and ethanol for 6 h, followed by washing with ethanol for 30 min

and air drying to eliminate water-soluble polymers and waxes. The fibers were then chemically treated to remove lignin and hemicelluloses to improve fiber surface roughness and compatibility when composite material was formed. (I) Alkali treatment induced such modification where fibers were immersed in 0.1 M NaOH in 50% volume of ethanol for 3 h at 45°C under continuous agitation. Furthermore, (II) successive bleaching process using hydrogen peroxide at pH = 11.5 (buffer solution) and 45°C: (a) 0.5% H₂O₂, (b) 1.0% H₂O₂, (c) 2.0% H₂O₂ and (d) 3.0% H₂O₂ for 3 h each one under continuous agitation were performed. Then, (III) hemicelluloses were removed by hydrolysis using a mixture of 10% w/v NaOH and 1% w/v Na₂B₄O₇·10H₂O at 28°C for 15 h, under continuous agitation. Then, (IV) acid hydrolysis was performed using 70% HNO₃ and 80% CH₃COOH, (1/10 v/v) as a catalyst for 15 min at 120°C.

Procedure 2

The bleaching was performed to remove the remaining lignin through treating with 0.7% (w/v) NaClO at pH 4 to 4.2 in acetic acid-sodium acetate buffer (fiber to liquor ratio 1:10) and stirred at 80°C for 2 h. The sample was filtered and the obtained solid was washed with distilled water, the residue was dried at 105°C. Then, hemicelluloses were removed by hydrolysis 3 g of obtained solid using 75 mL of 17.5% NaOH. The slurry was left for 35 min and 75 mL of distilled water was added and stirred for a few minutes. After being filtered and washed with distilled water until neutralization.

Table 1 showed the variation of the fiber treatment process prepared for the analyses in the current study. Untreated banana and water hyacinth fibers were given notation BNSF and WHCF, respectively. The nomenclature adopted for the different treatments is X-Y, where X is related to the fiber type (BNSF for banana stem fiber and WHCF for water hyacinth fiber) and Y is associated with the step of treatment: IIb for *Procedure 1-IIb*, III for *Procedure 1-III* and IV for *Procedure 1-IV*. Another samples used in this study, in order to assess the effectiveness of banana and water hyacinth fibers, is called α-BNSF-Y and α-WHCF-Y, respectively. In this case, the fiber obtained after completion of the selected chemical treatments (*Procedure 1-IIb*, *Procedure 1-III* and *Procedure 1-IV*) was bleached with 0.7% (w/v) NaClO and 17.5% NaOH.

Table 1. Notation and summarized treatment on banana stalk and water hyacinth by preconditioning, alkaline treatment and bleaching to isolate cellulose.

Notation		Treatment
Without treatment	BNSF	Untreated banana stalk fiber
Pretreatment and alkaline treatment	BNSF-PA	N-BNSF extracted with 2:1 (v/v) mixture of toluene and ethanol and treated with 0.1 M NaOH in 50% volume of ethanol
Bleaching I	BNSF IIb	PA bleaching with 0.5% H ₂ O ₂ and 1.0% H ₂ O ₂ ,
Bleaching II	BNSF III	BNSF IIb treated with 2% and 3.0% H ₂ O ₂ then with 10% w/v NaOH-1% (w/v) Na ₂ B ₄ O ₇ ·10 H ₂ O
Acid hydrolysis	BNSF IV	BNSF III treated with 70% HNO ₃ – 80% CH ₃ COOH (1/10 v/v)
Bleaching III	α-BNSF III	BNSF III treated with 0.7% (w/v) NaClO and 17.5% NaOH
	α-BNSF IV	BNSF IV treated with 0.7% (w/v) NaClO and 17.5% NaOH
Without treatment	WHCF	Untreated water hyacinth fiber
Pretreatment and alkaline treatment	WHCF-PA	N-WHCF extracted with 2:1 (v/v) mixture of toluene and ethanol and treated with 0.1 M NaOH in 50% volume of ethanol
Bleaching I	WHCF IIb	PA bleached with 0.5% H ₂ O ₂ and 1.0% H ₂ O ₂ ,
Bleaching II	WHCF III	WHCF IIb bleached treated with 2% and 3.0% H ₂ O ₂ then with 10% w/v NaOH-1% (w/v) Na ₂ B ₄ O ₇ ·10 H ₂ O
Acid hydrolysis	WHCF IV	WHCF III treated with 70% HNO ₃ – 80% CH ₃ COOH (1/10 v/v)
Bleaching III	α-WHCF IIb	WHCF IIb treated with 0.7% (w/v) NaClO and 17.5% NaOH
	α-WHCF III	WHCF III treated with 0.7% (w/v) NaClO and 17.5% NaOH

2.3 Characterization

2.3.1 Chemical composition

Chemical compositions of the untreated and treated banana and water hyacinth fibers were determined according to the following Technical Association of the Pulp and Paper Industry (TAPPI) procedures: extractives (TAPPI T264 cm-07), α -cellulose (TAPPI T203 cm-99), and lignin (TAPPI UM 250). Hemicelluloses content was determined using a common process. [39-41]

2.3.2 Scanning electron microscopy (SEM) analysis

Scanning electron micrographs of virgin and treated fibers were captured using Thermo scientific, Prisma. Before SEM analysis, the samples were coated with gold using the sputtering technique to make them conductive. All images were taken at an accelerating voltage of 20 kV.

