

RESEARCH ARTICLE

Isolation of Cellulose Nanofibers From Sunflower Seed Husks via Formic Acid Hydrolysis

Ainur Battalova¹ | Kydyrmolla Akatan¹ | Sana Kabdrakhmanova² | Zhanar Ibraeva³ | Beisebekov Madiar⁴ | Shaimardan Esbol⁴ | Kantay Nurgamit¹ | Asylkan Dzhumanazarova⁵ | K. S. Joshy⁶ | Sabu Thomas⁶

¹S. Amanzholov East Kazakhstan University, Ust-Kamenogorsk, Kazakhstan | ²Satbayev University, Almaty, Kazakhstan | ³Abai Kazakh National Pedagogical University, Almaty, Kazakhstan | ⁴Scientific Center of Composite Materials, Almaty, Kazakhstan | ⁵Institute of Chemistry and Phytotechnology, National Academy of Sciences, Bishkek, Kyrgyzstan | ⁶School of Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam, India

Correspondence: Kydyrmolla Akatan (ahnur.hj@mail.ru) | Asylkan Dzhumanazarova (dzhumanazarova@gmail.com)

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ABSTRACT

Nanocellulose has garnered great interest among researchers because of its biodegradability, renewability, biocompatibility, high strength and versatile functionality. The present study focuses on the development of an eco-friendly, benign method to extract cellulose nanofibrils (CNFs) from waste sunflower husks (SFHs) using formic acid hydrolysis. Both CNFs and microcrystalline cellulose (MCC) were obtained in high yields from SFHs. The enhanced colloidal stability of CNFs was evident from the ζ potential values, which ranged from -11.8 to -19.6 mV. Varying yields of CNFs were obtained by differing reaction times, though all were found to be thermally stable. SEM and TEM were used for the morphological analysis. The removal of non-cellulose constituents was confirmed by FTIR spectroscopy. The enhancement of crystallinity upon treatment was examined using XRD analysis. The thermal stability of the cellulose extracted was checked via TGA. The present method of extraction of CNFs and MCC from waste SFHs using formic acid could open a new way of bulk production of nanocellulose fibers for the manufacture of green, value-added products in high-end fields, including electronics, agriculture and biomedicine, among others.

1 | Introduction

Large-scale consumption of mineral resources increases and complicates social, economic and environmental problems. In the last quarter of a century, scientists around the world have begun to focus on the efficient use of environmentally friendly resources [1, 2]. In this regard, lignocellulosic materials have become viable for the production of inexpensive, biocompatible and biodegradable cellulose fibers [3]. The distinctive physical and chemical characteristics, fibril morphology, biocompatibility and biodegradability of cellulose nanofibers (CNFs) make them suitable for a number of practical applications [4]. In particular, CNFs in nanocomposite form are widely used in the production of aerogels and insulating materials, as well as in the

control of polymer viscosity for the production of films, energy-storage materials and membranes for water purification [5, 6].

In recent studies, agricultural waste was found to be a potential source of raw materials for the production of cellulose micro- and nanofibers [7]. Researches used banana peels, corn waste, palm leaves, bamboo, pineapple waste, rice straw and apple pomace [8–12] to obtain CNFs at yields of 25%–52%, fiber diameters of 20–95 nm and lengths of 300 nm–20 μ m.

Currently, mineral acids and mechanical processing methods are often used in the production of CNFs. Mineral acids destroy the amorphous part of cellulose, resulting in cellulose nanocrystals with high crystallinity and rod-like structure. Further, mechanical

treatment breaks down cellulose microfibrils into nanosize particles, by way of cleavage of the fibrils. However, these methods require undesirable energy consumption and the usage of a large number of reagents, thus adding to the overall cost of production, from an economic and environmental point of view [12]. In addition, if the degree of crystallinity of cellulose decreases during mechanical processing, hydrolysis with mineral acids has been found to reduce the thermal stability of the final product [9, 13, 14].

