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Abstract

Because of the environmental footprint of oil-based materials, the demand for bio-based renewable materials is hiked. The usage of agricultural waste to extract cellulose, minimized the dependent of hydrocarbon products which is an added value besides due to overpopulation the productivity is increased, which leads to an increase in agricultural waste that causes environmental pollution. In this work, various cellulosic materials, such as cellulosic textile fibers (CTF), microcrystalline cellulosic fibers, and nanocrystalline cellulosic fibers, were extracted from coffee waste to make them into valuable products. The morphological analysis of extracted cellulose is performed by scanning electron microscopy, and the Fourier transform infrared spectroscopy was performed to investigate the structure of extracted cellulose, which indicates the crystalline cellulosic components from the extraction process; X-ray diffractometer analysis shows the extracted cellulose was cellulose I and cellulose II. The cellulose that is extracted by ultrasonication with dimethyl sulfoxide has 88 % of cellulose with a crystallinity index of 74.5 %, and the thermal properties of raw coffee husk and extracted cellulose were compared by thermogravimetric analysis. Additionally, the dye uptake of the CTF shows its potential as a bio-adsorbent in the dye removal domain.

Keywords: Agricultural waste, bio-based material, coffee husk, textile fiber, microcellulose, nano cellulose.

1.Introduction

The need for petroleum-based resources is hiked, however, the resources are ephemeral along with there's a risk of climatic changes leading this petroleum-based industry unsustainable [1]. The agitation of this issue has continuously alarmed awareness leading to increased attention towards sustainable resources [2–4]. Due to rapid population growth, the rising trend of industrialization, and agricultural activities, a huge number of resources like agricultural wastes are generated [5–7]. A substantial amount of organic matter is comprised of agricultural wastes which lead to issues while disposal causes pollution, and destruction of sustainability [8,9]. The use of agricultural wastes that produce biobased materials can be an alternative solution for hydrocarbon-based materials [10–12]. As of now, agricultural wastes are underutilized [13]. Based on the Indian coffee report in 2019, the waste generation during the coffee processing is around 25 million metric tons (MMT) in the world, the waste generation the wet processing alone generates 16 MMT.

The generation of agricultural wastes is huge and extracting cellulose from these wastes and other biomass is the replacement of petroleum-based polymers [14]. One of the ways to ameliorate these conditions is the usage of biowastes shuns the depletion of natural resources. Nascently usage biowastes as a promising source for substitute of these petroleum-based polymers [14].

Coffee is the second globally consumed product after oil [15]. Coffee is an eminent beverage in the world, everyone likes to drink Coffee. During the first 11 months of the year 2020/21(October 2020 - August 2021), coffee exports amounted to 118.96 million bags (i.e., 60 kg of bags), an upsurge of 1.9% compared to the same period of the year 2019/20 [16]. Generally, the coffee bean has been extracted by different methods namely wet processing, dry processing, semi-dry processing, honey processing, anaerobic processing, and carbonic maceration [17,18]. From the above processing methods wet and dry processing are widely practiced around the world. In the dry processing method, about 1.8% of waste coffee husk was generated from fresh coffee fruits [19]. But, in the wet processing method, 40% of waste coffee husk has been produced from the coffee fruit. However, 50% of the world's coffee is produced by the wet processing method [20]. The waste management in wet processing was a challenging one. Coffee husk is one of the coffee processing wastes that account for 29% of total generation. Coffee husk is the first waste by-product during the processing of coffee, and it possesses about 29% of dry weight in the whole fruit [21].

Numerous value-added cellulose fibrous materials can be generated from the natural cellulose that are extracted from these kinds of agricultural waste [22–24]. The cellulose materials extracted from these wastes have adequate compatibility, a high degree of crystallinity, excellent mechanical properties, a large specific surface area, a high aspect ratio, and high thermal stability [25,26]. A massive amount of coffee by-products is disposed of from the coffee industry. They are enriched by carbohydrates, proteins, pectins, bioactive compounds like polyphenols further they are low-priced renewable resources [27]. As it is discussed, the coffee husk is abundant biomass, and it provides promising possibilities to extract the various cellulosic fibrous materials. Hence, this study aimed to isolate and characterize the cellulose fibrous materials from the coffee husk. As the extracted husk has promising possibilities to convert various value-added products like short textile fibers, fillers in the composite materials, and micro/ nano-scale materials such as micro/nanocrystalline cellulose, micro/nano fibrillar cellulose, paper industry, and sorbent materials to remove the hazardous substances, etc.

2. Materials and methods

2.1 Materials

The cellulose fibrous material extraction process was started by collecting the ripened coffee cherry from the agricultural fields in Yercaud, Tamilnadu, India. NaOH, H_2O_2 35% were purchased from Sigma Aldrich, India. All chemicals were of analytical grade and used without further purification. C.I. Reactive red 195 dyes supplied by Colorant dyes company, India.

2.2 Extraction of coffee husk by wet processing method

After collecting the required quantity of coffee cherries, first, it is carried out to the depulping process to remove the husk by wet processing method. Then the coffee husk can be dried in the atmospheric condition (i.e., sun-dried), and it is the raw materials to produce the CTF, MCCF and NCCF. The production of various cellulosic materials is explained below.

2.3 Production cellulosic textile fibers (CTF)

Ten grams of the coffee husk (based on oven-dried mass) were added for the delignification process (i.e., NaOH 12%), temperature (90°C), and time (120 min), prior to the delignification process, the various process parameters like alkali concentration, temperature and time of the treatment has been optimized. For the bleaching process, 3 grams per liter (g/L) of H_2O_2 has been used with alkaline pH (12) at 90°C for 60 min, in this work H_2O_2 is used as it replaces the conventional chlorine dioxide bleaching process. H_2O_2 oxidizes and removes the natural-colored substances, in addition, an alkaline medium helps to remove the residual lignin present in the husk. After the bleaching process, the fibrous materials appear bright and clean. After bleaching, the cellulose textile fiber (CTF) materials were subsequently washed with hot and cold water until they neutralized. The bleached CTF has been dyed using CI Reactive Red 195 dyes, chemical structure of the dyes is shown in Fig 1.

