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Extraction and Characterization of Cellulose Nanocrystals from Filter Paper by Sulfuric Acid Hydrolysis Method

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Abstract-Cellulose nanocrystals (CNCs) are nanomaterials derived from cellulose, which is the main component of plant cell walls. Nanocrystals are obtained through a process of mechanical or chemical treatment that breaks down cellulose fibres into smaller dimensions at the nanoscale. This study aims to investigate the hydrolysis of filter paper into cellulose nanocrystals (CNCs) using 60% (w/w) sulfuric acid (H_2SO_4) and identify the characteristics of the extracted CNCs. Filter papers are made from 100% premium pre-treated and high-quality cellulose fibres. The pulverized filter paper mixed the 60% (w/w) sulfuric acid in MLR 1:20 with strong agitation, and the mixture was heated at 50°C for 120 minutes. The mixture was diluted with cold distilled water in a 1:10 ratio to stop hydrolysis. The resulting mixture was centrifuged at 8000 rpm for 15 minutes to separate the CNCs. The precipitate was washed with distilled water using a dialysis membrane until the pH reached neutral. The properties of extracted CNCs have been discovered by Transmission Electron Microscopy (TEM) analysis, Fourier Transform Infrared (FTIR) analysis and X-ray Diffraction (XRD) analysis. The results of TEM analysis showed the needle-shaped morphology of CNCs and sizes ranging from 15–30 nm in diameter to 100–300 nm in length. The FTIR results revealed the functional groups present in the extracted CNCs. The XRD diffraction results showed the crystalline structure of the extracted CNCs. The results indicate that filter paper can be used as a source of cellulose for CNC extraction.

Keywords: Acid hydrolysis, Cellulose, Cellulose nanocrystals, Sulfuric acid, Filter paper

I. INTRODUCTION

The increasing worldwide environmental concerns have created an urgent need for novel and ecologically friendly materials. The historic dependence on non-renewable resources and environmentally hazardous products has accelerated a paradigm shift towards more sustainable alternatives. These innovative materials stress environmental friendliness throughout their entire existence from manufacture to use and disposal. (Samarawickrama et al., 2023; Pan, Li and Tao, 2020). Cellulose is an extraordinary biopolymer that forms the basis of plant cell walls and represents one of the most prevalent organic substances on Earth. Cellulose has a linear polymer structure consisting of repeating glucose units linked together by β-1,4-glycosidic bonds. These glucose chains form long, unbranched macromolecules, which can be several thousand glucose units long (Rahimi Kord Sofla et al., 2016; Dimas et al., 2020).

The linear structure and the regular arrangement of glucose molecules give cellulose remarkable properties. The most striking attribute is its sheer abundance, which is found in the cell walls of virtually all plants, providing structural support and rigidity. The versatility of this remarkable biopolymer extends to a wide array of applications from the production of paper and textiles to serving as a potential solution in biofuels, pharmaceuticals and sustainable packaging (Sacui et al., 2014; Chakrabarty and Teramoto, 2018). Cellulose's renewability and biodegradability underscore its importance in the ongoing pursuit of sustainable and environmentally friendly materials, embodying nature's ability to inspire innovation and meet the demands of a rapidly evolving world (Solihin et al., 2018).

The cellulose nanomaterials consist mainly of three basic structures of microfibrillated cellulose (MFC), cellulose nanocrystal (CNC) and bacterial nanocellulose (BNC). There have been changes in the extraction processes and appearance of these cellulose nanomaterials. Nanotechnology has emphasized cellulose nanocrystal (CNC) extraction from various renewable sources and its application in technical sectors (Samarawickrama et al., 2023; Egamberdiev and Norboyev, 2022). Cellulose nanocrystals (CNCs) are called cellulose nanowhiskers or nanocrystalline cellulose and have structural dimensions in nanoscale width and length. Cellulose nanocrystals (CNCs) possess unique nanoscale configurations that can adopt various morphologies of the rod of needle shapes. These CNCs are characterized by highly oriented molecules, strong crystallinity and a large surface area filled with numerous hydroxyl groups (Sheltami et al., 2012; Rashid and Dutta, 2020). The cellulose chains in the CNCs are packed into an ordered and compact structure, stabilized by both intramolecular and intermolecular hydrogen bonds. Furthermore, the structure of the CNCs exhibits a high level of reactivity, a hierarchical organization and multi-scale properties. CNCs have garnered significant attention for their physical and chemical properties, renewable nature, sustainability and utilization of composite materials (Owoyokun et al., 2021; Lee et al., 2019). The CNCs can be extracted using various acid hydrolysis methods, temperature-mediated oxidation, mechanical disintegration and enzyme-assisted hydrolysis. The most efficient method is acid hydrolysis and which involves immersing cellulose fibres in concentrated acid to hydrolyze the amorphous regions of the cellulose chains while keeping the crystalline parts intact (Razali et al., 2019; Bao et al., 2021).