2.3.3 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy studies on untreated and treated fibers were carried out using FTIR spectrophotometer (IR Prestige, Shimadzu). All the spectra were recorded with a scan rate of 32 scans per minute at a resolution of 4 cm^{-1} in the wavenumber region of 4000 cm^{-1} to 500 cm^{-1} at the atmospheric condition. The transmittance curve of FTIR was used to assess the microstructure of the natural fibers.

2.3.4 X-ray diffraction analysis (XRD)

Wide-angle X-ray diffractograms of untreated and treated fibers were recorded on a Rigaku SmartLab X-ray diffractometer. The system has a rotating anode generator with a copper target and a wide-angle powder goniometer. The generator was operated at 40 kV and 40 mA and the samples were scanned in the 2θ range of 5° to 90° at the rate of 3° min^{-1} .

The Crystallinity Index (CrI) of untreated and treated fibers was examined by using the XRD technique compatible with the computerized data acquisition facility. The CrI [42] of the fibers was calculated using equation (1):

$$CrI (\%) = \frac{(I_{002} - I_{am})}{I_{am}} \times 100 \quad (1)$$

Where I_{am} represents the low-intensity peak (110) which contributes amorphous fraction and the high-intensity peak (002) I_{002} , which contributes crystalline fraction.

The crystallite size (CS) of the fibers was calculated for untreated and treated fibers for the crystallographic plane (002) by using Scherer's formula expressed in equation (2) [43].

$$CS = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

Where K is the Scherrer constant (0.84), λ is the X-ray wavelength (0.154 nm), and θ is the Bragg

2.3.5 Thermogravimetric analysis (TGA)

Thermograms of untreated and treated fibers were recorded using a NETZSCH STA 449 F3 Thermal Analysis System for thermogravimetric analysis (TGA). Samples of approximately 5 mg were placed in a ceramic crucible and heated from room temperature to 700°C at $5^\circ\text{C}\cdot\text{min}^{-1}$. Purified nitrogen (99.9995%) at a flow rate of $100\text{ mL}\cdot\text{min}^{-1}$ was used as the carrier gas to provide an inert atmosphere and to remove the gaseous and condensable products, thus minimizing any secondary vapor-phase interactions.

2.3.6 Flexural strength of fiber-cement composite

The flexural strength of fiber-cement composites was also measured under a three-point bend. They were performed on three specimens for each series of composites, with dimensions of $10\text{ mm} \times 77\text{ mm} \times 200\text{ mm}$. The specimens were loaded continuously to failure at a stress rate of $0.1\text{ mm}\cdot\text{min}^{-1}$. The tests were carried out in an Instron (model 1185) servo hydraulic testing machine equipped with a 5 kN load cell.

3. Results and discussion

3.1 Physical properties of the untreated and treated banana stalk and water hyacinth

The physical appearance of the fiber

Figure 1 depicted different color of the banana and water hyacinth fibers after sequential treatment. During extraction, the mass of fibers was reduced. As reported by Thiripura and Ramesh [44], the extraction process could remove extractive compounds contained in the stalks of water hyacinth and banana except for lignin, cellulose, and hemicelluloses. The resulted fractions of WHCF IIB and BNSF IIB from successive treatment with 0.5% and 1% H_2O_2 had the darkest brown color (Figure 1(a)), indicating other impurities such as lignin and hemicelluloses in the fiber have not been removed yet, while it slightly changed into dark brown which was lighter than the untreated fiber. After the WHCF IIB and BNSF IIB was further successive treated with 2% and 3% H_2O_2 , alkaline treatment and acid hydrolysis could further remove lignin by breaking the ether bonds and increased the whiteness degree of fibers (Figure 1(b) and Figure 1(c)). Alkaline treatment was performed by cutting the chain to separate hemicelluloses from the main chain, namely cellulose. In addition, reaction with NaOH solution will also cause degradation of lignin molecules due to the termination of aryl-ether bonds, carbon-carbon, aryl-aryl, and alkali-alkali [45]. Bleaching III using NaClO (α -BNSF III and α -WHC IIB) (Figure 1d) was performed to remove the remaining lignin and hemicellulose. Hence, the lighter color of the fiber demonstrates that more lignin and hemicellulose were oxidized and removed during the treatment.

