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Research article

Isolation of Fiber-Cellulose and Characterization from Oil Palm Frond for 3D and 4D Printing Materials Application

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Abstract: The oil palm frond (OPF), a primary biomass derived from agricultural waste in oil palm production, holds significant potential for evolving into cellulose fiber. Leveraging natural materials for cellulose extraction aligns with environmental sustainability. In this study, we focus on separating cellulose fibers from OPF biomass. The OPF is divided into its leaflet and frond-axial parts, undergoing a sequence of steps: dewaxing, alkaline treatment, delignification, hydrogen peroxide treatment, and final filtration. These steps assess both efficacy and cellulose fiber outputs. Notably, the axial and leaflet portions yield cellulose fibers, effective as an initial extraction step before progressing to nanoscale slicing. Quantitatively, extraction yields indicate that 14.13% and 19.52% of the 100 g leaflet and frond-axial portions can be harvested. SEM images confirm well-dispersed individual fibers. Additionally, GCMS results reveal slightly higher carbon dioxide gas in the palm leaflet sample than in the palm frond-axial sample after five days of water soaking. This procedure efficiently initializes OPF for cellulose extraction, positioning it as an initial ingredient for subsequent 3D/4D printing material production.

Keywords: Oil Palm Frond (OPF); Cellulose Fiber; Morphology

1. Introduction

Over 100 million palm trees thrive globally, with oil palm fronds (OPF) constituting a significant biomass—accounting for 47% of total oil palm waste [1,2]. Despite being considered waste, OPF is a valuable raw material due to its affordability, accessibility, and abundance [3,4]. Notably, in the realm of additive manufacturing (AM) and 3D/4D printing technologies [5-9], a transformative landscape has emerged for rapid production and plastic recycling in personalized consumer goods, automotive components, medical devices, aerospace applications, and energy-related products [10,11]. Leveraging its mechanical strength akin to steel, OPF cellulose stands out as an excellent reinforcement option for 3D/4D printing materials. Moreover, its biodegradability and renewable nature position natural fiber as a sustainable and ecologically acceptable bio-composite material for biomedical and industrial purposes [12].

Oil Palm Fronds (OPF) constitute agricultural waste generated during the regular pruning of palm trees, which occurs approximately every 20 days when fresh fruit bunches (FFB) are harvested. Only a small portion of OPF is repurposed for composting, while the majority is incinerated on-site [13].

Unfortunately, this practice contributes to air pollution and poses risks to human safety. Efficient waste management strategies are essential to address these challenges and mitigate environmental concerns. Oil Palm Fronds (OPF) possess a high fiber content due to their inherent spongy and fibrous nature. Consequently, they are well-suited for cellulose fiber synthesis. Within OPF, vascular bundles and parenchyma contain a mixture of extractives, cellulose, hemicellulose, and lignin. These other components must be selectively removed through enzymatic, chemical, mechanical, or chemo-mechanical treatments to obtain cellulose fibers. In essence, cellulose comprises a homopolymer of β-D-glucopyranosyl repeating units connected by 1,4-glycosidic bonds [14].

This work aims to extract cellulose fibers from oil palm frond (OPF) biomass. Using cost-effective and straightforward chemical extraction methods, we have divided the OPF into leaflet and frond-axial parts. Our investigation assesses the efficiency and cellulose fiber yields for leaflet and frond-axial portions.

2. Materials and Methodologies

2.1 Raw Materials and Sample Preparation

The oil palm frond (OPF) waste biomass has been obtained from a palm plantation in Suratthani Province, Thailand. Initially, we sorted out the leaflets from the frond. Subsequently, both components were shredded and dried under ambient conditions for 72 hours. Afterward, the raw materials were dried at room temperature for 24 hours and then cut into smaller pieces with an average length of 0.2 mm. Finally, the samples were oven-dried at 100±2°C.

2.2 Extraction of Cellulose Fiber

Raw cellulose fibers underwent dewaxed in Soxhlet equipment for 6 hours with 200 mL of 70% (v/v) ethyl alcohol, with a fiber-to-solvent ratio of 1:10 (g/L). After proper rinsing to eliminate alcohol residues, the dewaxed fibers are suspended in a 10% sodium hydroxide solution. The beaker, wrapped in aluminum foil, is autoclaved at 121°C and 1.5 bar pressure for an hour. These steps prepare the cellulose fibers for further use. Finally, the fibers retrieved from the supernatant were thoroughly rinsed with double-distilled water.