Moreover, cellulose nanocrystals (CNCs) may be extracted utilizing a variety of powerful acids such as hydrobromic, sulfuric, phosphoric, hydrochloric and nitric. However, the hydrolysis process mainly employs sulfuric acid due to its ease of use and faster reaction time than other strong acids (Ramírez-Casillas et al., 2018; Eyley and Thielemans, 2014). The length of the cellulose crystals obtained through hydrolysis depends on the starting material's levelling-off degree of polymerization (LODP). Studies suggest that gentler hydrolysis conditions can eventually achieve the same LODP as the starting material. However, it may take longer reaction times resulting in lower material losses. (Chen et al., 2016; Bettaieb et al., 2015). The surface charge of the CNCs will vary depending on the choice of sulfuric acid that introduces sulfate half-ester groups to the CNC, while other acids can't form ester groups properly. The CNC extraction process can use sulfuric acid (H_2SO_4) concentrations such as 65%, 45% and 30% (w/w) of H_2SO_4 solution. The CNCs extracted using the acid hydrolysis method have a functionalized surface, remarkable crystallinity and colloidal solid stability in the water (Romruen et al., 2022; Agarwal et al., 2021). The CNCs are mainly extracted from cellulose-rich natural sources. These sources serve as the primary reservoirs for CNC extraction and play an essential role in manufacturing this potential nanomaterial. Plant-based fibres are the most commonly used sources for extracting CNCs. These fibres are derived from plants and serve as primary sources for producing CNCs. (Sai Prasanna and Mitra, 2020; Gadzama et al., 2020). These sources for CNC extraction underline the importance of sustainable and renewable materials in nanotechnology. The fantastic features of CNCs make them particularly appealing materials for various industrial applications. The CNCs are a potential alternative in multiple sectors due to their unique properties like great mechanical strength, large surface area and biodegradability (Rhim, Reddy and Luo, 2015).

Cellulose Nanocrystals find applications across diverse manufacturing sectors, including paints, coatings, adhesives, foods, cosmetics, transparent paper and pharmaceuticals (Afshari and Ziyadi, 2018; Kusmono and Affan, 2022). In the present study, we extracted CNCs from Filter Paper using a 60% (w/w) sulfuric acid hydrolysis technique. Filter papers are porous papers that have been specially created for a variety of filtration purposes. These papers are made with 100% premium quality cellulose fibres. Filter papers are frequently utilized in labs, industries and daily settings. Because they effectively separate particulates from liquids or gases (Kusmono et al., 2020; Beyene et al., 2018). The extracted CNC characterization was performed using analysis methods of Transmission electron microscopy (TEM), Energy Dispersive X-ray (EDX), Fourier transform infrared (FTIR) and X-ray diffraction (XRD).

II. METHODOLOGY

A. Collection of the materials and chemicals

The 98% Sulfuric acid (H_2SO_4, Sisco Research Laboratories Pvt. Ltd, India) and filter papers (No. 1 grade) and dialysis membrane tubing (Carolina Dialysis Tubing, USA – Molecular weight cut off 12,000-14,000 Dalton) used in this work were purchased from local chemical suppliers in Sri Lanka. The distillation water dispenser in the laboratory (laboratory water distiller- wall mounted type, Bionics Scientific Technologies, India) was used to prepare distilled water. All chemicals used in this study were analytical grade and could be used without additional purification.

B. Extraction process of CNCs

The 5 grams of filter papers were ground into small pieces and added dropwise to 60% H_2SO_4 (w/w) at room temperature in an MLR of 1:20 (W/V) with vigorous magnetic stirring. The mixture was then heated at 50°C for 120 minutes with strong agitation. After hydrolysis, the mixture was diluted with cold distilled water (4°C) in a 1:10 (v/v) ratio to stop hydrolysis. The resulting mixture was then repeatedly centrifuged at 8000 rpm for 15 minutes to separate the CNCs from the solution. The supernatant was discarded and the precipitate was washed with distilled water using a dialysis membrane until the pH reached neutral (pH 6.5-7.5). Finally, the washed precipitate was freeze-dried to obtain the CNCs (Kusmono et al., 2020; Sai Prasanna & Mitra, 2020).