Phase analysis

XRD studies of the untreated and treated BNSF and WHCF were carried out to investigate the fibers crystalline behavior of the fibers. The XRD pattern of the untreated and treated BNSF and WHCF

fibers are shown in Figure 2. The diffractograms of the fibers reveal two main reflections, corresponding to 2θ values of around 16° and 22° , respectively. The low-intensity peak (110), which contributes amorphous fraction (I_{am}), occurs at 2θ closer to 17.8° . It indicates the presence of amorphous materials in the fibers. The high-intensity peak (002), which contributes crystalline fraction (I_{002}), occurs at around $2\theta = 22.59^\circ$ and it indicates the content of α -cellulose in fibers. Figure 2 shows that the intensities of (002) and (110) crystallographic planes of both fibers are increased significantly as the fibers are treated under different processing conditions. The sharp peak in the X-ray diffraction pattern of final fiber (α -WHCF III and α -BNSF IV) obtained after Bleaching III exhibits a higher crystallinity due to the more efficient removal of non-cellulosic polysaccharides and dissolution of amorphous zones. The CrI of both α -WHCF III and α -BNSF IV is found to be 99%, which is higher than the untreated (77% for BNSF and 83% WHCF) fibers and is calculated by using equation (1). Thus, the above results demonstrate that successive treatment took place

preferentially in the amorphous region and the rearrangement of the crystalline regions in such a way that the fibers exhibited a more crystalline nature after treatment [46]. This is in conformity with the results of chemical analyses, as well as FTIR studies.

CS value of BNSF, BNSF IIb, BNSF III, BNSF IV, α -BNSF III, and α -BNSF IV fibers is found to be 18.8, 16.1, 22.0, and 27.0 Å, respectively. While the CS of water hyacinth fibers keeps changing from 70.0 Å for untreated, to 61.0 Å for WHCF IIb, to 35.9 Å for WHCF III, to 18.0 Å for WHCF IV, until 42.0 Å for α -WHCF IIb, and 33.0 Å for α -WHCF III. This is happened due to the removal of cementing materials from the natural fiber. The reduction in CS means an increase in the fiber aspect ratio which has a direct benefit to the improvement of the composite properties [47]. With the higher crystalline size, the structure tends to reduce the moisture absorption capacity and chemical reactivity of the fibers and it enhances the mechanical properties of the fibers [48].

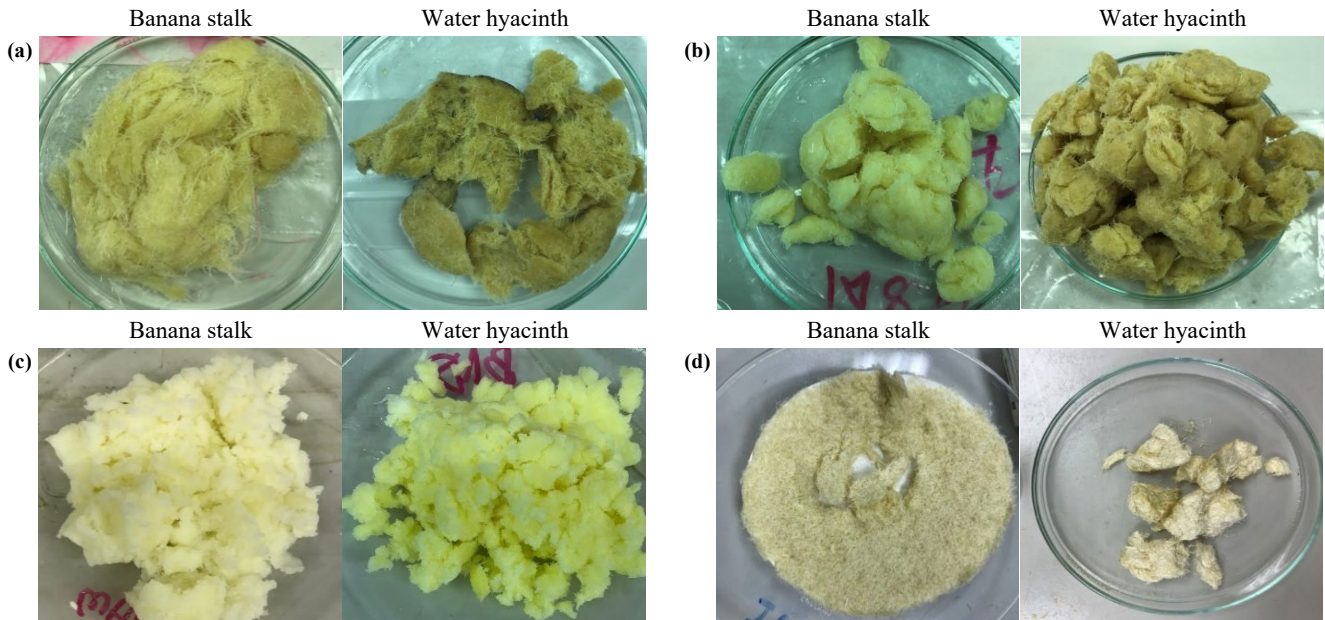


Figure 1. Isolation process result obtained by successive extraction of the 0.1 M NaOH treated by (a) Bleaching I (b) Bleaching II (c) Acid hydrolysis and (d) Bleaching III.