The properties and applications of CNFs depend on the raw material and the method of production [15, 16]. Sunflowers are a leading crop in Kazakhstan, as they are farmed for oil extraction. Such farming has spread over millions of hectares, and accounts for around 5% of all agricultural land in the country. Some studies have established that up to 50% of microcrystalline cellulose (MCC) and 35% of cellulose nanocrystals are currently obtained from sunflower husks (SFHs) [17, 18]. Therefore, obtaining cellulose fibers by processing sunflower seed waste, which accumulates in large quantities, can solve the problem of handling the husks, which is urgent from an environmental and economic standpoint. In addition, the usage of organic acids in processing, which are less hazardous than mineral acids and do not require large amounts of water for neutralization, is consistent with environmental protection principles.

Therefore, the novelty of the present study is the extraction of cellulose fibers derived from SFHs through the use of formic acid hydrolysis. Hence, via the present extraction method, agricultural waste can be recycled in the high yield extraction of CNFs, which can then be utilized in biomedical and agricultural applications, among others. The results obtained are comparable with those observed with the extraction of CNFs using mineral acids, but with the immense advantage that any waste can be recycled for further usage.

2 | Experimental Section

2.1 | Materials

Hydrogen peroxide ($\geq 15\%$, H_2O_2), acetic acid ($\geq 55\%$, CH_3COOH), formic acid (FA) ($\geq 96\%$, HCOOH), and sulfuric acid (H_2SO_4) 98% were obtained from Sigma-Aldrich (Bangalore, India). All reagents were of analytical grade and were used without additional purification.

2.2 | Methods

2.2.1 | Preparation of Peroxyacetic Acid (PAA)

PAA was prepared based on the methodology set forth by Kydyrmolla et al. [17]. The resulting PAA was stored in freezer at $5^\circ\text{C} \pm 0.5^\circ\text{C}$. The concentration of the PAA obtained was 15%.

2.2.2 | Chemical Composition of Sunflower Seed Husks (SFHs)

The mineral composition of raw SFHs was determined using X-ray fluorescence (XRF) spectroscopy on an EDX3600H (Skyray

Instruments, China). In order to determine the amount of water-soluble hydrocarbons, $5 \pm 0.001\text{ g}$ of raw material was heated for 2 h, with continuous stirring in 50 mL of distilled water. After this process, the SFHs were filtered, dried at $80^\circ\text{C} \pm 2^\circ\text{C}$ for 5 h, and then the mass was measured on an LV 210-A analytical scale (Sartogsm, Russia). The quantity of hydrolyzable hydrocarbons in water was determined from the difference between the initial mass and the final mass.

In order to determine the ash content of SFHs, 5 g of MCC was burned in an 8.2/1100 L muffle furnace (SNOL, Lithuania) at $700^\circ\text{C} \pm 5^\circ\text{C}$ for 90 min. The mass of ash (SiO_2) was measured on an LV 210-A analytical scale (Sartogsm, Russian) until an average value was obtained. The ash content was determined from the difference between the initial mass and the final mass.

2.2.3 | Extraction of Microcrystalline Cellulose (MCC) From SFHs by Organosolvent Oxidation

MCC was obtained from SFHs via the procedure outlined by Battalova et al. [18]. 10 g of SFHs was weighed out, and SFH: PAA was prepared in a volume of 1:14 g/mL. MCC was produced under continuous intensive stirring by boiling the raw material at a temperature of $90^\circ\text{C} \pm 5^\circ\text{C}$ in a rotatory flask, and then allowed to cool in a condenser, resulting in delignification. The MCC obtained was cooled to a temperature of $25^\circ\text{C} \pm 2^\circ\text{C}$, filtered, and neutralized with distilled water. The neutralized MCC was dried at a temperature of $80^\circ\text{C} \pm 2^\circ\text{C}$ for 6 h until a constant weight was reached.