C. Characterization processes of the extracted CNCs

1) TEM and EDX characterization process

A Transmission Electron Microscope (TEM, JEM-2100 Transmission Electron Microscope, Japan) was used to analyze the surface morphology and structure of extracted CNCs. The sample image analysis was performed at a 200kV voltage using magnifications. The elemental compositions of extracted CNCs were evaluated using an Energy Dispersive X-ray (EDX) analysis (EDAX element detector, USA) and linked with the TEM machine (Sai Prasanna & Mitra, 2020).

2) FTIR characterization process

A Fourier transform infrared (FTIR) spectrometer (FTIR Bruker Vertex 80, Bruker Corporation, USA) was used to identify chemical structures and functional groups in the extracted CNCs. The FTIR analysis of the extracted CNC sample was performed in FTIR – ATR type with transmission mode in the 600-4000 cm^{-1} range (Dimas et al., 2020).

3) XRD characterization process

An X-ray diffraction Spectrometer (Rigaku Ultima IV X-ray diffraction Spectrometer, UK) was used to analyze the crystal structure of extracted CNCs. The XRD powered at 40 Kv/40 mA equipped with a Copper (Cu) Kα radiation source (λ= 0.154 nm). The diffraction pattern was obtained at a scan speed of 2°/min with a diffraction angle of 2θ in the range of 10°-60° (Rashid and Dutta, 2020).

III. RESULTS AND DISCUSSION

A. TEM and EDX analyses

TEM and EDX analyses were used to determine details of the appearance and the elemental composition of the extracted CNCs. A TEM image (200 nm) of CNCs extracted using the 60% H_2SO_4 hydrolysis method is shown in Figure 01. It is possible to see needle-shaped CNC individual particles with diameters ranging from 10 to 30 nm and lengths ranging from 100 to 200 nm. The elemental compositions of the extracted CNCs were confirmed by EDX analysis. The EDX analysis is shown in Figure 02 and it showed distinctive peaks due to C, O and S. The EDX analysis discovered an atomic percentage of 5.61% for S, 46.12% for O and 48.27% for C (Kumar et al., 2020; Song et al., 2019).

B. FTIR analysis

The FTIR spectrum (Figure 03) was made on the extracted CNCs to find possible changes in the functional groups. According to Figure 03, the peak at 3321 cm^{-1} corresponded to the strong stretching vibration of the OH (Kumar et al., 2020). Also, the peaks 2282 cm^{-1} and 1642 cm^{-1} corresponded to the C-H bending and C=O bending vibration groups present in extracted CNCs (Draman, Daik and Mohd, 2016; Dimas et al., 2020). The peaks 1442 cm^{-1} and 1328 cm^{-1} corresponded to the C-O bending and the C-O-C stretching vibrations in extracted CNCs (Song et al., 2019; Kusmono et al., 2020).

