Chemical Composition and Extraction of Micro Crystalline Cellulose from Outer Skin Isolated Coffee Husk

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Coffee husk (CH) is a sustainable and abundantly available cellulosic waste material. Its fiber consists of cellulose as the major structural part which leads to potential utilization for the manufacturing of microcrystalline cellulose (MCC) products that can be utilized for different industrial applications. In the present study, chemical composition of outer skin-isolated coffee husk was determined and sequential treatments of various untreated (UT) sample, ethanol—toluene treated sample through dewaxed (DW) treatment, sodium hydroxide (NaOH)—treated sample through alkali (AT) treatment, and sulfuric acid (H₂SO₄)—treated sample through bleaching (BL) treatment have been carried out. The Micro Crystalline Cellulose (MCC) has been extracted through hydrogen peroxide (H₂O₂) after BL treatment. The BL treatment for MCC extraction process was conducted without chlorine and additional harsh acid treatment, respectively. The characterization of chemically treated samples was carried out to investigate their morphological, physico-chemistry, and thermal behavior through a scanning electron microscope (SEM), Fourier transform infrared—ray (FTIR), X-ray diffraction (XRD), thermo gravimetric analysis (TGA), and differential temperature analyzer (DTA).

From the chemical composition analysis; the cellulose, hemicellulose, lignin, and extractive content were determined and its values were (52.9%), (12.5%), (24.3%), and (9.4%), respectively. In the morphological examination, the great untreated (UT) fiber sample was greatly reduced into a micro-sized BL sample, revealing that (from FTIR analysis) the lignin and hemicellulose contents were greatly removed during chemical treatments and the presence of a micro crystalline cellulose region with 54.7% yield. Also, the sample AT and BL showed the lowest amorphous region in X-RD due to the removal of hemicellulose and lignin. The highest crystallinity index has been determined for the BL sample, i.e., 89.9%. Additionally, the thermal analysis shows that the AT and BL sample has great thermal stability than other (UT and DW) samples at high temperature. Therefore, the outer skin separated coffee husk was prepared from agricultural waste was subjected to eco-friendly chemical treatments to yield MCC. Thus, the extracted MCC is expected to be reliable for replacing other plant materials for the production of crystalline nanomaterial and reinforcing constituent for the fabrication of bio composite.

1. Introduction

Coffee is one of the most widely held commercial commodities next to petroleum [1]. Ethiopia is the first in Africa and sixth of the globe’s largest producers and exporters of coffee [2], and a large amount is consumed by local consumers [3]. Currently, according to the International Coffee Organization report, over 2.3 billion cups of coffee are used up every day across the world, and the world’s coffee yield has reached an average of 171.9 million of 60 kg bags per year [4]. Basically two varieties of coffee called as Robusta and Arabica are responsible to support 100% production in the world. They vary typically in their chemical constituents, and on the other hand, produce comparable volumes of waste [5]. Coffee cherry produces 30–50% coffee husk based on the processing method [6]. Currently, an estimated 400,000 to 550,000 metric tons of coffee has been produced per year in Ethiopia [7]. Among these, more than 100,000 tons are estimated to be coffee husks [8, 9].
Coffee husk is the coffee industry residue that is produced during the dry processing method [10], which contains cellulose, hemicellulose, and lignin in unlike proportions based on the geographical location and coffee hulling process [11]. The effects of these different conditions affect the chemical composition and physical properties of natural fibers [12]. Additionally, the caffeine and tannins contents, which are toxic in nature of this waste are disposed of by the environment and contaminate the land and rivers [13]. Furthermore, they are not used for animal food because of tannins which are considered as anti-nutritional compounds and other applications in Ethiopia [14]. So, due to disposal problems and lack of reutilization, these husks are traditionally burned in the fields leading to pollution or smoke which is identified as the cause of major health-hazardous [15]. Coffee wastes can be made up of husks, pulp and skin, coffee parchment, coffee mucilage, coffee silver skin, and spent coffee grounds [16]. Studies are under progress on the reprocessing of these by-products of coffee industries as these are important for environmental friendly motives and for the hopeful real purpose of this enormous extent of lignocellulose material. In processing, the coffee parchment and pulp separation are dissimilar in wet and dry processing. In wet processing, the pulp and outer skin are removed from cherries, and parchment is removed after drying. However, in the dry processing, the dried green coffee cherries and the skins (outer skin, pulp, and parchment) are isolated in a single process.