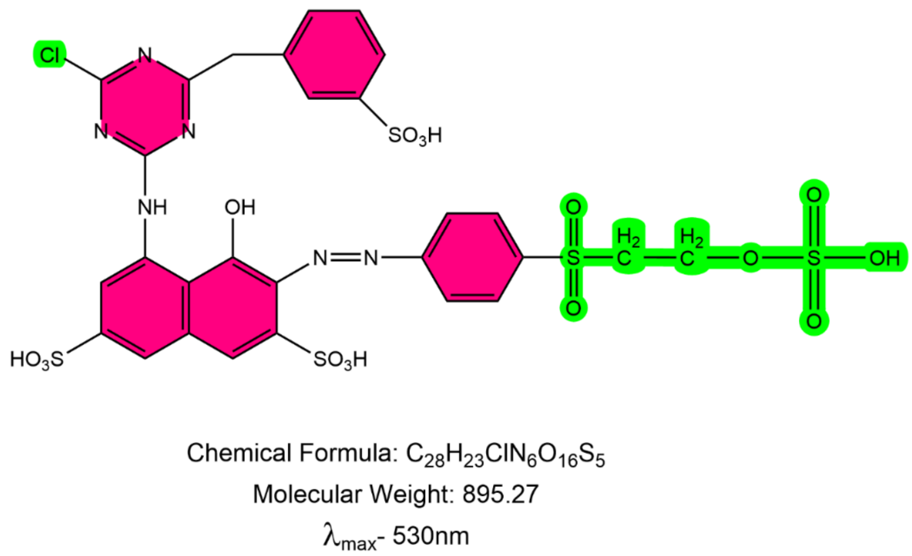

Fig. 1 Chemical structure of reactive red 195 dyes (hetero-bifunctional reactive dyes).

2.4 Microcrystalline cellulosic fibers (MCCF)

Once the coffee husk has been extracted from the de-pulping, it was carried out for vacuum dryer at 80°C was maintained to dry the coffee husk for 5 min and then milled in the laboratory bead milling crushed to powder form. The non-polar and polar components of these powders were extracted by utilizing Soxhlet extraction with Hexane and Chloroform (H:C; 5:1) ratio. The residuals solvents present in the sample were removed by drying the extracted lignocellulose powder at room temperature. Prior to the present work, we have already optimized the process with respect to the solvent ratios. After Soxhlet extraction, the 5 grams of pre-treated dried powder has been mixed with 45 mL of deionized water to carry out microwave digestion (i.e., Samsung MS23) at 800W for 5 min. Further, it is mechanically stirred for 15 min and filtered to remove undissolved cellulosic materials, later it can be treated again in the micro-oven, this process was repeated until the removal of all impurities from cellulose (Fig 2). Later, the micro cellulose compounds were carried out for the bleaching process with 5% (v/v) H_2O_2 at 90°C for 15 min. After the bleaching process, the bleached MCCF was freeze-dried in atmospheric conditions.

2.5 Production of nanocrystalline cellulose fiber (NCCF)

In this process nanocrystalline cellulose was extracted from MCCF, it is starting by soaking the 10 g of MCCF in the 50 mL of DMSO solution for 24 h. This soaked MCCF was mechanically reduced their size by using of high-speed ball milling machine, this process was carried out for 90 min (Spex 8000 M, 440C hardened steel balls of 1/4 in diameter). Later it was carried out to ultrasonic treatment (15 min at an output power of 1500W, 20kHz; (Sonic Newtown, CT, 20kHz, Model 1500W) to remove the impurities in the milled MCCF solution, this process was repeated two times. Finally, the NCCF extracted during the centrifugation process, it carried out with deionized water for 30 min at 10000 rpm, this process was also repeated 5 to 8 times. The obtained NCCF was freeze-dried and placed in a refrigerator at -20°C until needed.