2.2.4 | Extraction of Cellulose Nanofibers (CNFs) From MCC

Varying weight ratios of MCC and FA, including 1/20, 1/30 and 1/40 g/mL, were tried in order to obtain the best yield of CNFs from 1 g of processed MCC, with an 88% mass fraction of formic acid. MCC was boiled for 6 h with intensive stirring at a temperature of $90^\circ\text{C} \pm 2^\circ\text{C}$ in a rotary flask equipped with a condenser. The CNFs obtained were neutralized with distilled water, while being kept at a temperature of $25^\circ\text{C} \pm 2^\circ\text{C}$ in an OPN-8 centrifuge (Dastan, Kyrgyzstan) running at a speed of 3000 rpm. The neutralized CNF suspension was ultrasonicated using a 3000F ultrasonic homogenizer (Scientz, China) at a power of 40 KHz for 15 min, and then lyophilized in an LGJ-12S freeze dryer (Beijing Songyuan Huaxing Biotechnology, China). Afterwards, the yield was calculated using the following equation:

$$\eta = (m_{\text{MCC}} - m_{\text{CNF}}) / m_{\text{MCC}} \times 100\% \quad (1)$$

Where, m_{MCC} is the mass (grams) of MCC extracted from SFHs; and, m_{CNF} is the mass (grams) of the CNFs obtained.

The dry mass of the CNFs was measured with an accuracy of 0.0001 g on an LV 210-A analytical balance (Sartogsm, Russia). The entire extraction process is shown in Figure 1.

2.2.5 | Preparation of CNF Film

The purified CNFs were dispersed in water, poured onto a flat plastic surface, and then dried at $25^\circ\text{C} \pm 2^\circ\text{C}$ for 24 h. A colorless

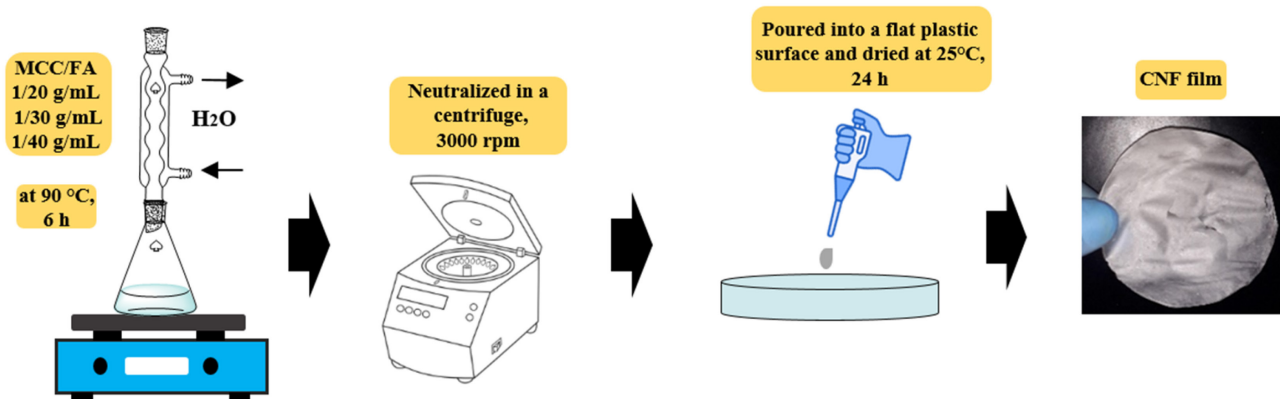


FIGURE 1 | Extraction of CNFs.

film, with a thickness of $21 \pm 1 \mu\text{m}$, formed (Figure 1). The samples were stored in an vacuum desiccator, so as to prevent absorption of moisture and carbon dioxide, then used for further characterization.

2.2.6 | Particle Size

The average particle size and ζ potential of the CNF solutions were determined using dynamic light scattering analysis on a Zetasizer NanoZS 90 (Malvern, UK). Aqueous suspensions of the CNFs (2wt%) were dispersed for approximately 10 min using a U-sonic UZTA-0.15/22-0 ultra sonic bath (Alena, Russia) at 30 KHz. Three samples of each of the above-mentioned selected ratios were analyzed in triplicate were analyzed.