Enormous natural materials have received increased attention from the research community due to their properties, including rice husk [17], cotton products [18], bagasse [19], and wastes of oil palm fruit [20], peanut hulls [21], and wheat straw [22]. The literature reveals that the use of these natural resources is sustainable for countries with sufficient amount. Ethiopia has various agricultural residues such as wheat, barley, teff, maize, chat, sugarcane, enset, and coffee. These wastes are mainly exploitable for energy consumption in the country [9] and other reutilization areas further require investigations. The residues of these crops have a high environmental impact and health hazards due to poor disposable problems. The demands are increasing for wood based products, including cellulose, MCC, wood-based reinforcing material, and their composite products for various industries such as medical and automotive. Cellulose is a highly crystalline and ordered structure which forms strong material with excellent properties [23]. Its derivative MCC is a microsized and tasteless naturally available substance found from purified and partially depolymerized cellulose. Due to its exceptional properties such as biodegradability, chemical inactivity, high surface area for bonding with resins, high sorption, absence of toxicity, and great hygroscopicity, MCC has gained attention for various applications such as cosmetics, pharmaceutical, bio composite reinforcement, and beverage[24, 25]. The extraction techniques for MCC particles are several including mechanical treatment, biological treatment, and chemical treatment. Among these techniques, chemical treatment (e.g. acid hydrolysis) is the conventional method for extraction of MCC [26]. The stringent environmental protocols concerning the utilization of protected forests drive the investigation of cellulose, MCC, wood-based reinforcing materials, and their composite products from agricultural residues to satisfy the demand of the industries. Therefore, to lessen deforestation and utilize efficiently agricultural residues (wastes), overlooking available renewable resources offers the commercial product through the production process. Interestingly, few researchers have focused on the use of agricultural residues to extract cellulose and fiber to fabricate paper, paperboard, and bio composite materials. Additionally, researchers have investigated agricultural residues, such as wheat straw [27], peanut hull [21], and rice husk [28], in the fabrication of particleboard, fibers, biomass energy, and composite material. Till now, numerous studies on different areas of coffee industry residues/coffee husk have been reported for various industrial applications. Some of the recently reported research works are presented in Table 1. From Table 1, it is palatable that coffee industry residues can yield different products and compounds.

The previous literature reveals that there is almost no report on the extraction of MCC and chemical composition analysis from outer skin-isolated coffee husk. The current study has been conducted to systematically determine the potential of outer skin-isolated coffee husk fiber for supplementing environmental protection and health. The major objective of this research is to explore the chemical composition and potential of microcrystalline cellulose extracted from outer skin-isolated coffee husks through a modified user-friendly procedure for industrial utilization. The resultant microcrystalline cellulose properties were studied in terms of structure, morphology, crystallinity, and thermal stability.

2. Materials and Methods

2.1. Materials. Coffee husk fibers were collected from bale zone Dello Menna, the southern part of Ethiopia, in the form of short fiber, in 2022. The reagents used were toluene, ethanol, sodium hydroxide, hydrogen peroxide, and sulfuric acid. All reagents were purchased from techno tech, Addis Ababa, Ethiopia, and were used without further purification.

2.2. Preparation of Samples. From the collected coffee husk fiber part, the pulp and parchment were separated from the outer skin via strip (manually). The coffee husk (pulp and parchment) isolated from the outer skin was washed away with distilled water and dried up in an oven at 70°C intended for 2 days, then cooled in a desiccator for 30 minutes to prevent moisture absorption of the fiber. Finally, it was crushed with a grinding machine and put through a sieve using a sieve dimension of 2 mm. Figure 1 confirms the collected coffee husk, outer skin-isolated coffee husk, and sieved outer skin-isolated coffee husk.