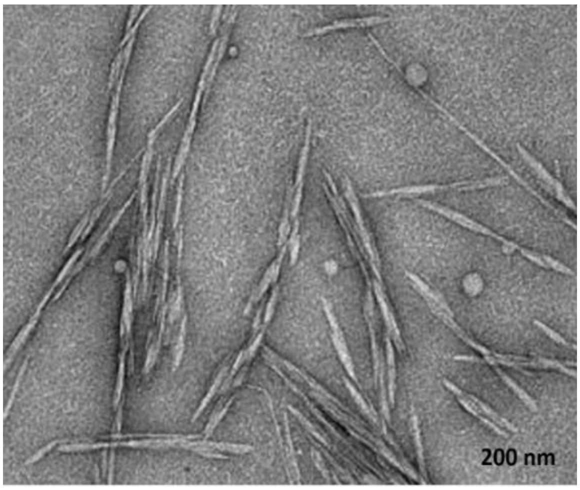

Figure 01: TEM image of extracted CNCs

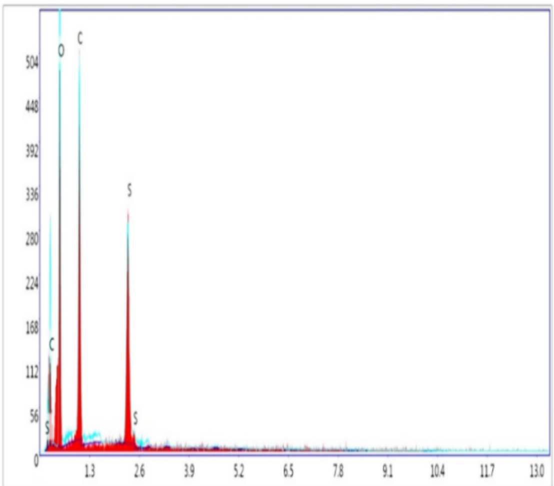

Figure 02: EDX spectrum of extracted CNCs

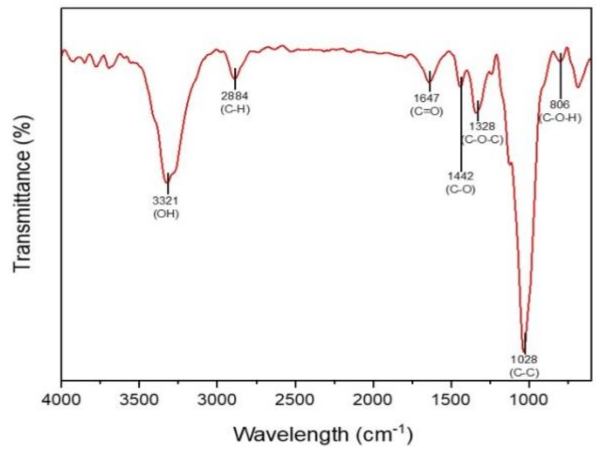

Figure 03: FTIR spectrum of extracted CNCs

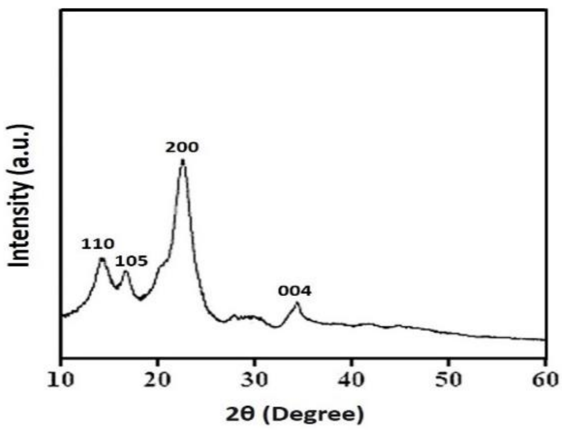

Figure 04: XRD spectrum of extracted CNCs

The peaks 1442 cm^{-1} and 1328 cm^{-1} corresponded to the C-O bending and the C-O-C stretching vibrations in extracted CNCs (Song et al., 2019; Kusmono et al., 2020). Moreover, the peak at 1028 cm^{-1} corresponded to the C-C strong stretching vibration in the extracted CNCs. The peak at 806 cm^{-1} corresponded to the bending vibrations in the extracted CNCs (Samarawickrama et al., 2021; Song et al., 2019). The FTIR analysis revealed that the filter paper was from correctly extracted CNCs.

C. XRD analysis

The XRD pattern of extracted CNCs is shown in Figure 04. The XRD peaks were detected at the 2Ɵ values of 14.8°, 16.5°, 22.7° and 35.1° corresponding to the crystal planes of (110), (110), (200) and (004) that indicate the formation of CNCs. The strong and distinct peaks indicated that the extracted CNCs are crystalline in nature and free of impurities. The results are almost similar to the results obtained for CNCs by other researchers (Di Giorgio et al., 2020; Alobaidi et al., 2015).

IV. CONCLUSION

The procedure for extracting cellulose nanocrystals (CNCs) from filter paper using 60% sulfuric acid was successful. The TEM analysis provided clear evidence of the formation of needle-shaped CNC particles with diameters ranging from 10-30 nm and lengths between 100-200 nm. The functional groups present in the extracted CNCs were identified by analyzing the FTIR spectrum. The XRD spectrum confirmed the distinctive crystalline cellulose point of the extracted CNCs. The potential of CNCs for various engineering and manufacturing applications is vast and promising.

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