After autoclaving, the fibers underwent delignification by immersing them in a 1:1 (v/v) combination of 20% formic acid and 10% hydrogen peroxide. This mixture was preserved in a water bath at 85°C for 2 hours before being filtered to collect purified fibers. Initially, the fibers were cleaned with 10% formic acid and successive washings using double-distilled water. The resulting extracted cellulose fibers exhibited a pale yellow hue. Subsequently, a 10% hydrogen peroxide solution was applied to the cellulose fibers for 90 minutes at 60°C. The pH of the cellulose fiber suspension was adjusted using a 10% solution of sodium hydroxide. After filtration and repeated cleaning, the insoluble portion of cellulose was gathered, and the yield (w/w based on dry weight) was computed.

2.3 Characterizations

We examined the morphology of the extracted fibers and assessed the impact of sample treatments using scanning electron microscopy (SEM). Specifically, we employed the FEI Quanta 450 FEG SEM, operating at 5.0 kV high voltage under coverage pressures ranging from 9.4×10^{-4} to 1.1×10^{-3} Pa. Additionally, we verified carbon levels released during our procedures and from the samples using gas chromatography (GC) and mass spectrometry (MS). For this purpose, we utilized the GCMS-HSS instrument in our study.

3. Results and Discussion

3.1 Cellulose Fiber from Extraction Processes

To separate and remove dissolved polysaccharides and other constituents from water, we finely chopped and dried oil palm leaflets and frond samples in 2-L bottle containers. Each bottle was filled with water and allowed to soak for a week, softening the samples and facilitating the separation of polysaccharides and soluble substances. Subsequently, we filtered the samples using a sieve tool and rinsing with clean water and additional filtration 2–3 times. Figure 1 illustrates the two types of fibers obtained: those from the oil palm

frond sample exhibit a brunette color (Figure 1(a)), while the oil palm leaflet sample fibers appear green (Figure 1(b)). Finally, the dewaxing procedure yields the fibers shown in Figure 1(c).

Next, we examine the delignification results using two fiber samples from the previous procedure. These samples are placed in two-liter round-bottom bottles, each containing a 10% sodium hydroxide solution of 1,000 ml and a 30% hydrogen peroxide solution of 250 ml. We assemble the reflux apparatus kit and allow the solutions to boil for 3 hours, during which a significant amount of air bubbles may form, and vigorous boiling can occur. After boiling, we let the mixture cool down, then strain and rinse it with clean water multiple times. Finally, we squeeze the fibers until they are completely dry. The cellulose fibers produced through this delignification process exhibit a white color for the leaflet's fiber (see Figure 1(d)). However, the OPF fiber products from the frond part (Figure 1(c)) appear darker. This difference is attributed to the higher lignin content in the OPF frond, making alkali treatment more challenging than the leaflet portion. Consequently, the lignin in OPF frond fibers is more densely packed than in the leaflet fibers.

Figure 1. Samples of two types of fibers: (a) from palm fronds and (b) from palm leaflets after soaking for one week. The fibers resulting from the dewaxing procedure are shown in (c) and sourced from (a). Additionally, (d) illustrates the characteristics of palm fibers after bleaching and lignin removal from the source (b).

Figure 2. Characteristics of OPF fibers: (a) after undergoing the digestion process, and (b) and (c) after being squeezed until the leaflet and frond fibers are completely dry, respectively.

3.2 The Process of Digestion to be Small-Scaled Cellulose

Each sample type from the previous step was combined with 500 mL of a 20% acetic acid solution and 150 mL of a 30% hydrogen peroxide solution in a 2-L Erlenmeyer flask. The flask's mouth was sealed with a glass funnel. Both samples were immersed in a hot water bath at 85°C for 90 minutes, followed by cooling, filtration, and multiple rinses with clean water. Figure 2(a) illustrates the characteristics of OPF fibers after passing through this digestion process. Finally, the material was squeezed until the fibers were completely dry, as depicted in Figures 2(b) and 2(c) for the leaflet and frond. Subsequently, the cellulose fiber products were oven-dried at 110°C for 2–3 hours. The extraction results indicate that the yield percentage of cellulose from leaflet and frond oil palm biomasses (100 g each) is 14.13% (14.13 g) and 19.52% (19.52 g), respectively.