2.3. Chemical Composition Analysis. The chemical composition investigation of the lignocellulosic components present in the outer skin isolated coffee husk fibers was
carried out in three steps, which follow the conventional methods of the Technical Association of Pulp and Paper Industry (TAPPI) and standards which involves an analytical approach (gravimetric method) to find extractive, hemicellulose, lignin, and cellulose contents. For a piece of sample, three replicates were conducted to determine the average value. This step was then followed for microcrystalline cellulose extraction.

**Step 1.** The extractive content was investigated through the TAPPI standard technique (T-264 om-82) [30]. In a Soxhlet extraction, about 20 g of dry outer skin isolated coffee husk was added to a beaker filled with 750 mL of the solution combination (1:1, ethanol: toluene). The extract was collected and placed in an oven at 110°C with the aim of drying up for precede weighing. This extractive-free dried coffee husk was considered as a base for the subsequent processes. The yield of extractive was determined by expression (1).

\[
\text{% of Extractives} = \frac{W_i - W_f}{W_i} \times 100, \tag{1}
\]

where \( W_i \)—is the weight (gm) of oven-dried sample before extraction and \( W_f \)—is the weight (gm) of the oven-dried sample after soxhlet.

**Step 2.** The content of the lignin sample was calculated by putting in the residue in a sulfuric acid solvent of 72% as per TAPPI approach (T-222 om-83) methodology [41]. About 3 gram of extraction-free sample was immersed in a beaker, to the 51 mL of sulfuric acid (72%) solvent was placed, rigorously stirred in electromagnetic stirrer at room temperature for 8 hours. Then, this hydrolyzed sample was washed away using distilled water till the PH became neutral and was dehydrated in an oven for 3 hours at 105°C. The lignin content was determined by expression (2).

**Table 1:** Recently reported research work conducted on coffee industry residues.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Objective</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffee silver skin</td>
<td>Nanocellulose extraction</td>
<td>Bio-nanocomposite film development for food packaging</td>
<td>[29]</td>
</tr>
<tr>
<td>Parchment</td>
<td>Micro fibrillated cellulose extraction</td>
<td>Composite reinforcement</td>
<td>[30]</td>
</tr>
<tr>
<td>CH/thermoplastic starch films</td>
<td>Composite film development</td>
<td>Food packaging material</td>
<td>[31]</td>
</tr>
<tr>
<td>Spent coffee ground/poly (vinyl alcohol)</td>
<td>Thermoplastic starch composite film development</td>
<td>—</td>
<td>[32]</td>
</tr>
<tr>
<td>CH/starch/poly lactid acid</td>
<td>Bio-based composite development</td>
<td>Building materials (roofing and ceiling tile)</td>
<td>[33]</td>
</tr>
<tr>
<td>CH/polypropylene</td>
<td>Composite material development</td>
<td>Internal automotive parts and lightweight furniture</td>
<td>[34]</td>
</tr>
<tr>
<td>Ground coffee waste/oxobiodegradable high density polyethylene</td>
<td>Polymer composite material development</td>
<td>—</td>
<td>[35]</td>
</tr>
<tr>
<td>CH/linear low-density polyethylene</td>
<td>Green composite material development</td>
<td>Rigid packaging (food tray, cups and containers)</td>
<td>[36]</td>
</tr>
<tr>
<td>CH/poly lactid acid</td>
<td>Development of polybutylene adipate terephthalate composite</td>
<td>Substitute neat poly butylene adipate terephthalate</td>
<td>[37]</td>
</tr>
<tr>
<td>Coffee husk/polybutylene adipate terephthalate</td>
<td>High-density polyethylene composite</td>
<td>—</td>
<td>[38]</td>
</tr>
<tr>
<td>Coffee hull/high-density polyethylene</td>
<td>Polyethylene composite</td>
<td>—</td>
<td>[39]</td>
</tr>
<tr>
<td>CH/high-density polyethylene</td>
<td></td>
<td>—</td>
<td>[40]</td>
</tr>
</tbody>
</table>