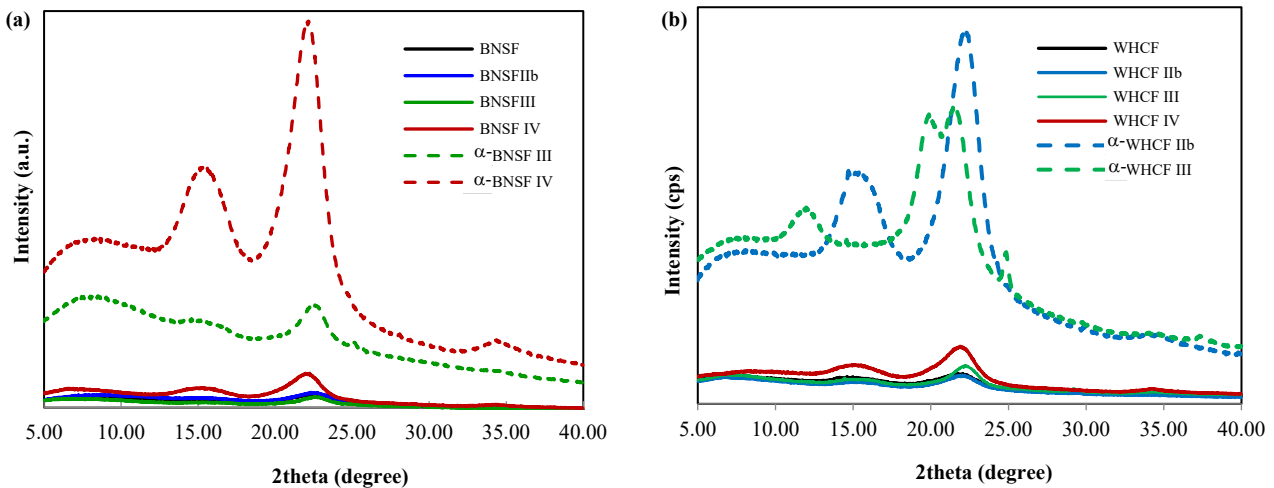


Figure 2. XRD patterns of untreated and treated (a) BNSF and (b) WHCF obtained from different stages of the cellulose extraction process.

Scanning electron microscopy (SEM)

The effect of sequential treatment on the morphology of BNSF and WHCF fibers was obtained from SEM studies. Figure 3 and Figure 4 show the SEM images of untreated and treated BNSF and WHCF. Both untreated BNSF and WHCF fibers are glued with lignin and hemicelluloses which cause all the fibrils associated with bundles. Impurities could be seen deposited on the fiber surface. The surface of the fiber is found to be smooth due to the presence of waxes and oil (Figure 3(a) and 4(a)).

Due to the alkali treatments performed on the raw BNSF or WHCF, the fibril surface is exposed, making hemicelluloses and lignin accessible to chemical treatment, and also surface impurities were removed. The treatments aided in breaking down the lignocellulosic components and solubilized the lignin and hemicelluloses to expose the hidden cellulose. During Bleaching I and II, the hemicelluloses

are hydrolyzed and become water soluble. The lignin gets depolymerized. As a result, defibrillation of the fiber occurs because of the removal of the cementing materials which can be seen from the SEM images (Figure 3(b-c) and c and Figure 4(b-c)).

Acid treatment after the bleaching process helps to disintegrate the fibrils further. Figure 3(d) and Figure 4(d) show the SEM photographs of the individualized microfibrils after acid treatment. It can be seen from the SEM that the size of both BNSF and WHCF fibers is reduced from several meters to less than 10 mm. Thus, acid treatment helps in defibrillating the fiber diameter to micron range. Bleaching III helps to further remove the remaining lignin present in the fibers, which helps in further defibrillation. Sodium hypochlorite and sodium acetate buffer allow the removal of lignin. Lignin is rapidly oxidized by chlorine. Lignin oxidation leads to lignin degradation and leads to the formation of hydroxyl, carbonyl, and carboxylic groups, which facilitate lignin solubilization in an alkaline medium (data not shown).