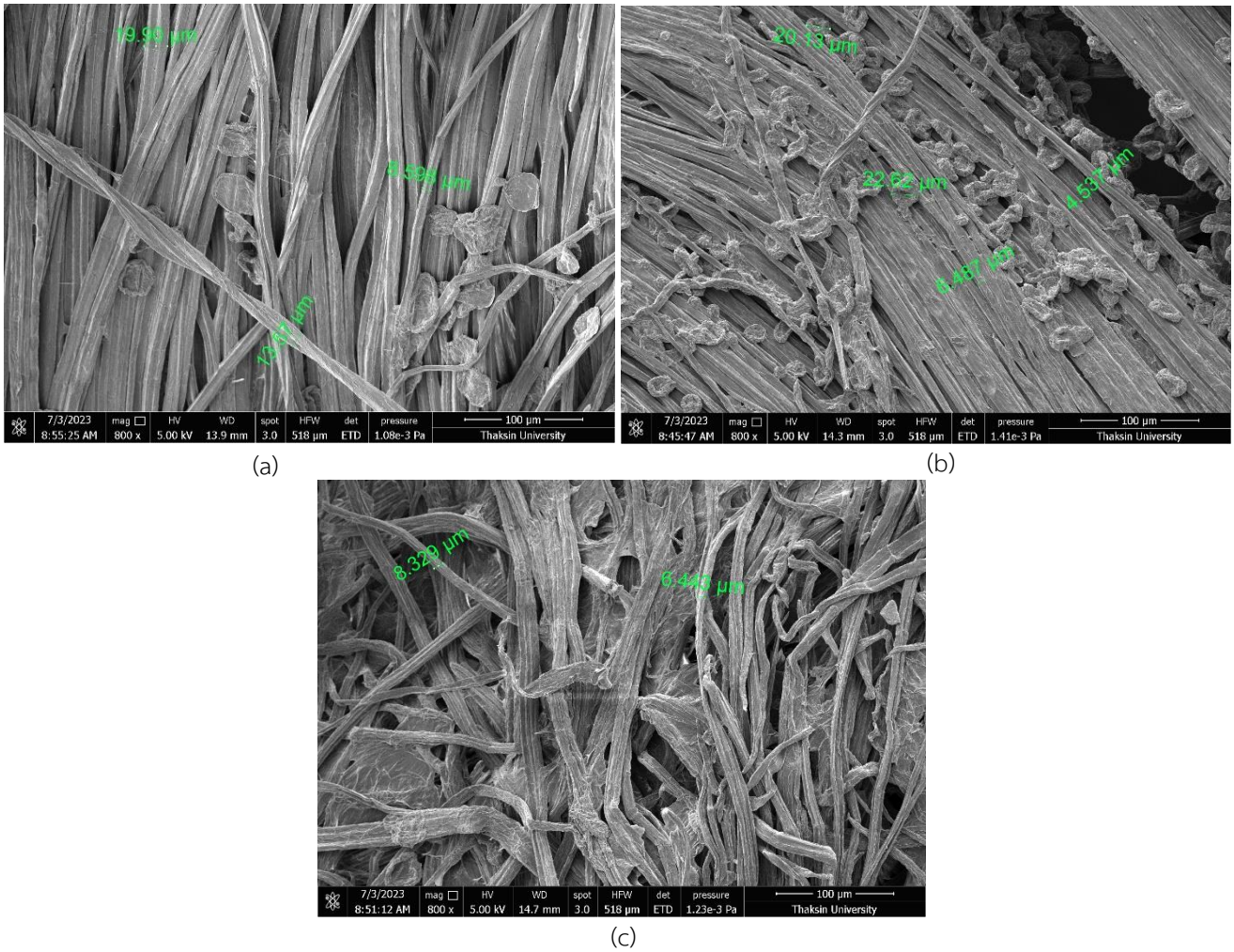
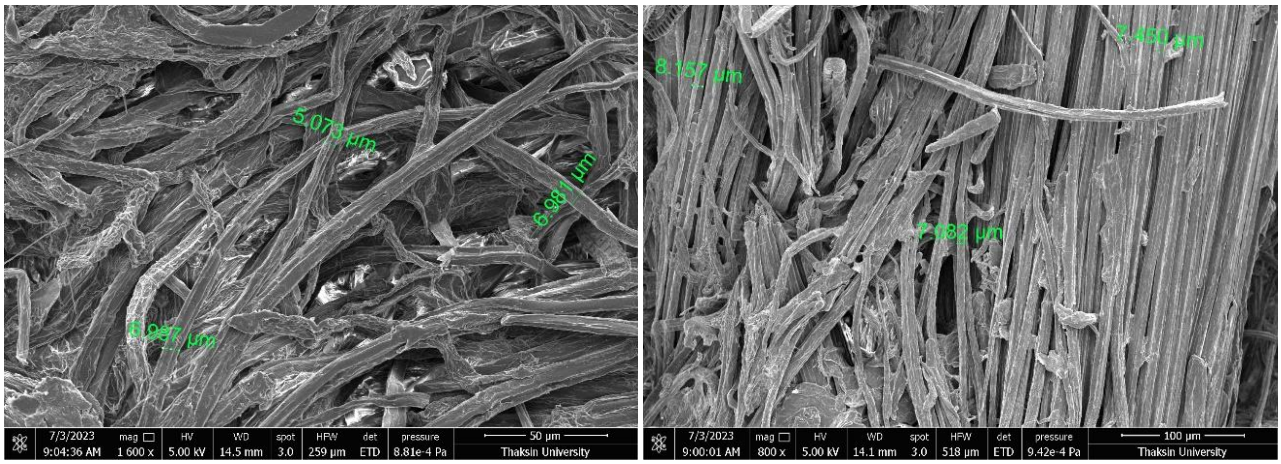