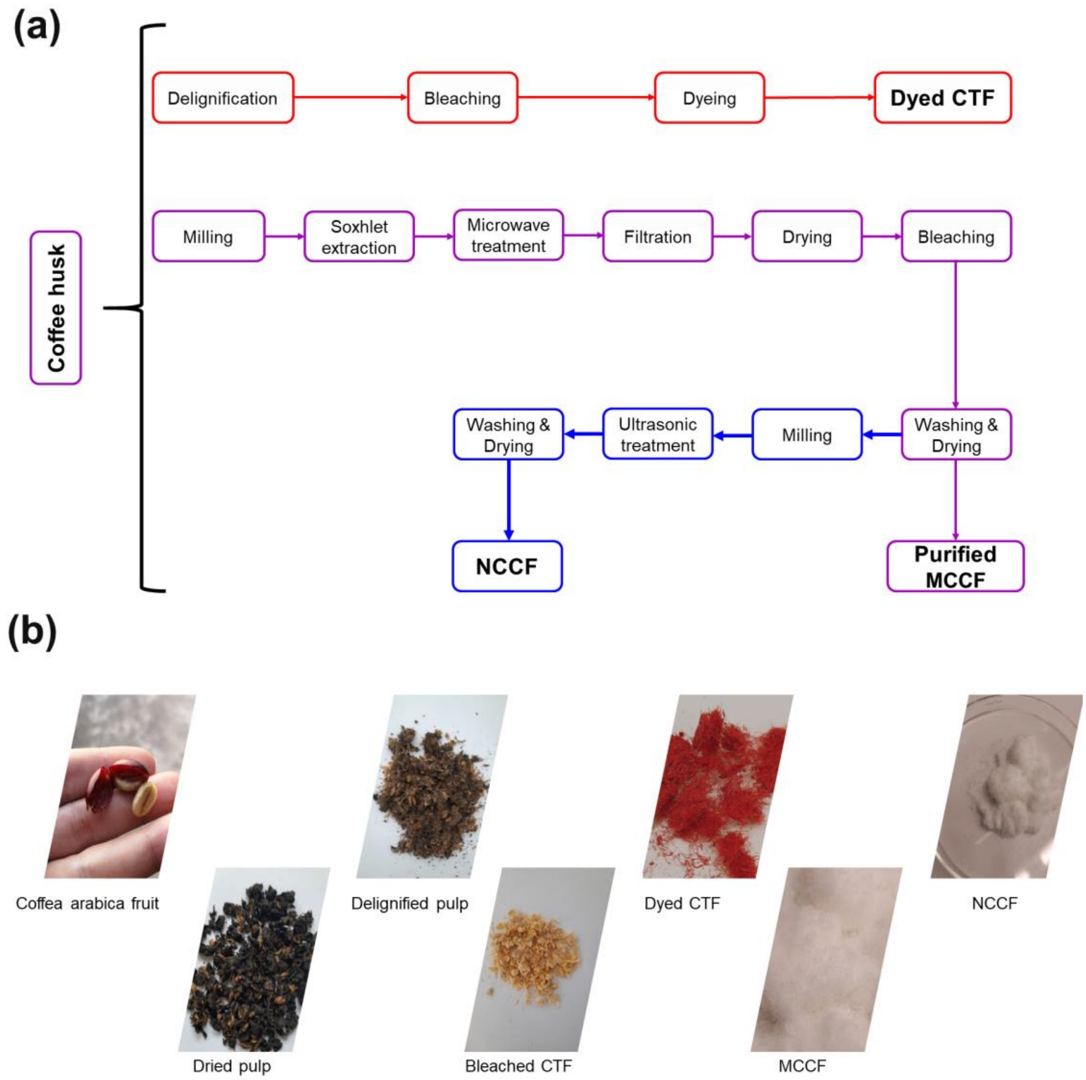

Fig. 2. Stages are involved to prepare dyed CTF (cellulose textile fibers), MCCF (microcrystalline cellulose fibers) and, NCCF (nanocrystalline cellulosic fibers) (a); photographs of various cellulosic materials (b).

2.6 Testing and Characterization

Chemical composition of cellulose fibrous materials

The chemical composition of untreated and extracted cellulosic fibers, microcrystalline cellulose and, nanocrystalline cellulosic fibers were identified with a different method. The lignin content of the fibrous materials was analyzed as per the TAPPI standard (T-222 om-88) [28]. Cellulose content has been measured by the dissolution of fibrous materials in 67% H_2SO_4 (v/v) [29]. To find the hemicellulose, the fibrous materials have been dissolved with NaOH as described in the literature [30]. The coffee husk biomass was transferred to a pre-weighed dry porcelain crucible and heated at 600 °C for 5 h. After cooling down, it was weighed (W_2) and ash content (%) was determined. In a pre-weighed dry porcelain crucible, the coffee husk and extracted other cellulosic materials was transferred and heated for 5h at a temperature of 600°C. After this process it was weighed (W2) and ash content (%) was found.

Scanning Electron Microscope (SEM)

Tescanvega 3 SEM was used to study the morphological properties of fibrous materials extracted from coffee husk at various stages of treatments. The surface of the fibrous material was sputter-coated with a thin layer of gold to make the fibrous materials conductive in a vacuum chamber before starting the measurement. The SEM images were taken at the required magnification range to observe the surface changes clearly at 10.0 kV electron voltage.

Fourier transform infrared spectroscopy (FT-IR)

The FT-IR instrument which is used to know about the composition and functional group of the fibrous materials is made by Thermo Fisher and model Nicolet is 10. General information regarding changes in the chemical structure can be obtained by FTIR analysis, which has been extensively used for structural analysis of different materials during chemical treatments. The experiment was carried out in the wavenumber range of 500 to 4000 cm^{-1}.

X-ray diffraction (XRD)

The structural characteristics of various stages of coffee fibrous materials were estimated by an X-ray diffractometer Panalytical X'Pert Pro (40 mV, 40 mA), was used with Cu Kα (λ = 1.5418 Å) radiation and graphite monochromator scanned in the axis of 2θ range varying from 3° to 60° at a speed of 10° per minute. The Segal method has been associated to analyze the crystallinity index (ICr) of the cellulosic fibrous materials to estimate the structural changes before and after the treatment [31].

$$ICr\ (\%) = \left(\frac{I_{200} - I_{am}}{I_{200}}\right) \times 100 \tag{1}$$

The ICr and I_{200} represent both crystalline and amorphous materials where ICr is the crystalline index and I_{200} is the height of 200 peaks, the term that refers only to amorphous materials is I_{am} which refers to the lowest height between 200 and110 peaks [32].

Thermogravimetric analysis (TGA)

Thermal Analyzer STA7200 was used for the TGA to know about the thermal properties of the coffee fibrous materials. The experiments were carried out in presence of nitrogen gas with a furnace temperature of 40-800°C.

Color measurement of cellulosic textile fibers

Generally, the alkali treatment has a great influence on the structural changes in the fiber which makes the fiber more absorbent [33]. Therefore, to understand the influence of the delignification process on the extracted fibers were dyed with reactive dyes and color strength and ΔE* (CIE LAB 1976) values are measured by using of reflectance spectrophotometer Spectraflash-600 (datacolor) with standard illuminant D65 and (LAV/Spec. Excl., d/8, D_{65}/10°) conditions.