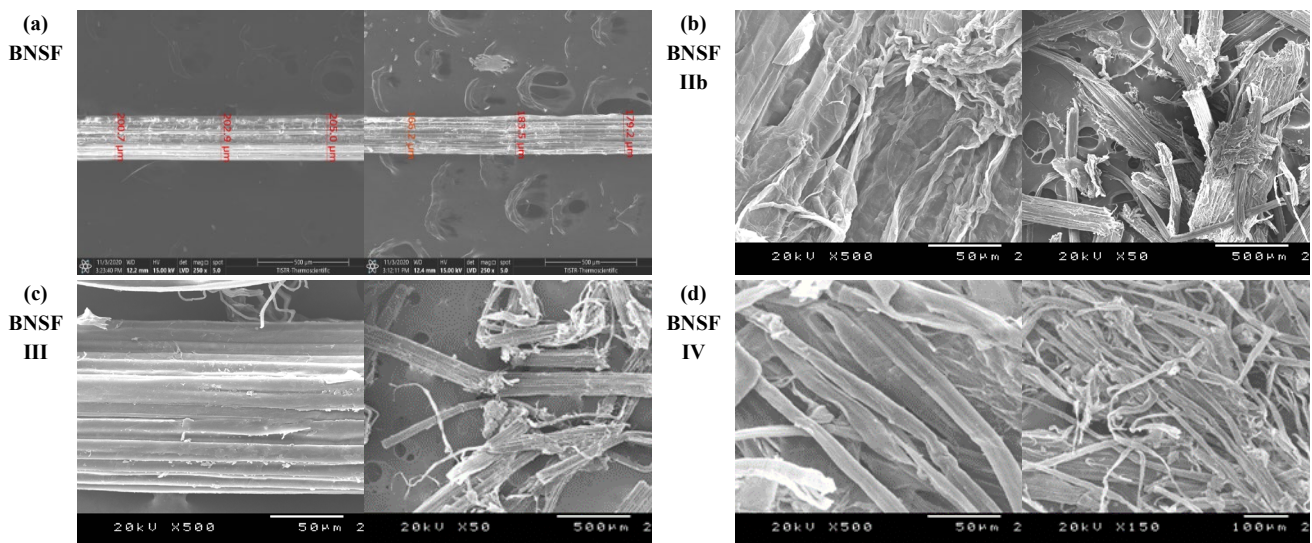


Figure 3. SEM images of BNSF fraction obtained from different stages of the cellulose extraction process (a) untreated, (b) Bleaching I, (c) Bleaching II, and (d) Acid hydrolysis.

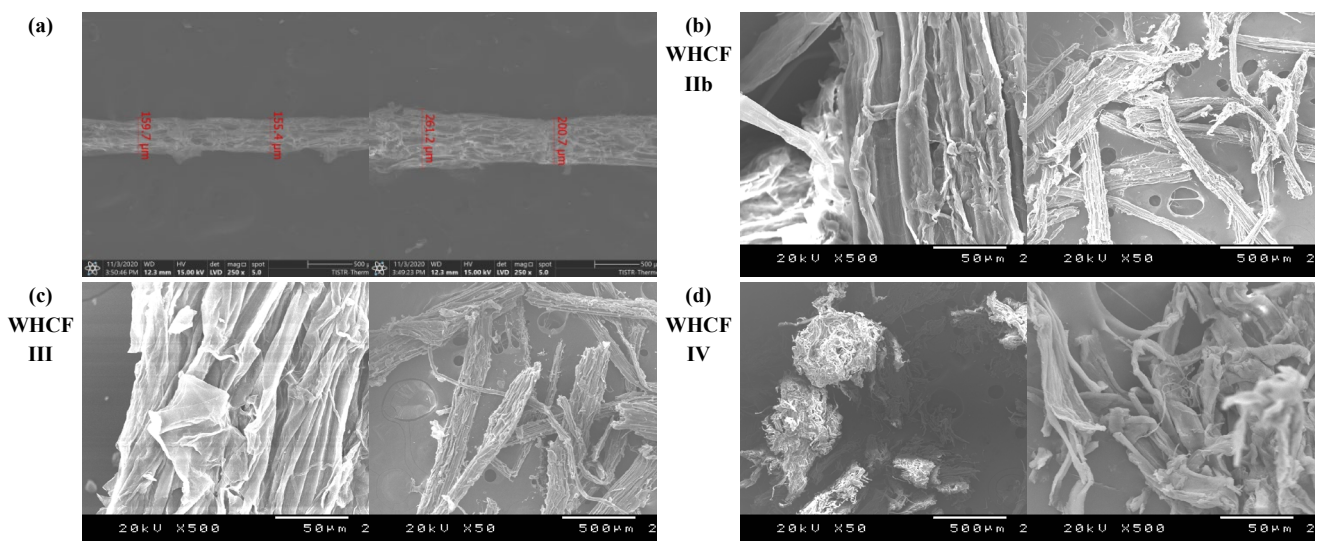


Figure 4. SEM images of WHCF fraction obtained from different stages of the cellulose extraction process (a) untreated, (b) bleaching I, (c) bleaching II, and (d) acid hydrolysis.

3.2 Chemical composition of the untreated and treated banana stalk and water hyacinth

Chemical composition of the fiber

The major botanical components are presented in Table 2. The obtained data show that the untreated fibers contained 55.14% cellulose and 14.41% lignin for BNSF and 58.71% cellulose and 5.24% lignin for WHCF. The extractive contents, acetone and hot water, of banana and water hyacinth were 4.44% and 3.36%, respectively. The cellulose content of 55.14% and 58.71% was an indication of an average but tolerable yield. The values of the extractives were relatively low. The lignin content of banana was higher than water hyacinth suggesting higher chemical consumption of liquor during chemical treatment.

After Bleaching I, the fibers had α -cellulose and hemicelluloses as 51.62% and 33.80% respectively for banana stalk and 54.49% and 42.96% for water hyacinth. When Bleaching I fibers (BNSF IIb) undergo the Bleaching II process, we can see that there is a further decrease in the percentage of hemicelluloses as well as an increase in the percentage of the α -cellulose component present in the fiber (BNSF III). However, unlike to the BNSF, yield of hemicelluloses and holocellulose of WHCF III slightly dissolved. The yield of α -cellulose decreased from 54.49% to 43.18% obtained by this Bleaching II procedure for WHCF III. Lower yield of purified cellulose revealed that more severe treatment conditions with 2% and 3% H₂O₂ and 10% w/v NaOH-1% (w/v) Na₂B₄O₇·10 H₂O, used in this study, did do damage to the cellulose, although it is more reactive toward lignin and hemicellulose than toward the carbohydrates. Similar observations have been reported by Singh [49]. In addition, the structural differences (Hard-soft structure) between WHCF and BNSF lead to differences in the breaking of glycosidic bonds.