Figure 3. SEM micrographs of the raw frond-axial part of OPF reveal the following fiber thicknesses: (a) approximately ~8.6 – 19.9 µm, (b) approximately ~4.5 – 6.5 µm, and (c) approximately ~6.4 – 8.3 µm.

This result can be compared with the fronds and leaves, which yielded 2.90 g and 3.01 g, respectively, using the familiar extraction technique described by Mehanny et al. [2]. In contrast, the extraction yields from different methods applied to rice straws, corncobs, pineapple leaves, and pineapple peel biomass materials were 32.26%, 38.18%, 16.60%, and 9.05% (w/w), respectively [15]. Notably, our method demonstrates the effectiveness in extracting sufficient yields compared to other studies involving similar biomasses for cellulose production. The chosen procedures stand out due to their simplicity, reproducibility, and low operational costs. While it may perform well in cellulose yield, it exhibits attractive characteristics. Sufficient amounts of these cellulose products could potentially support material experiments for 3D/4D printing in subsequent stages.

3.3 Scanning Electron Microscopy (SEM)

The morphology of OPF fibers in leaflet and frond-axial samples has been examined using SEM. The treatment applied to the fibers significantly impacts their morphology. When extracting frond-axial fibers, various non-cellulosic and macromolecular substances—such as hemicelluloses, lignin, pectin, and wax—can be removed by exposing the fiber surface. SEM micrographs (see Figure 3) depict the extracted fibers from the frond-axial portion, which still exhibit an average size in the large micro-scale range (4.5–20 µm). In contrast, SEM images of the extracted cellulose fibers from the leaflet portion (see Figure 4) show an average size in the range of 5.1–8.2 µm.



(a) (b)

Figure 4. SEM micrographs of the raw leaflet part of OPF reveal the following fiber thicknesses: (a) approximately ~5.1 – 7.0 µm and (b) approximately ~7.1 – 8.2 µm.

Our extraction method demonstrates sufficient efficiency to serve as an initial step before further processing into nanoscale particles. These nanoscale particles can enhance reinforcement in mechanical strength, resulting in lighter, biodegradable, and more resilient materials suitable for 3D/4D printing. Such materials find applications in novel products and surface-modified assembly, enabling rapid tooling and scalable production. However, it's important to note that OPF fiber surfaces are coated with fatty materials, wax, impurities, and globular projections called tyloses. Despite this, the alkaline treatment effectively reduces roughness by eliminating contaminants from the fiber surface. Specifically, the interaction with sodium during treatment removes contaminants like wax and cuticles [16].

3.4 Gas Chromatography—Mass Spectrograph (GC-MS)

We employed this technique to verify whether our extraction process releases low levels of carbon. Since the waste generated during our procedure consists of organic compounds acting as non-toxic solvents, it is environmentally friendly. Simultaneously, this approach minimizes water contamination and allows for