2.2.7 | UV Analysis of CNF

The optical absorption spectra of the CNF aqueous solutions obtained were recorded on a PE-5400 UV spectrophotometer (Promecolab, Russia), with a scanning speed of 240 nm/min and a wavelength of 190–1000 nm.

2.2.8 | FTIR Analysis

FTIR analysis was performed on an FT-801 spectrometer (Simex, Russia), with a resolution of 1 cm^{-1} and a wavelength $4500\text{--}4700 \text{ cm}^{-1}$ in accordance with the standard method and using an accessory to measure attenuated total reflection (ATR) and specular-diffuse reflection (SDR), at a temperature of 25°C and the number of scans at 100.

2.2.9 | XRD Analysis

The crystallinity of CNF samples was examined using X-ray diffraction on an X'PertPRO diffractometer (Malvern Panalytical Empyrean, Netherlands), using monochromatized copper ($\text{CuK}\alpha$) radiation, with a scan range of 0.02° , and K-Alpha1 of $0.1542 \text{ \AA}$. The XRD operated at a measurement angle of $10^\circ\text{--}40^\circ$, a voltage of 40 kV, and a current of 30 mA.

The crystallinity index (CI) was measured utilizing the Segal method, and calculated by the following equation [14, 17]:

$$\text{CI} (\%) = (I_{200} - I_{\text{am}}) / I_{200} \times 100\% \quad (2)$$

Where, I_{200} is the 2θ value at the maximum intensity of the lattice diffraction peak between 21° and 23° ; and, I_{am} is the 2θ value at the minimum between peaks at 15° and 20° .

2.2.10 | SEM Analysis

The surface morphologies of the CNF film obtained were evaluated using a Quanta 200i 3D SEM (FEITM, Netherlands). Measurements were carried out in high vacuum mode using a secondary electron detector at an accelerating voltage of 15 kV. The surface of the CNF film was coated with gold nanoparticles to improve the transfer of electrons.

2.2.11 | Thermogravimetric Analysis

The changes in the characteristics of the CNF film samples due to heat were analyzed using TGA on a Lab Sysevo differential thermogravimetric analyzer (Setaram, France). The atmosphere was argon, the temperature range was $30^\circ\text{C} \pm 5^\circ\text{C}$ – $700^\circ\text{C} \pm 5^\circ\text{C}$, and the heating rate was $10^\circ\text{C}/\text{min} \pm 1^\circ\text{C}/\text{min}$. The final mass of the samples was approximately $25 \pm 2 \text{ mg}$.

3 | Results and Discussion

3.1 | Chemical Composition of SFH

Quantitative analysis of the composition of chemical components in the initial raw SFH sample was performed, the results of which can be found in Table 1.

3.2 | Characteristics of MCC Obtained From SFHs

The moisture content of the MCC was determined in accordance with Russian state standard (GOST) 16,932, β -cellulose content—GOST-6840, residual lignin content—GOST-11960,

and hemicellulose content—GOST-9002. The yield of MCC by the organosolvent oxidation method was equal to $45\% \pm 2\%$. The remaining contents of lignin and hemicellulose were determined to be $1.8\% \pm 0.1\%$ and $11.6\% \pm 0.5\%$, respectively, with β -Cellulose at $68\% \pm 3\%$ and humidity at $2.1\% \pm 0.1\%$.

3.3 | Extraction of CNFs From SFHs via Formic Acid Hydrolysis

CNF film obtained by hydrolysis of SFHs using 1/20 g/mL of FA is shown in Figure 2. First, SFHs were ground into a fine powder that contained all the cellular components, including lignin, cellulose and hemicellulose. The SFH powder was repeatedly processed in order to remove lignin and hemicellulose, thus the microcrystalline cellulose obtained could be homogenized and purified in order to extract CNFs.