**Figure 1:** (a) Waste coffee husk. (b) Outer skin isolated waste coffee husk (coffee pulp and parchment). (c) Ground outer skin isolated coffee husk.
where \( W_i \) is the weight of oven-dried sample before extraction and \( W_L \) is the weight of oven-dried sample after extraction.

\[
\text{% of Lignin} = \frac{W_i - W_L}{W_i} \times 100, \tag{2}
\]

\[
\text{% of Hemicellulose} = \frac{W_j - W_b}{W_j} \times 100, \tag{3}
\]

where \( W_i \) is the weight of the oven-dried sample before extraction and \( W_b \) is the weight of the oven-dried sample after extraction.

Then, the cellulose percentage was calculated by

\[
\text{% Cellulose} = 100 - (\% \text{hemicellulose} + \% \text{lignin} + \% \text{extraction}). \tag{4}
\]

2.7. Bleaching. For the removal of lignin and remaining amount of hemicelluloses, extracting MCC was carried out with the dewaxed and alkali-treated sample placed in sulfuric acid (7 wt%) solvent for 3 h at room temperature under stirring with 1:20 fiber to liquid ratio (g/mL). Further purified cellulose was treated with hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) solvent (11%, v/v), and the pH was tuned to 11 by 8 wt% NaOH. The solution was forcefully agitated constantly for 4 hours at 50°C temperature and a 1:25 sample to a solvent ratio. The microcrystalline cellulose sample obtained from this bleaching process was filtered and washed away with distilled water till the pH reaches neutral. The treatment of each process is carried out twice in the same settings and weighed for taking the sample yield. The outer skin-isolated CH, MCC extraction, and chemical composition analysis has been illustrated in Figure 2.

2.8. Fourier Transform IR-Spectroscopy. Infrared spectroscopy investigation was carried out to obtain the existence of chemical variations which occurred in the intended (UT, DW, AT, and BL) samples. The peaks were obtained with Jasco FT/IR-6600 type A analyzer (Easton, Maryland, USA), at scanning speed of 2 mm/sec in the range of 400–4000 cm\(^{-1}\) (standard) and 4 cm\(^{-1}\) resolution.

2.9. X-Ray Diffraction (XRD). The XRD pattern of untreated and chemically treated samples was recorded using MAXima_X XRD-7000 X-ray Diffractometer (Japan) with Cu Kα radiation. The X-ray was operated at 30 mA and 40 kV with a scan rate of 3 min\(^{-1}\) and in the range of 5–60. The crystallinity index (CI) was investigated by the XRD amorphous subtraction method developed by Ruland for the first time and states the ratio of the sum of areas under the peaks of the crystalline component \( I_c \) to the overall area under all peaks \( I_{tot} \).

\[
\text{Crystallinity index} (\%) = \frac{I_c}{I_{tot}} \times 100. \tag{5}
\]

2.10. Scanning Electron Microscope (SEM). Surface morphology of coffee husk-derived cellulose and microcrystalline cellulose was observed through JOEL, JCM-6000 plus scanning electron microscope (JOEL Ltd., Tokyo, Japan), operating under 10 KV accelerating voltage.

2.11. Thermo Gravimetric (TG) and Differential Thermal (DT) Analyzer. The thermal endurances of the samples were carried out using BJHENVEN thermo gravimetric analyzer, HCT-1 model. For analysis, the samples were heated between 0 and 500°C under a nitrogen atmosphere at 10°C/min.

2.12. Determination of Average Molecular Weight and Degree of Polymerization. The average degree of polymerization, DP, of extracted MCC was determined by the viscometry method at 25°C in 6 wt% NaOH/4 wt% urea solvent using...
Ostwald viscometer [45, 46]. The flow time was recorded and relative viscosity, $\eta_r$, was determined based on recorded flow time (ratios of time flow of extracted MCC solution and CED solvent). Then, intrinsic viscosity, $\eta_I$, was determined according to the following equation in cm$^3$g$^{-1}$.

$$\log \left[ \frac{\eta_r - 1}{C} \right] = \log [\eta] + 0.13 [\eta]C,$$

where $C$ is solution concentration of the sample in g mL$^{-1}$.