From Bleaching II fiber to acid hydrolyzed fiber, there is an increase in the percentage of α -cellulose (74.43% for BNSF IV and 71.56% for WHCF IV). Therefore, the reinforcement ability of these fibers is expected to be much higher than other fibers, which have less percentage of cellulose content, which formed a microcrystalline structure with high order crystalline regions and low order amorphous regions [50].

These characteristics have been proved in the following section of XRD analysis. As we go from raw fiber to the final fiber, we can see that there is a decrease in the percentage of hemicelluloses content. This proves that the sequential treatment diminishes the intermolecular binding possibilities, which in turn leads to an increase in the solubility of hemicelluloses content.

3.3 FTIR analysis

The FTIR spectra of four fractions of Banana and four distinct fraction water hyacinth fibers in various forms shown in Figure 5 and Figure 6, showed the characteristic peak expected for cellulose, hemicelluloses, and lignin moieties. In particular, the bands at 3271 cm⁻¹ due to the O-H stretch vibration of the intermolecular hydrogen bonding associated with cellulose fibers [51]. This band became sharp and intense after bleaching and further on acid hydrolysis of the fiber and it appears at 3271 cm⁻¹. This is due to the increase in the crystallinity in the fibers, showing the increase in the percentage of cellulose components. Also, the intensity has been attributed to the removal of impurities from the surface of the fibers by sequential extraction thus exposing the more reactive -OH group.

The results of the IR spectrum of banana and water hyacinth display peaks at a wavelength of 1765 cm⁻¹ to 1700 cm⁻¹, which indicates the presence of acetyl and ester in carboxyl group chain of the acid p-coumeric acids as well as indicating the presence of lignin and hemicellulose. This result is in agreement with previous work presented by Thiripura and Ramesh [44]. There are also peaks at a wavelength of 1600 cm⁻¹ to 1500 cm⁻¹, which indicates the presence of the C=C group on the aromatic ring of lignin. Hemicelluloses are seen from the presence of the peak at a wavelength of 1620 cm⁻¹ and 1273 cm⁻¹.

During sequential extraction process, the intensity peaks at 1707 cm⁻¹, 1620 cm⁻¹, and 1598 cm⁻¹ are reduced from raw to the final fiber. It clearly indicates the less percentage content of hemicelluloses lignin and hydroxyl groups, which are advantageous, because higher contents will affect the mechanical properties of the fibers. This supports the chemical analysis data as shown in Table 1.

Table 2. Physical properties and chemical composition of untreated and treated cellulose fibers from BNSF and WHCF.

Fiber type		Chemical composition					Physical properties	
		α -Cellulose ^a (wt%)	Holocellulose ^b (wt%)	Hemicellulose ^c (wt%)	Lignin ^d (wt%)	Extractive ^e (wt%)	Crystallize size ^f (Å)	CrI ^g (%)
Banana	N	55.14	-	-	14.41	4.44	18.8	77
	IIb	51.62	85.43	33.80	-	-	16.1	62
	III	67.66	86.15	18.49	-	-	22.0	73
	IV	74.43	94.40	19.96	-	-	27.0	96
	α -III	96.00	-	-	-	-	21.0	84
	α -IV	100.00	-	-	-	-	27.0	99
Water hyacinth	N	58.71	-	-	5.24	3.36	70.0	83
	IIb	54.49	87.31	42.96	-	-	61.0	88
	III	43.18	85.42	42.24	-	-	35.9	80
	IV	71.56	92.90	21.34	-	-	18.0	90
	α -IIb	96.00	-	-	-	-	42.0	97
	α -III	98.00	-	-	-	-	33.0	99

^a Based on TAPPI T203 cm-99

^b Based on the chlorination method.

^c Calculated by the difference between holocellulose and α -cellulose quantities.

^d Based on TAPPI UM 250 and TAPPI T222 om-11

^e Based on TAPPI T264 cm-07

^f Crystallinity index, % CrI = (I₀₀₂-I_{am}) × 100/ I_{am}

^g Crystallite size, CS = Kλ/βcosθ

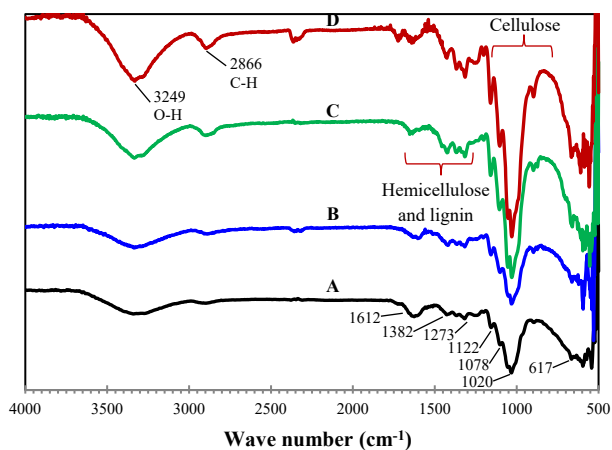


Figure 5. FTIR spectra of BNSF fraction obtained from different stages of the cellulose extraction process (a) bleaching I, (b) bleaching II, and (c) acid hydrolysis.