3. Results and Discussion

3.1 Chemical composition of extracted cellulosic materials

In the production of MCCF and NCCF, it is observed that coffee husk has a substantial potential to be a renewable source. The NCCF production was facilitated by subjecting these MCC's to DMSO soaking and ball milling aided ultra-sonication treatment through the sonic breaking of MCCF. Acoustic cavitation leads to the creation, growth, and collapse of bubbles in the process of ultra-sonication which is in the liquid state. The shockwaves are created on the cellulose fiber surface of localized hot spots during the process rendering the erosion laterally towards the axial direction forming cellulose nanofibers [34–36].

Table 1 depicts the chemical composition of coffee husks and their derived cellulosic materials. For an enhanced view it is been compared with MCCF, NCCF other cellulosic biomass (i.e., corn cob). A similar number of cellulosic compounds is contained in both the coffee and corn cob to form a similar solid yield for both products later to the production of MCCF and NCCF. A huge number of impurities like hemicellulose and lignin, pectin, wax particles, and extractives, in addition to lignin and hemicellulose, are estimated to be present in the raw husk samples as a known fact. Subsequently, resulting in the presence of cellulose content low ranging between 34 and 37% (w/w) of untreated samples was observed.

The untreated coffee husk has 34.22% of cellulose, the low cellulose content is almost similar to the other agricultural waste products like 34% corn cob [37], rice husk 35% [38], 40.8%, and sugarcane bagasse 40% [37]. A high amount of cellulose content ranging from 73 to 78% (w/w) was observed on the raw cellulose source during the extraction. Due to lignin and hemicellulose impurities removal from raw coffee husk samples, the cellulose content is increased in the treated agricultural waste samples [39].

Table 1. Chemical composition of various cellulosic materials extracted from coffee husk and other biomass [37,40,41]

Sample	Coffee husk (% w/w) (this work)	Corncob (% w/w)
Untreated raw samples		
Cellulose	34.22 ± 2.54	34.11 ± 1.47
Lignin	22.25 ±0.75	15.08 ± 1.32
Hemicellulose	20.17 ± 1.44	20.17 ± 2.43
Ash	1.65 ± 0.35	30.06 ± 1.36
MCCF		
Cellulose	74.54 ±1.55	83.13 ± 2.63
Lignin	8.14 ± 1.77	3.43 ± 1.17
Hemicellulose	2.48 ± 0.40	1.59 ± 0.84
Ash	2.15 ± 1.33	11.85 ± 1.21
NCCF		

Sample	Coffee husk (% w/w) (this work)	Corncob (% w/w)
Cellulose	88.44 ± 3.22	91.43 ± 1.27
Lignin	1.98± 0.60	0.31 ± 0.08
Hemicellulose	1.24 ± 0.25	0.51 ± 0.02
Ash	1.53 ± 1.64	7.75 ± 1.12

NCCF production is involved in further treating sonication and washing, to acquire at most purified cellulose ranging from 85 to 90% (w/w). The reduction of lignin and hemicellulose from MCCF is due to the strong involvement of this process. Perhaps, observed NCCF noted for all investigated agricultural waste were observed to agree with the above investigation [13,14,40,41].

Rather than a coffee husk, corn cob's ash content was determined to be higher resulting to attribute to mineral-rich content in corn cobs. During the NCCF conversion process, the mineral content of corn cob is reduced which indicates the removal of impurities like lignin which is due to microwave digestion, sonication, and continual washing.

3.2 Surface morphology of extracted cellulosic materials

Scanning Electron Microscope (SEM) provides ultra-high-resolution imaging at low accelerating voltages and small working distances. The Tescanvega 3 SEM is used for the examination of the top surface of microfibres obtained. The SEM images of coffee husk, delignifed and bleached fiber were also observed and mentioned in the below Fig.3. The SEM image of the coffee husk confirms that the fiber is a cellulosic polymer with a fibrillary sheet packing as shown in Fig. 3. The image of the external fiber surface taken at 5, 10, 20, 100 μm confirms the applicability of these fibers in husk and paper industries and its allied industries.