Average degree of polymerization was then determined from the following formula:

$$DP^{0.905} = 0.75 [\eta].$$

3. Results and Discussion

3.1. FTIR and Chemical Composition. The chemical composition of outer skin-isolated coffee husk was determined using the gravimetric method and was determined to be 9.4% extractives, 12.5% hemicellulose, 24.3% lignin, and 52.9% of cellulose yield. This yield value is higher than the cellulose yield of wheat straw (32.5%) [47], coffee husk (24.5%) [48], and parchment (22%) [30] and lower than the yield values of cellulose extracted from coffee husk through chlorine-based extraction techniques (61.8%) [49] reported in the literature. Furthermore, the yield value is comparable to yield values of cellulose extracted from bagasse (55.2%) [50] and kenaf fiber (53%) [51]. The obtained cellulose from outer skin isolated CH is compared with other renewable source and has been summarized in Table 2 and Figure 3 which shows different samples of outer skin-isolated coffee husk in order to determine their chemical composition and changes.

3.2. FTIR. Infrared spectroscopy is a simple technique used to obtain information continually on chemical changes that takes place throughout chemical treatments. Figure 4 shows the IR spectra of untreated (UT) sample (a), dewaxed sample (b), alkali-treated sample (c), and bleached sample (d). Table 3 exhibits all IR spectra of detected peaks and their representations.

FTIR analysis shows UT sample and DW sample spectra exhibited matching absorption bands. The spectra at 1030 cm$^{-1}$ shows the O–H and C–O stretching vibration of polysaccharide occurred in cellulose, and the peak at 1630 cm$^{-1}$ is may be caused by water absorption of the samples [58]. The spectrum at 1739 cm$^{-1}$ is a typical behavior of the carbonyl C=O stretching of the uronic ester and acetyl groups of polysaccharides. It is moreover associated to the p-coumaric acids of hemicellulose or/and lignin [59], and the removal of this spectra after continuous chemical treatments shows the elimination of excessive content of hemicellulose and lignin from the samples. Additional sign of hemicellulose and lignin elimination through the treatment is the substantial reduction in the absorption of the small spectra at 1220 cm$^{-1}$ which is associated to the C-O stretching of the aryl group in hemicellulose and lignin. A small spectra exhibited at 1430 cm$^{-1}$ can be associated to the CH$_2$ symmetric bending of cellulose [57]. The absorption in the range of 3600–3100 cm$^{-1}$ is associated to the O–H stretching vibration and hydrogen bonds of the hydroxyl groups. The cellulose did not show the absorption band located at 1739 cm$^{-1}$, which is a typical behavior of the stretching vibration of C=O and C-O. The alkali treatment removed these groups from the spectra.
Finally, the FTIR spectra of BL sample shown in Figure 4 shows the delignification process of sample and further extraction of MCC. In this spectra, the elimination of almost the remaining lignin was proven by the removal of peak at 1516 cm\(^{-1}\), and the peak band around 3440 and 2920 cm\(^{-1}\) is related with the characteristic values of purified cellulose and the broadened peak and sharp peaks in the BL sample implying enhanced cellulose content and increasingly exposed cellulose content in the sample [60]. In addition, the spectra around 1430 cm\(^{-1}\) are connected to the crystallinity of cellulose and are related to CH\(_2\) symmetric stretching. Additionally, the spectra at 898 matching to the C–O–C pyranose ring skeletal stretch, \(\beta\)-glycosidic bond stretch, and C–H asymmetric deformation [61]. This peak appearance on