The effect of formic acid hydrolysis under different reaction conditions and time intervals is outlined in Table 2. The weight of MCC was kept constant with varying percentages of FA, which resulted different yields of CNFs. The highest yield of CNFs, 71.09 ± 2 , was obtained at the lowest ratio of FA 1/20. The size

of the CNFs obtained in this ratio was found to be 4530 ± 50 nm in length and 38 ± 2 nm in width, with a stable ζ potential of -15.8 mV. The higher concentrations of FA, 1/30 and 1/40, reduced the percentage yield of CNFs to 49.18 ± 2 and 60.91 ± 2 , respectively, with respective particle lengths of 4017 ± 50 and 4017 nm, widths of 405 ± 15 and 548 ± 15 nm, and ζ potentials of -14.7 and -11.8 mV. Therefore, depending on the reaction conditions, the percentage yields, sizes and ζ potentials differed. The highest CNF yield, at more than 70%, was reached with the lowest ratio of FA, thus indicating that FA could be used as a very good hydrolysis agent for production of high yield and high purity cellulose nanofibers.

Liu et al. synthesized nanocellulose from bleached corncob residue under different hydrolysis conditions, using sulfuric acid, formic acid, (TEMPO)-mediated oxidation, and pulp refining [19]. Longer rod-like CNFs, with a highly crystalline nature, were obtained during FA hydrolysis. Whereas, in the case of sulfuric acid hydrolysis, less crystalline and shorter rod-like CNFs resulted. In (TEMPO)-mediated oxidation, the thinnest fibers were obtained. The pulp refining process resulted in long, flexible and highly networked CNFs.

Wu, Meiyang, et al. reported the effect of formic acid/choline chloride (F-DES) eutectic solvents in the efficient isolation of CNCs and CNFs from lignocellulose pretreatment, followed by ball milling [20]. They observed that the combination of pretreatment and fibrillation effectively resulted in a yield of CNCs plus CNFs at almost 95%. During this process, the dimensions of fiber aggregations also decreased.

Another recent study by Lin et al. provides an effective method for the production of nanocellulose, xylooligosaccharide and nanolignin from a three-step fractionation of corncob using formic acid-NaOH pretreatment or citric acid-NaOH pretreatment [21]. In this study, the nanocellulose that was obtained had high transparency and remarkably high swelling in water. The formic acid-NaOH pretreatment was observed to be more efficient compared to the citric acid-NaOH pretreatment in the production of nanocellulose.

3.4 | UV Spectroscopy

The transparency of the synthesized CNF solutions was compared using UV-visible spectra in a wavelength range of 300–900 nm (Figure 3). The CNF solution prepared using the least amount of FA was the most transparent, followed by those with 30 and 40 weight ratios, respectively. Transparency in the UV spectra is related to the structure and dimensions of the CNFs. The high transparency of CNF_{1/20} is due to its uniform nano-sized fibers.

The spectra of the three samples did not show the absorption of the electron transitions of the π - π^* (C=O) bond of the aromatic ring at a wavelength of 260–280 nm (Figure 3). This is explained by complete removal of lignin and hemicellulose [22], which can be clearly seen in the FTIR spectrum shown in Figure 4.

In a study by Zhao et al., between the UV regions 200–400 nm, the CNFs completely blocked the UV radiation, thus almost no

TABLE 1 | Chemical composition of the initial SFH sample.

Compounds	Quantity, %
Na	0.3
K	8.5
P	2.1
Ca	4.2
Si	2.51
N	1.4
C	52
O	35
Water soluble hydrocarbons	3
Ash content	2.5