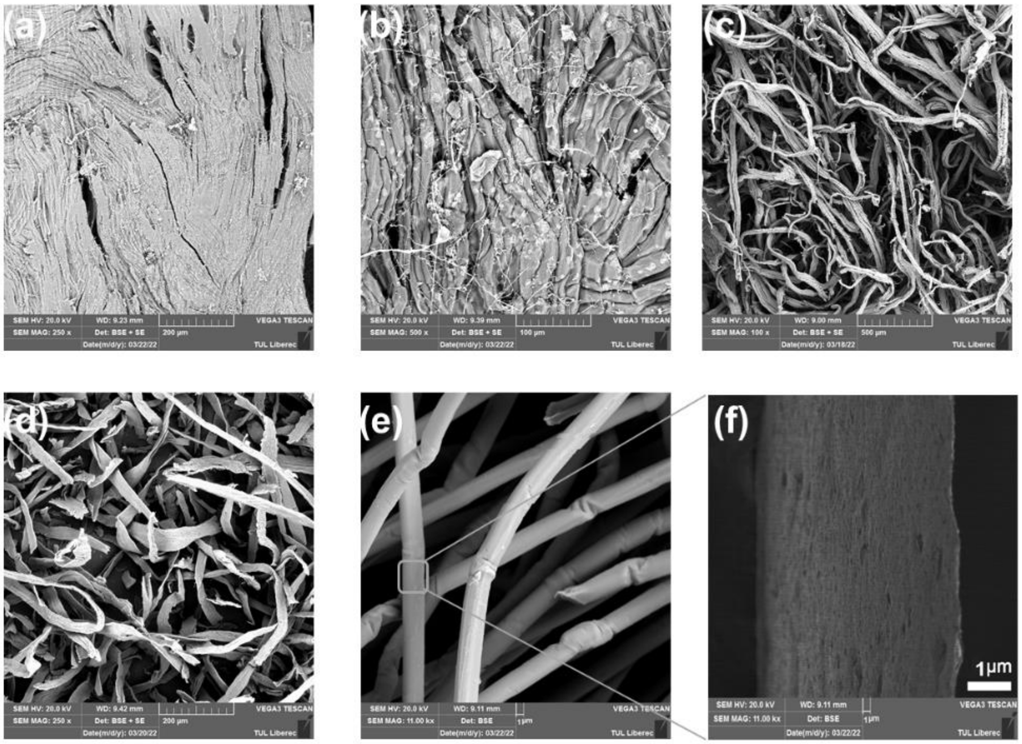

Fig. 3. SEM micrographs of coffee pulp (a); delignified pulp (b); textile fibers (c); MCCF (d) and NCCF (e&f).

3.3 FT-IR analysis

The FT-IR instrument used in this experiment for analyzing is made by Thermo Fisher and model Nicolet is 10. The FT-IR spectra of raw coffee husk, dyed CTF, MCCF, and NCCF are shown in Fig. 4. From the graph, the absorption bands are associated with stretching and vibrations of chemical groups of cellulose, lignin, and hemicellulose. The bleached CTF/ dyed CTF spectrum shows the broad and intense band at 3500 to 3260 cm^{-1} is assigned to the intramolecular and intermolecular stretching vibration of hydroxyl (O-H) groups in the cellulose molecules. The C-H stretching vibration of alkyl groups of cellulose lies in the band at 2910 cm^{-1}. The small peak in the raw husk at 2850-2857 cm^{-1} indicates the asymmetric methyl and methylene stretching in lignin and hemicellulose. The ester group that lies in either hemicellulose or lignin of untreated fiber is observed at the peak of 1735 cm^{-1} and C=O stretching in unconjugated ketone, carbonyl, and aliphatic groups of hemicellulose and lignin. The band around 1639 cm^{-1} resembles the O-H group to the absorbed water (Table 2). The band around 1650 to1500 cm^{-1} faintly corresponds to the C=C aromatic skeletal vibrations of lignin. The band at 1465 cm^{-1} shows the C-H deformation in the lignin molecules. C=O stretching and aromatic skeletal vibration of lignin and CH and OH bending of carbohydrates lies in the band between 1415-1425 cm^{-1}. Phenol that presents in the raw fiber lies between 1310-1390 cm^{-1} and at 1320 cm^{-1} corresponds to syringyl of lignin.

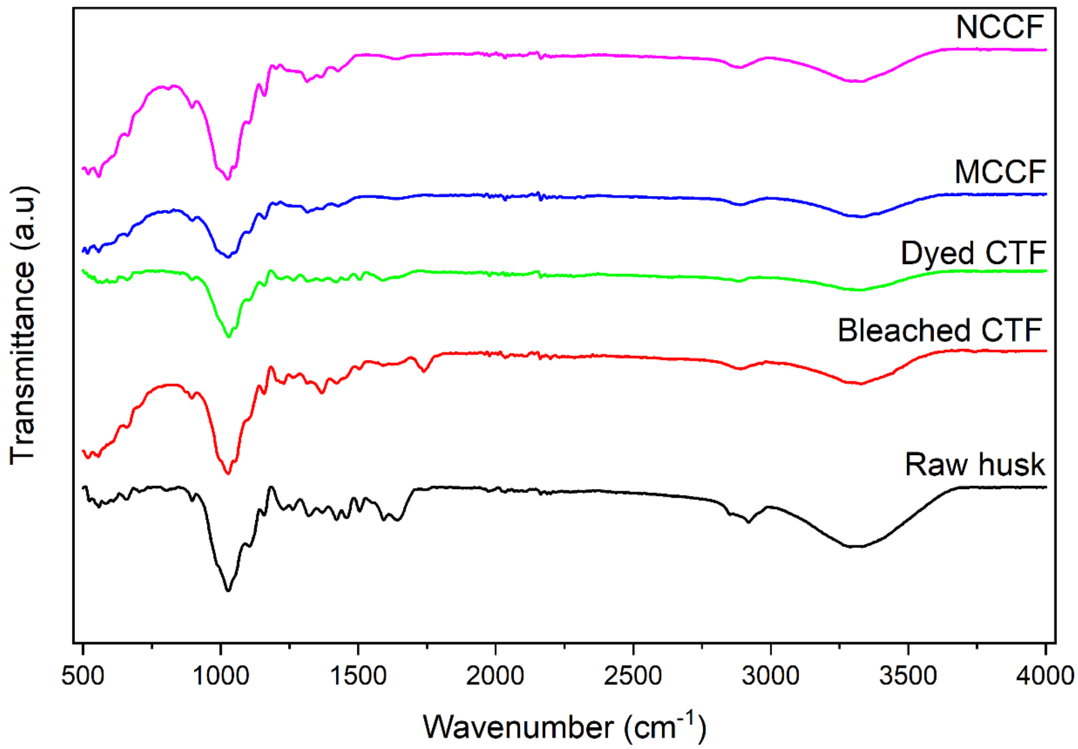

Fig. 4. Fourier transform infrared spectroscopy (FTIR) spectra of various cellulosic materials extracted from the coffee husk.

The absorption bands between 1315-1340 cm^{-1} in the MCCF attribute the CH_2 wagging in the cellulose. The absorption band between 1370-1375 is associated with CH bending of cellulose and hemicellulose (Table 2). The band at 1285 cm^{-1} corresponds to -COO vibration of acetyl group in the hemicellulose or aryl alkyl ether present in the lignin and the band at 1268 cm^{-1} shows the Guaiaryl in lignin. C-O stretching and O-H in the plane of cellulose were observed at the band 1240 cm^{-1}. The aromatic skeletal vibration of lignin in the untreated fiber is shown by the peaks that emerge between 1200 and 1300 cm^{-1} [42].