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Renewable source</th>
<th>Cellulose content (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Wheat straw</td>
<td>32.5</td>
<td>[47]</td>
</tr>
<tr>
<td>2</td>
<td>Coffee husk</td>
<td>24.5</td>
<td>[30]</td>
</tr>
<tr>
<td>3</td>
<td>Parchment</td>
<td>22</td>
<td>[30]</td>
</tr>
<tr>
<td>4</td>
<td>Bagasse</td>
<td>46</td>
<td>[50]</td>
</tr>
<tr>
<td>5</td>
<td>Kenaf</td>
<td>53</td>
<td>[51, 52]</td>
</tr>
<tr>
<td>6</td>
<td>Giant reed</td>
<td>35.52</td>
<td>[53]</td>
</tr>
<tr>
<td>7</td>
<td>Jute</td>
<td>60</td>
<td>[54]</td>
</tr>
<tr>
<td>8</td>
<td>Sisal</td>
<td>73.5</td>
<td>[52]</td>
</tr>
</tbody>
</table>

Figure 4: Infrared spectra of UT, DW, AT, and BL samples.
the BL sample spectra confirms the breaking of cellulose chains and extraction of MCC.

3.3. X-Ray Diffraction Measurements. It is an important method to characterize the structure of crystalline material. Figure 5 represents the XRD patterns of chemically-un-treated and treated outer skin isolated coffee husk samples. The samples showed outstanding peaks around 16.7°, 22.4°, 34.6°, and 44.1°, which match all peaks with standard diffrac tion data (JCPDS Card Number: 00-003-0192) that corresponds to the crystallographic plane of (110), (200), (004), and (100) [55, 62]. This JCPDS Card Number: 00-003-0192 refers to coated cellulose-II type structure, and these planes reveal that each cellulose sample has a cellulose type structure [63], and the bleached (BL) sample shows coated cellulose-II type structure. The peak observed at 16.12° was related to the cellulose crystals domain, and it has increased intensity for alkali-treated (AT) and bleached (BL) samples. It was suggested that the two-cycle NaOH—alkali treatment and H₂SO₄ and H₂O₂—based bleaching processes promote highly ordered coated cellulose-II crystallites in outer skin isolated coffee husk through improving intra and inter-molecular hydrogen bonding. The peak 22.2° 34.6 and 44.0

**Table 3: The IR spectra of detected peaks and their representations.**

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Spectra</th>
<th>Represents</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1030</td>
<td>All</td>
<td>C-O-C pyranose ring skeletal vibration</td>
<td>[43]</td>
</tr>
<tr>
<td>1141</td>
<td>BL</td>
<td>C-O-C stretching at the b-(1→4)-glycosidic linkages</td>
<td>[55, 56]</td>
</tr>
<tr>
<td>1220</td>
<td>UT</td>
<td>C-O stretching of the aryl group in hemicellulose and lignin.</td>
<td>[56]</td>
</tr>
<tr>
<td>1430</td>
<td>AT, BL</td>
<td>C-H bond of cellulose</td>
<td>[57]</td>
</tr>
<tr>
<td>1516</td>
<td>UT, DW</td>
<td>C-C aromatic ring stretching vibrations of lignin</td>
<td>[55]</td>
</tr>
<tr>
<td>1630</td>
<td>AT, BL</td>
<td>OH bending of the absorbed water</td>
<td>[58]</td>
</tr>
<tr>
<td>1739</td>
<td>UT, DW</td>
<td>C=O stretching in hemicellulose</td>
<td>[59]</td>
</tr>
<tr>
<td>2920</td>
<td>AT, BL</td>
<td>C-H stretching</td>
<td>[57]</td>
</tr>
<tr>
<td>3440</td>
<td>AT, BL</td>
<td>-OH groups stretching of cellulose</td>
<td>[60]</td>
</tr>
</tbody>
</table>

**Table 4: Crystalline index of UT, DW, AT, and BL samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>The total area of crystalline peaks</th>
<th>Areas of all peaks</th>
<th>Crystalline index (CI %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UT</td>
<td>5207.2</td>
<td>7462.2</td>
<td>69.7</td>
</tr>
<tr>
<td>DW</td>
<td>6611.9</td>
<td>8667.5</td>
<td>76.2</td>
</tr>
<tr>
<td>AT</td>
<td>6386.1</td>
<td>7863.2</td>
<td>81.2</td>
</tr>
<tr>
<td>BL</td>
<td>8394.4</td>
<td>9328.3</td>
<td>89.9</td>
</tr>
</tbody>
</table>