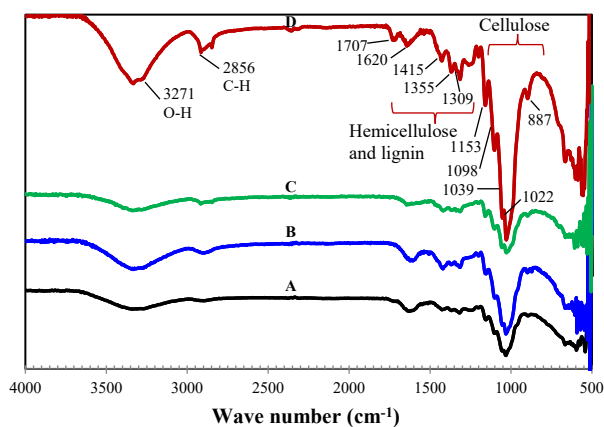


Figure 6. FTIR spectra of WHCF fraction obtained from different stages of the cellulose extraction process: (a) bleaching I, (b) bleaching II, and (c) acid hydrolysis.

3.4 Thermal behavior of treated and untreated banana stalk and water hyacinth

Figure 7 and Figure 8 showed the TGA curves of BNSF and WHCF fibers extracted with 1% H₂O₂, 3% H₂O₂, and 70% HNO₃ and 80% CH₃COOH. All the six thermograms of BNSF and WHCF extracted by Bleaching I (BNSF I Ib and WHCF I Ib), Bleaching II (BNSF II and WHCF II), and acid hydrolysis (BNSF IV and WHCF IV) gave only one main decomposition stage ranging between 250°C and 350°C. It was observed that small weight loss occurred between

25°C to 100°C due to the evaporation of moisture for all the treated fibers. The TGA curves of six fractions extracted with Bleaching I, Bleaching II, and on further acid hydrolysis process started to decompose at 226.1°C (BNSF I Ib), 240.3°C (BNSF II), and 258.0°C (BNSF IV) for treated banana and 210.2°C (WHCF I Ib), 216.6°C (WHCF II), and 236.5°C (WHCF IV) for treated water hyacinth. At 50% weight loss from the decomposition temperature was observed at 300.5°C, 310.2°C, and 329.8°C for BNSF I Ib, BNSF II, and BNSF IV, respectively, and 325.9°C, 329.9°C, and 342.1°C for WHCF I Ib, WHCF II and WHCF IV, respectively.

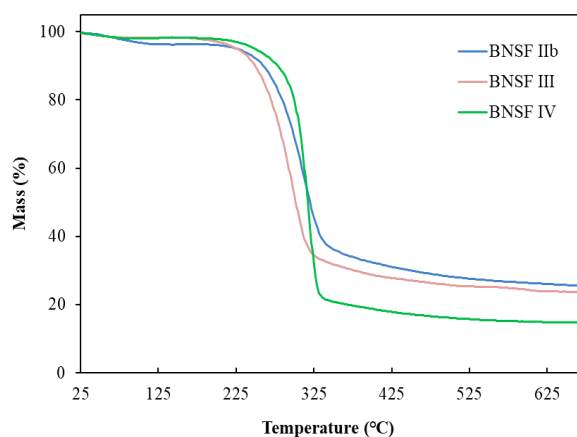


Figure 7. TGA curves of BNSF fraction obtained from different stages of the cellulose extraction process (a) bleaching I, (b) bleaching II, and (c) acid hydrolysis.

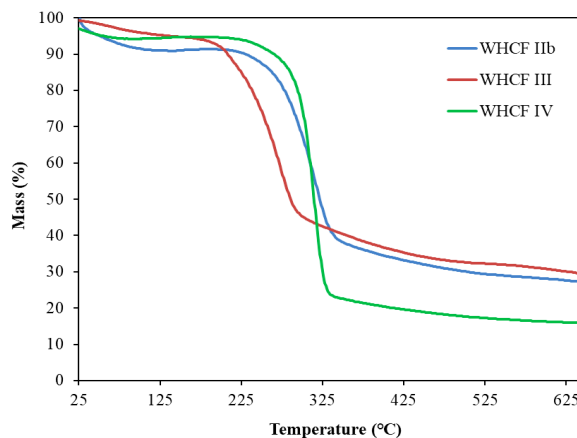


Figure 8. TGA curves of WHCF fraction obtained from different stages of the cellulose extraction process: (a) bleaching I (b) bleaching II, and (c) acid hydrolysis.

Table 3 Thermogravimetric (TG) results for treated BNSF and WHCF fibers.

Fiber	Initial degradation temperature	Temperature for 20% weight loss (°C)	Temperature for 50% weight loss (°C)	Residue (%)
BNSF I Ib	226.1	278.2	300.5	24.95
BNSF II	240.3	298.4	310.2	23.57
BNSF IV	258.0	314.9	329.8	14.66
WHCF I Ib	210.2	278.0	329.9	26.22
WHCF II	216.6	293.0	325.9	28.30
WHCF IV	236.5	317.7	342.1	15.63

Table 4 Three point-bending strength of natural fiber reinforced cement with BNSF and WHCF at different stages of treatment process.