Table 2. Assignment of peaks corresponding to different functional groups present in the various cellulosic materials extracted from the coffee husk.

Name of the molecules	corresponding peaks (cm^{-1})	corresponds to
Lignin	1720	C = O
	1650-1515	Lignin and extractives: aromatic ring vibration.
	1415-1425	Lignin: C = O stretching and aromatic skeletal vibration. Carbohydrates: CH and OH bending.
	1465	C-H deformation
	1310-1390	Phenol
	1320	Syringyl
	2850-2857	Lignin and hemicellulose: asymmetric methyl and methylene stretching.
	1268	Guaiacyl
Hemicellulose	1710-1731	Hemicellulose: C = O stretching in unconjugated ketone, carbonyl, and aliphatic groups. Extractives: C = O stretching in ester carbonyl.
	875-930	Glycosidic bond
Cellulose	1370-1375	Cellulose and hemicellulose: CH bending.
	1240	C-O stretch and O-H in plane
	1155	Cellulose: C-O-C asymmetric stretching
	2910	CH
	900	Glycosidic bond
	890	Cellulose: C1-H deformation
	1075-1155	Cellulose: C-O-C asymmetric stretching
	3260-3500	OH intramolecular and intermolecular stretching
	1315-1340	Cellulose: CH_2 wagging.

The absorption band that lies between 1075-1155 cm^{-1} corresponds to the C-O-C asymmetric stretching at the β (1,4) glycosidic linkage of the cellulose molecule. At the band 1105 cm^{-1}, it is observed that the stretching vibrations of C-OH in D-glucose units and this band is a significant characteristic for the cellulosic component which is enhanced in bleached fibers. The band at 1020 cm^{-1} is associated with the C-O stretching and C-H deformation of the pyranose ring skeletal vibration of the cellulose. The C-H deformation of cellulose lies at the band of 890 cm^{-1}. The band at 900 cm^{-1} related to the C-O-C stretching at the β 1,4 glycosidic linkage between sugar units of the cellulose. However, in the delignified husk the intensity of the absorption band around 1526, 1486, 1344, and 1285 cm^{-1} are dimmed this clearly shows the maximum removal of the hemicellulose and lignin in MCCF which is previously confirmed in the chemical composition section.

3.4 XRD analysis

The data from the XRD diffractograms of various cellulosic materials that extracted from coffee husk shows the peaks of 2θ = 15.2° and 21.6° which indicates the presence of cellulose type I (i.e., crystal planes 1 1 0 and 2 0 0 was observed) and at the peaks of 2θ = 12.5° and 22.8° implies the presence of cellulose II (Fig. 5). The intense peaks at 25.7, 25.2, 25.8 and 26.1 of raw coffee husk, dyed CTF, MCCF, and NCCF indicate the mixture of polymorphs of cellulose type I (typical peaks at 2θ = 15.2° and 22.8°) [43].

The two peaks on X-ray diffractograms of dyed CTF are at $2\theta = 13.8°$ and $2\theta = 16°$ corresponds to the (1 0 1) and (1 0 1¯) crystallographic planes. The above said two peaks became intense when the crystalline cellulose content is high and if the fiber has more amorphous material (such as lignin, hemicellulose, pectin, and amorphous cellulose) then the peaks are broadened [44]. From Fig. 5 the peaks of dyed CTF at 14° and 16° are intense, it clearly shows the alkali treatment (and the pretreatment process with NaOH) of dyed CTF remove some impurities like amorphous materials as shown in (Fig. 5).

Cellulose II is observed in the diffractograms of MCCF and NCCF at the angle of 12.6°, 18.5°, 20.2°, 22.8°, and 40.2° [45]. X-ray diffractometer is used to analyze the changes in cellulose crystallinity of fibrous material with respect to the treatment in all stages and a Segal formula was used to calculate the degree of crystallinity. It is noted that the crystallinity index of all extracted fibrous materials has surged (i.e., 55.8 %-raw husk). The crystallinity index of CTF, MCC and NCCF were 63.7% ± 2.8%, 72.1% ± 3.1%, 74.5% ± 2.2%. From the above-mentioned values, it is clear that NCCF has high crystallinity than the other cellulosic materials extracted from coffee husk, which represents the removal of lignin and hemicellulose that took place during the chemical treatments. In addition, the crystallinity index (CI) values of NCCF have higher crystallinity than MCCF, which agrees with the further treatment of the NCCF production process.

The crystallinity degree of fibers was increased with the sharpness of diffraction peaks. The crystallinity index varied significantly among the coffee husks. As the crystalline index increased, the rigidity of cellulose increased, and, thus, the mechanical properties also increased. Therefore, these MCCF and NCCF could be used as reinforcement in the micro/nanocomposite field, as it would improve the mechanical properties of nanocomposites.