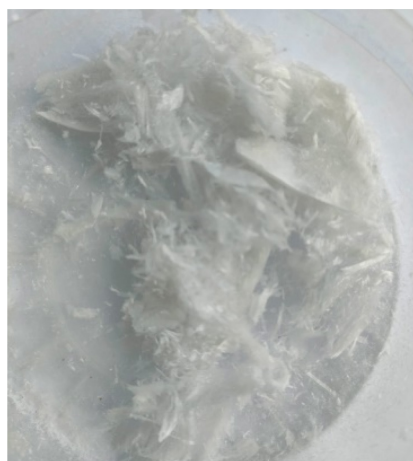
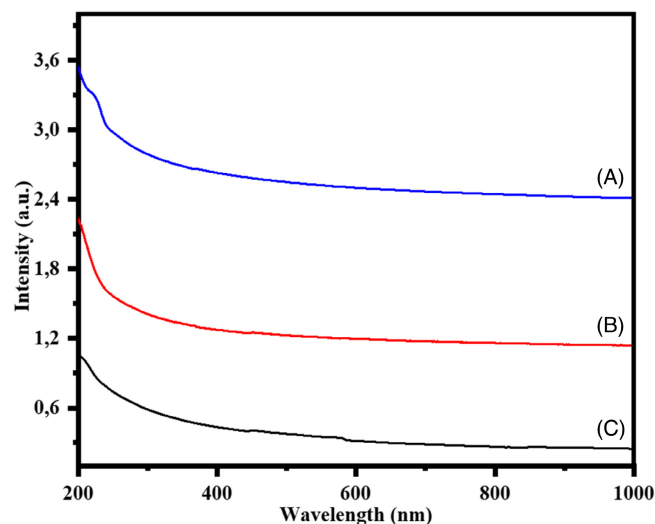
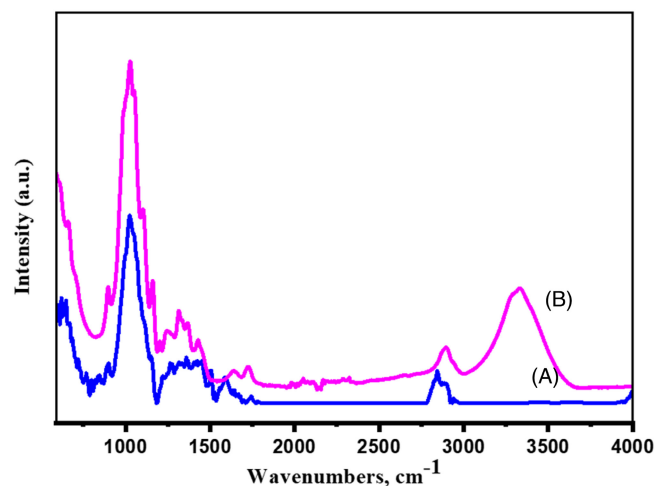


FIGURE 2 | CNF_{1/20} film sample obtained from MCC.

TABLE 2 | Effects of formic acid-based hydrolysis conditions on yield and properties of CNFs prepared from SFHs.

Samples	Reaction time, h	Yield, %	Crystallinity index (CI), (%)	Zeta-potential, mV	Average particle size, nm	
					Length	Width
MCC	—	45 ± 2	68 ± 4	—	2354 ± 150	205 ± 30
CNF _{1/20}	6	71.09 ± 2	74.9 ± 4	−15.8	4530 ± 50	38 ± 2
CNF _{1/30}	6	49.18 ± 2	70 ± 4	−14.7	4017 ± 50	405 ± 15
CNF _{1/40}	6	60.91 ± 2	71.5 ± 4	−11.8	5205 ± 50	548 ± 15

**FIGURE 3** | UV spectra of the: (A) CNF_{1/20}; (B) CNF_{1/30} and (C) CNF_{1/40}.**FIGURE 4** | FTIR spectrum of the (A) SFH and (B) MCC samples.

UV transmittance was observed [23]. This analysis completely agrees with the observations of the current study.

3.5 | FTIR Spectroscopy

The result of a comparative study of the chemical composition of raw SFHs and the MCCs obtained from them using IR spectroscopy

is shown in Figure 4. The SFH spectrum in Figure 4A corresponds to the structure of lignocellulosic materials. The C—O, C—O—C, C—H₂ bonds in the cellulose, lignin and hemicellulose molecules, respectively, are observed between 600 and 1600 cm^{−1}. The small peak at 1740–1760 cm^{−1} is characteristic of the signal from C=O bonds in the lignin and hemicellulose molecule, while the larger peak at 2890 cm^{−1} shows the C—H bond [24] in cellulose.