**Figure 5: X-ray diffraction pattern of untreated (UT), dewaxed (DW), alkali-treated (AT), and bleached (BL) sample of outer skin isolated coffee husk.**
were observed to be sharpened gradually and also had high intensity for both AT and BL samples as compared to UT and DW samples. This was likely due to the alkali treatment and bleaching processes that removed residual compounds and produced coated cellulose-I crystalline structure with 54.7% yield. Accordingly, the highest crystalline index of cellulose possessed 89.9% with the BL sample, followed by the AT with 81.2%, DW with 76.2%, and lastly UT with 69.7% as shown in Table 4. Thus, the outer skin-isolated coffee husk-bleached sample could offer it as a promising agent in bio composite reinforcement application.

3.4. Morphological Properties of Chemically Untreated (UT) and Treated (DW, AT, and BL) Samples. Figure 6 exhibits SEM micrograph of CH fiber subjected to dewaxing, alkaline, and bleaching treatment. Figures 6(a) and 6(b) show the feature of any typical lignocellulosic fiber characteristics which clearly shows surface impurities. The dewaxed sample Figure 6(b) further exhibits the microfibers in pack form more densely with a rough surface, and the alkali-treated sample in Figure 6(c) exhibits less dense microfibers with a smooth surface, and fibers try to isolate each other. This indicates partial hemicellulose, lignin, and surface impurity removal at this stage, while the smooth structure of cellulose was still preserved [50]. The two-cycle bleaching process in Figure 6(d) causes the fiber to split into isolated cellulose microcrystalline. According to reported pieces of literature, the acidic attack disintegrates the cellulose structure into individual small microcrystalline size, and penetration of acidic ions into the inner part of fiber could depolymerize the cellulose by degrading the amorphous regions [60]. The chemically-treated cellulose microcrystalline average diameter are about 2-3 μm but the exact length is difficult to determine. The reduction in diameter refers to the disappearance of hemicellulose, lignin, and other impurities [64]. This extracted CH cellulose microcrystalline is less in diameter than those extracted from various sources such as sisal [65], coconut [66], and wheat straw [67] with different extraction methods which uses harsh acid and chlorine-based extraction methods.

3.5. Thermal Stability. Figures 7(a) and 7(b) exhibit the TGA and DTA curve, respectively, and environmentally friendly chemical treated and untreated outer skin-separated coffee husk samples. Initially, all samples, mainly UT and DW samples, demonstrated a decreased weight curve in the range of 30–135°C, which is a typical characteristic of adsorption of water and disappearance of constituents of low molar mass [68]. However, AT and BL samples showed increase in the same way with a flattened curve, and the weight loss was also relatively low. This was probably caused by water adsorption of the high amount of cellulose content in both samples. Consequently, AT and BL samples exhibit higher decomposition temperatures than UT and DW samples for the reason of the existence of microcrystalline cellulose structure that increases the thermal endurance of samples from high temperatures [63]. The second range 135–250°C is associated with the degradation of hemicellulose which contains numerous saccharide types that form amorphous structures and thermally less stable lignocellulosic components [30]. The third range 250–375°C corresponds to a portion of hemicellulose and cellulose. Cellulose is a highly crystalline and ordered structure that forms strong material with thermal stability [69]. Finally, the degradation takes place at the range of 375–520°C related to lignin, which is more thermally stable and difficult to degrade [70]. The DTA curve tries to show a slight an endothermic reaction at the initial stage of the curve due to the sample’s dehydration around 100°C, then undergoes a sharp exothermic reaction between temperature around 270°C–375°C. The sharp exothermic reaction at this temperature range indicates the degradation of cellulose and remaining hemicellulose. Variation in the structure of cellulose due to heat primarily takes place through depolymerization (begins at 310°C due to breaking the chain at 1,4 glycosidic bond), dehydration (occurs at initial range of degradation temperature, 280°C), and the formation of Glucosan [71]. Additionally, the exothermic peak around the temperature of 410°C and above indicates the release of lignin from the samples. Finally, the curve BL sample shows that the temperature resistance is highly relative to other samples. This indicates that the two stage bleaching process highly improves the thermal resistance of the sample. The weight loss in each range of the samples is summarized in Table 5. The weight loss of sample BL in the range initial, second, and final was lower than other samples, and in the third range AT sample, the loss was low.