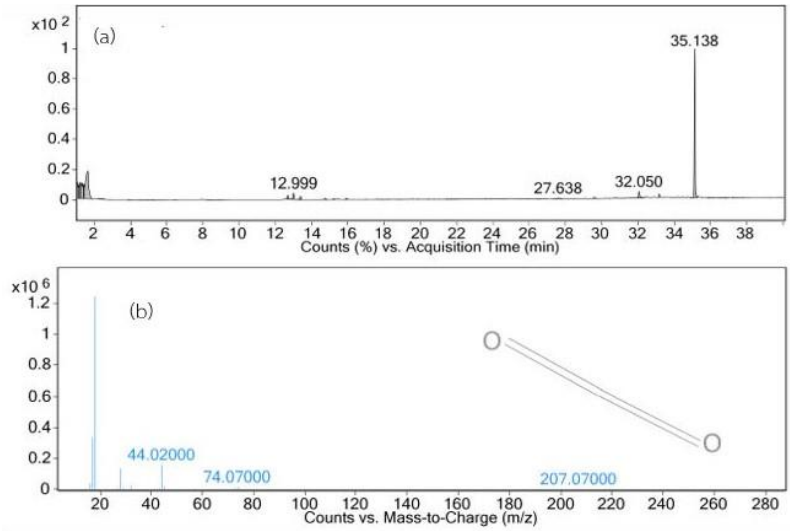


Figure 5. The chromatogram (a) and the spectrum (b) display the results of analyzing carbon dioxide (CO_2) released from frond-axial palm samples soaked in water for five days. Gas chromatography and mass spectrometry techniques were employed for this analysis.

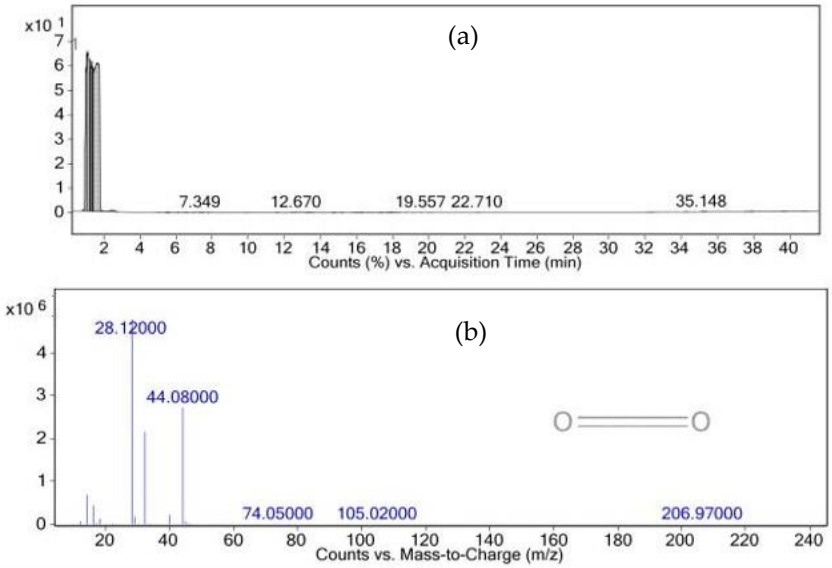


Figure 6. The chromatogram (a) and the spectrum (b) display the results of analyzing carbon dioxide (CO_2) released from leaflet palm samples soaked in water for five days. Gas chromatography and mass spectrometry techniques were employed for this analysis.

recycling. The analysis revealed a carbon dioxide peak at retention time (RT) equal to 35.138 minutes for the palm frond-axial crushed sample (see Figure 5(a)) and 35.148 minutes for the palm leaflet crushed sample (see Figure 6(a)). Additionally, we observed an ionized molecular species with a mass of 44.02000 m/z for the palm frond-axial crushed sample (see Figure 5(b)) and 44.08000 m/z for the palm leaflet crushed sample (see Figure 6(b)). Notably, this mass corresponds to the molecular weight of carbon dioxide gas (44.0100 m/z).

These findings indicate that soaking palm samples in water for five days produces trace carbon dioxide levels. Interestingly, the palm leaflet crushed sample exhibited slightly higher carbon dioxide gas production than the palm frond-axial crushed sample. Overall, both samples exhibit minimal carbon dioxide release.

4. Conclusions

The study revealed that using our procedure, cellulose fibers extracted from the frond-axial and leaflet parts of oil palm fronds (OPF) are efficient as an initial extraction step before further processing into nanoscale particles. Our methodology significantly improves the separated fibers compared to their original raw material. Specifically, the extraction yields for leaflet and frond-axial parts per 100 g of raw material are 14.13% and 19.52%, respectively. SEM images confirm that individual fibers are well-dispersed. Gas chromatography-mass spectrometry (GCMS) results indicate that the palm leaflet sample produces slightly more carbon dioxide than the palm frond-axial sample after soaking in water for five days. However, both samples exhibit minimal carbon dioxide release. Consequently, our method effectively enables OPF extraction for subsequent cellulose material synthesis.

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