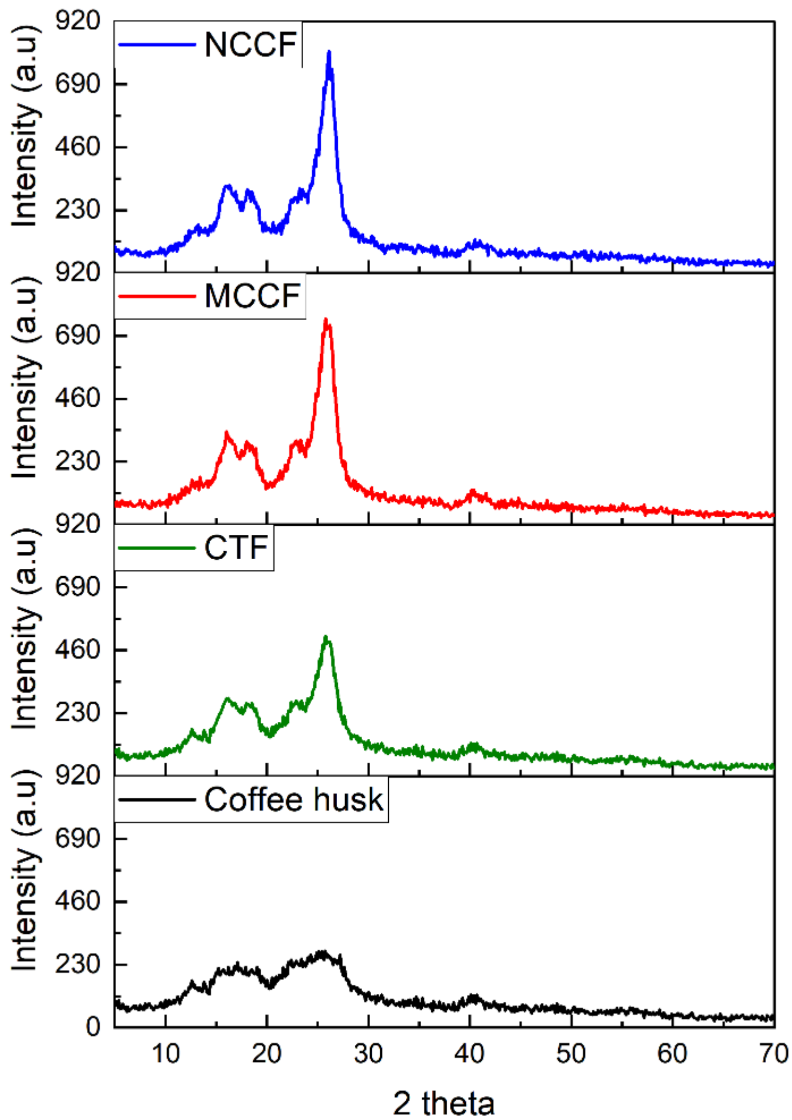

Fig. 5. X-ray Diffractograms of various cellulosic materials extracted from the coffee husk.

3.5 Thermogravimetric analysis (TGA)

To know about the thermal stability the coffee husk fiber is subjected to evaluate by using Thermo-gravimetric analysis. The analysis can be done before and after pre-treatment and the weight loss percentage towards the temperature is given in Fig. 6. Based on the weight percentage change as a role of temperature in the curve can be divided into three steps. In the initial step, the weight loss of 5.1% has been taken place at room temperature to 270°C this is due to the evaporation of moisture in the sample. Meanwhile, the weight loss was relatively high in the second degradation that lies between 274-450°C. The degradation of some fraction of hemicellulose, lignin, and cellulose was happened due to oxidative thermal degradation. The onset temperature of thermal degradation for the raw coffee husk is 274°C. In this degradation step the maximum weight loss of 36.6%, this thermal degradation associated with the cleavage of glycosidic linkage in the cellulose molecule leads to loss of cellulose structure. Furthermore, rapid depolymerization of cellulose and lignin was observed in the final degradation step that lies between 450 to 797°C, the weight loss percentage in this degradation step was about 11.9%. In bleached and dyed CTF they show similar results, at the temperature of 200°C the weight loss in bleached pulp is 3.5% whereas in dyed pulp it is 4.6%. In the temperature between 200 to 500°C major weight loss of 24.9% in bleached pulp and 21.3% in dyed pulp is occurred. In the final stage, the weight loss percentage of bleached and dyed pulp is 8.7% and 9.4% respectively in the temperature between 500-797°C. The overall weight percentage loss of both bleached and dyed pulp is less than the raw coffee husk this shows the effective removal of impurities in the pulp. The MCC and NCCF have high cellulose content as discussed above (in the Chemical composition section), which refers to it are having fewer impurities as a result both MCC and NCCF has high thermal stability. The weight loss percentage is 1.7% for MCCF and 2.2% for NCCF at 200°C as in the previous one major weight loss of 17.8% and 14.1% for MCCF and NCCF at the temperature between 200-500°C. In the final step of the temperature between 500-797°C weight loss percentage of 7.6% for MCCF ad 7.3% for NCCF. From the above results and the results, it is confirmed that the NCCF has the overall lowest weight loss percentage of 23.6% followed by MCCF has 27% which indicates the high crystalline cellulose content that is previously confirmed by XRD analysis.

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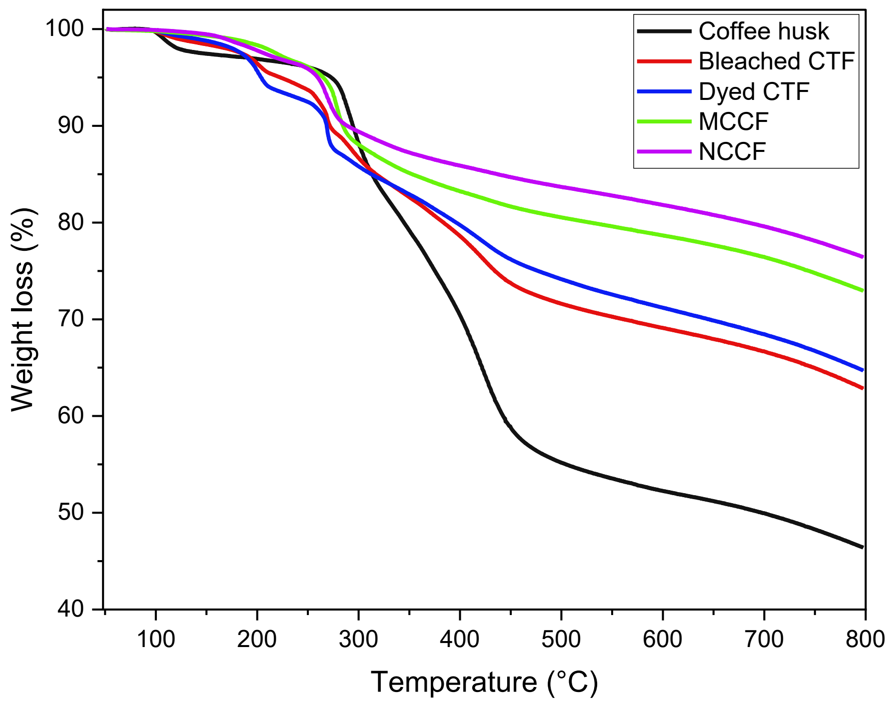