Fiber	Flexural strength (MPa)	Flexural extension (mm)	CrI (%)	α -Cellulose (wt%)	Fiber
Banana	BNSF IIb	9.80 ± 0.93	0.79 ± 0.082	62.7	51.62
	BNSF III	8.50 ± 0.90	0.68 ± 0.080	73.5	67.66
	BNSF IV	9.00 ± 1.08	0.76 ± 0.066	96.3	74.43
	α -BNSF IIb	10.01 ± 0.98	0.76 ± 0.082	97.2	97.41
	α -BNSF III	10.50 ± 1.18	1.03 ± 0.067	98.9	98.72
	α -BNSF IV	10.43 ± 0.58	0.70 ± 0.057	99.5	99.15
Water hyacinth	WHCF IIb	7.09 ± 1.46	0.6 ± 0.150	88.6	54.49
	WHCF III	7.77 ± 1.12	0.48 ± 0.079	80.4	43.18
	WHCF IV	7.01 ± 0.51	0.62 ± 0.130	90.3	71.56
	α -WHCF IIb	10.49 ± 1.05	0.97 ± 0.078	97.6	97.50
	α -WHCF III	12.33 ± 1.76	0.71 ± 0.055	99.4	98.52
	α -WHCF IV	13.89 ± 1.05	1.06 ± 0.078	99.7	99.01
No fiber (control)	-	8.65 ± 1.32	-	-	-
Commercial fiber cement (reference)	-	6.16 ± 1.08	1.00 ± 0.070	-	-

Table 3 listed degradation temperature and percentage residue analyzed from the TG curves. The % char residue of BNSF IV had the lowest percent of residue at 700°C which was 14.66%, showing a low percentage of lignin [52,53]. The same trend occurred in treated WHCF.

Overall, the sequential treatment on both BNSF and WHCF fibers improved their thermal stability, showed by the shifted curves to a higher temperature compared to the initial fiber. Less degradation peaks for treated BNSF and WHCF proved the removal of some components, such as lignin and hemicelluloses, from the fiber during treatment [54]. Further, the results indicate that sequential extraction is an effective condition for bleaching of lignin and diminishing the hemicelluloses making treated BNSF and WHCF fibers can be used as reinforcement.

3.5 Mechanical properties of the composites

The flexural properties are summarized in Table 4. The flexural strength was consistently maintained at the range of 9 MPa for BNSF IIb, BNSF III, and BNSF IV composites and 7 MPa for WHCF IIb, WHCF III, and WHCF IV composites with variation treatment done on the fibers. The flexural strength of the composites made of WHCF and BNSF shows slightly change in comparison with normal concrete mixture without fibers. This was attributed to the poor adhesion between the reinforcement with matrix and this incompatibility was due to the treatments applied to the fibers. However, the change in flexural properties was about (-) 19% to 13%.

The flexural strength of the composites containing α -BNSF and α -WHCF obtained from Bleaching III exhibit between 62% and 125% more than the commercial composite and between 15% and 60% more than unreinforced cement. Bleaching III conducts an increase in the mean value of the composite strength, but the difference is not statistically significant to conclude an enhancement of the strengthening effect of the fibers due to their purity and crystallinity. Strengths slightly increase with increasing crystallinity of fiber in each stage, in the case of α -WHCF composites. The best properties were obtained

from α -WHCF IV composites. For α -BNSF composites, the effects of Bleaching III do not significantly increase the strengths of the composites. The spread of values of flexural extension for such composites tends to be quite large, as shown in Table 4 (0.6 mm to 1.06 mm). The extension of α -WHCF IV composites shows the highest flexural extension which is comparable to that of commercial fiber cement.

In conclusion, it can be stated that the addition of α -BNSF and α -WHCF reinforcement (2.33 wt%) can produce a composite product with flexural strength values of approximately 10 MPa, which is adequate for building applications.

4. Conclusions

In summary, a method for cellulose extraction from natural fibers was developed. Characterization of the synthesized fibrils was done by different techniques. From the chemical examination, the major constituents of these fibers were found to be cellulose. Chemical analysis of obtained BNSF and WHCF after each stage of sequential extraction showed an increase in cellulose content and a decrease in lignin and hemicelluloses content. Successive bleaching helped with cellulose purification. The SEM measurement exposes, during fiber treatment, the morphologies of the compounds and the fibrils change at every stage of each sequential extraction procedure, due to the removal of hemicelluloses and wax contents after treatment. The FTIR studies give evidence for the dissolution and chemical modification that occurred during the additional stage of the sequential extraction process. XRD studies were done to investigate the fiber size and percentage crystallinity of the modified fibers. The XRD studies also revealed that there is a reduction in the size of fibers during the additional stage of the sequential extraction process. The percentage crystallinity of the fibers was also found to be increased from raw fibers, Bleaching I, Bleaching II, acid hydrolysis to Bleaching III process. The XRD studies also reveal that as the additional stage of the sequential extraction process proceeded there was an increase in the percentage crystallinity of the banana and water hyacinth fibers.

The flexural strengths of the composites reinforced with α -BNSF and α -WHCF present differences with plain cement. Maximum tensile strength of 13 MPa was obtained for composites reinforced with 2.33% (weight fraction) of α -WHCF fibers. The value is greater than twice the strength of plain cement. The comparison results confirm that these fibers represent a valid alternative to those as reinforcement in cement composites for building applications.

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