3.6. Average Molecular Weight and Degree of Polymerization. The η and extracted MCC average DP was determined to study the effect of H2O2 treatment on the cellulose structure. During the first bleaching cycle using H2SO4, the η and DP are 901 and 1340, respectively. For the second bleaching cycle, using H2O2 for preparation of MCC, the η and DP significantly reduced to 365 and 281, respectively. This could be described by the degradation of amorphous region for the extracted MCC. The result shows that the DPs of extracted MCC are in the range (150–300) of currently available commercial MCC, and the DPs of extracted MCC higher than DPs of commercial MCC i.e.117.2 and MCC extracted from bacterial cellulose has DP250 [72]. The molecular weight (Mw) of extracted MCC from outer skin isolated CH was determined by multiplication of DP of extracted MCC with (Mw) of unit cellulose, 162 [73], then the (Mw) of extracted MCC is around 21,300 g/mol. With considering to the plenty of coffee husk waste material, large scale fabrication of MCC with adequate DP and (Mw) could be realized.
Figure 6: SEM micrograph of untreated (a), dewaxed (b), alkali-treated (c), and bleaching (d) sample of outer skin-isolated coffee husk fiber.
Figure 7: (a) TGA and (b) DTA curves of UT, DW, AT, and BL samples.
4. Conclusion

In this study, the systematic extraction of MCC from outer skin-isolated coffee husk was carried out using an environmentally-friendly extraction method. The extraction was conducted effectively by means of the cooperative chemical treatment method of dewaxing (toluene, ethanol), alkali (NaOH), bleaching (H₂SO₄), and chlorine and harsh acid free—MCC extraction (H₂O₂). FTIR results showed the cellulose structure which refers to the elimination of a significant quantity of hemicellulose and lignin throughout the chemical treatments. Extracting MCC by means of weak acid and chlorine-free treatment shows the extraction process to be environmentally kind with ensuing protection of harm chemicals. Therefore, this process can be further realized to other lignocellulosic materials as well. The XRD analysis had demonstrated the crystalline structure of the extracted microcrystalline cellulose, though TGA offered clarity in terms of stability in its thermal property. The morphological examination confirmed the rod-shape-like fibers of the separated cellulose, and additional homogeneity in the structure of microcrystalline cellulose was realized after the bleaching process. From the present investigation, it is possible to conclude that outer skin-isolated coffee husk is excellent source for the fabrication of MCC in abundance with excellent thermal property and great crystallinity index through this environmentally friendly and economically feasible procedure. These extracted MCCs could be reliable for replacing other plant materials for the production of crystalline nanomaterial and for different industrial applications such as hygroscopic agents in cosmetics, fillers, and binders in medicine formulations, reinforcing elements for the production of bio composite for building and automotive industries.

Data Availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

Nehemiah Mengistu: Investigation, writing original draft, Devendra Kumar Sinha: Writing, review and editing, Getenet Asrat: Supervision.

Table 5: Weight loss of the samples at each range.

<table>
<thead>
<tr>
<th>(%) of weight loss in each ranges</th>
<th>UT</th>
<th>DW</th>
<th>AT</th>
<th>BL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial range</td>
<td>7.7</td>
<td>6.1</td>
<td>3.5</td>
<td>3.3</td>
</tr>
<tr>
<td>Second range</td>
<td>3.4</td>
<td>4.0</td>
<td>3.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Third range</td>
<td>48.0</td>
<td>60.8</td>
<td>45.2</td>
<td>46.9</td>
</tr>
<tr>
<td>Final range</td>
<td>20.1</td>
<td>26.2</td>
<td>22.3</td>
<td>17.9</td>
</tr>
</tbody>
</table>

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References


[41] M. Alotaibi, B. A. Alshammari, N. Saba et al., “Characterization of natural fiber obtained from different parts of date

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