Fig. 6. Effect of change in temperature on weight loss of various cellulosic materials.

3.6 Physical properties of cellulose CTF from coffee husk

Fig. 7 shows the diameter of the coffee fiber that is measured by an optical microscope with 10X magnification. From the Microscopic observation, based on the diameter the fibers are categorized into two types, namely coarse and fine. The average diameters of both coarse and fine fibers were observed throughout the length at various places. For each fiber 50 readings were taken and likewise, 20 fibers were measured, the diameter of untreated coarse and fine fibers was tabulated in Table 3.

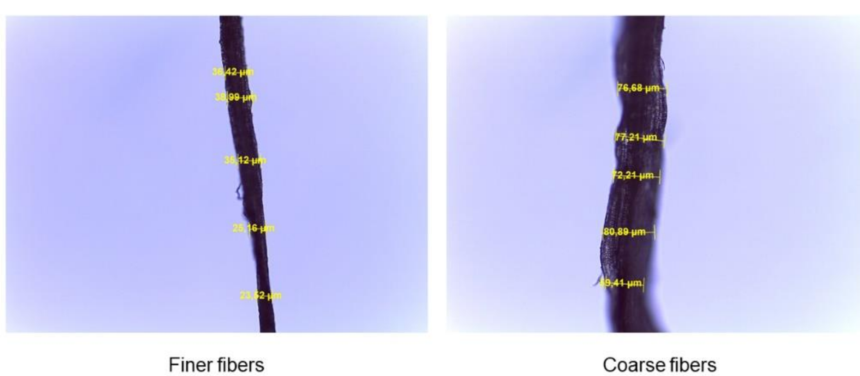

Fig. 7. Microscopic images of coarse and finer CTF.

From the results, it is evident that coarse & fine fibers are found in the range of 10-20% & 80-90% respectively. It was observed that the diameter of raw fiber was observed between 23.15 to 80.89 µm, the detailed description of the fiber diameter measurement is shown in Table 3.

Table 3. Mean diameters of delignified, bleached and dyed CTF.

Fiber type	Mean diameter (µm)	Mean fiber length (mm)	Tenacity (N/tex)
Delignified CTF	59.44 ± 32.25	31 ± 2.6	0.08 ± 0.01
Bleached CTF	58.32 ± 22.5	27 ± 1.8	0.09± 0.01
Dyed CTF	58.25 ± 9.98	25 ± 2.1	0.09± 0.01

3.7 Dyeing properties

The color of the dyed coffee fibers has been influenced by the effectiveness of alkali treatment. This is since CTF have an equal ratio of cellulose and impurities like hemicellulose and lignin [33]. The results of the optical properties of extracted CTF are shown in Table 4, color strength of the dyed CTF was measured with the maximum wavelength (λ_{max}- 530 nm). The CTF was dyed with reactive dye with the concentration of dyestuff (3% on weight of the material). For better understanding, the same quantity of dyes was used to dye the plain cotton fabric and observed the color strength values of both cotton and CTF from coffee husk. It was evident that after the scouring and bleaching the fibers were ready to absorb a large number of dyestuffs as similar to cotton fabric, it can be confirmed by its color strength values (K/S values).

Table 4. Color values of raw fibers, bleached and dyed fibers

Fiber Type	L*	a*	b*	K/S	
Bleached CTF	88.77	1.11	33.25	-	

Dyed CTF	47.42	30.92	-	5.8	
Dyed cotton fabric	35.72	53.14	20.7	7.5	

Note: K/S denotes the color strength (i.e., a ratio of reflectance and absorption with respect to the scattering of the sample during the color measurement). Cotton fabric was dyed together with coffee fiber (i.e., same bath).

4. Conclusion

In this work, various forms of cellulosic materials (i.e., CTF, MCC, NCCF) were extracted from the coffee husk, which was characterized by SEM, FT-IR, TGA, XRD. The morphological analysis was analyzed by SEM that shows the detailed image of the fibers. The crystalline nature of the extracted cellulose fibers was carried out by XRD which indicates the crystallinity of cellulose and the effective removal of hemicellulose and lignin in CTF, MCC, and NCCF. For reference, the cellulose, hemicellulose, and lignin contents were analyzed in all raw husk, MCC and NCCF and compared these values to the cellulose that extracted from the corn cob where NCCF extracted from coffee husk shows the cellulose content of 88.44 ± 3.22. To know about the sorption properties the CTF was dyed with reactive red 195 where the bleached fibers have the absorbing property as same as cotton. Hence it was a promising source that can be used as short textile fibers, fillers in the composite materials, and micro/nano-scale materials such as micro/ nanocrystalline cellulose, micro/nano fibrillar cellulose, paper industry. In addition to that, it is possible to make activated carbon as the extracted fibrous material has a considerable amount of carbon so that it is used in various fields like in energy storing and used as an absorbent in the textile industry where dye pollution is a substantive, so it became a dye absorbent.

Conflict of interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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