Figure 4B shows the resulting MCC spectrum. The absorption regions indicate the following: the peak at 655.9 cm^{−1} shows the C—OH bond out-of-plane bending; the small peak between 891 and 1153.6 cm^{−1} shows the C—O—C bond in the β-(1,4)-glycoside; the large peak between 1014.7 and 1153.6 cm^{−1} is due to the high-intensity signals of C—O and C—C bonds in the aromatic ring; the dip at 1053.3 cm^{−1} is the C—O bond in the pyranose ring, which is subject to chronic oscillations of the C bond; small peaks at 1253.9, 1307.9 and 1365.8 cm^{−1} indicate C—H groups; the small jump at 1412.1 cm^{−1} shows the C—H₂ group; a small peak at 1635.9 cm^{−1} is due to the O—H in the water molecule being sorbed from the air in the cellulose; and, the medium broad peak between 2889.8 and 3337.8 cm^{−1} appears because of CH and OH groups [17, 18].

A study by Nehra et al. reported results that compare well with the present study [25]. They derived nanocellulose from wheat straw. A comparison of the major peaks indicates similarities. A broad peak at 3345 cm^{−1} shows O—H stretching, which closely mirrors the result of 3337.8 cm^{−1} in present study. A CH stretching vibration was observed at 2930 cm^{−1}, whereas the present study indicated 2889.8 cm^{−1}, and C=O stretching was seen at 1650 cm^{−1}, though the present research measured it at 1635.9 cm^{−1}. Theivasanthi et al. also reported similar IR spectra for CNFs, in which study O—H stretching was observed at 3342.64 cm^{−1}, C—O stretching at 1050 to 1120 cm^{−1}, and a C=O carbonyl vibration was seen at 1728.22 cm^{−1} [26].

Figure 5 shows the relative FTIR spectra of CNF and the MCC samples obtained with different ratios of FA. A broad peak at 3332 cm^{−1} corresponds to the OH group of CNFs, and the smaller peak at 2898 cm^{−1} is representative of the CH stretching vibrations of cellulose [20]. The less intense peak at 1720 cm^{−1} is due to the C—O stretching vibrations of cellulose. Small peaks at 1315.5, 1333.4 and 1368.3 cm^{−1} are due to the C—H groups, while the slightly larger one at 1428.4 cm^{−1} is from the C—H₂ group [18]. C—O—C stretching vibrations are observed as a strong absorption band at 1028 cm^{−1}. The less intense peaks at 1360, 662 and 562 cm^{−1} correspond to CH rocking vibrations of the CNFs [21]. For different weight ratios of FA, there was no structural difference or functionality observed in the IR spectra, despite variations

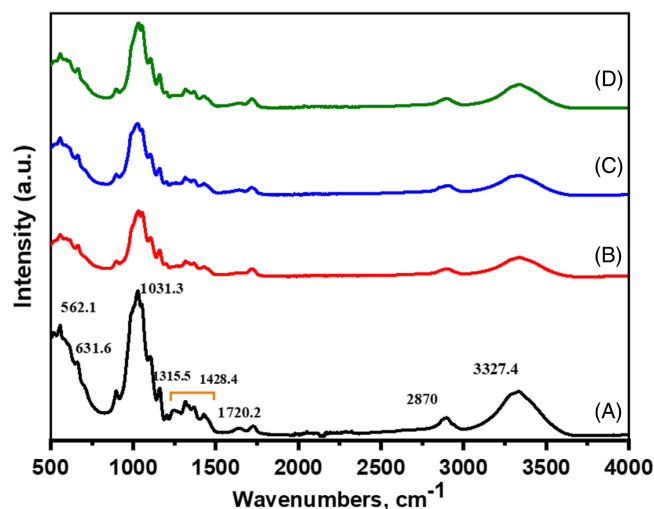


FIGURE 5 | FTIR spectra of: (A) MCC; (B) CNF_{1/20}; (C) CNF_{1/30} and (D) CNF_{1/40}.

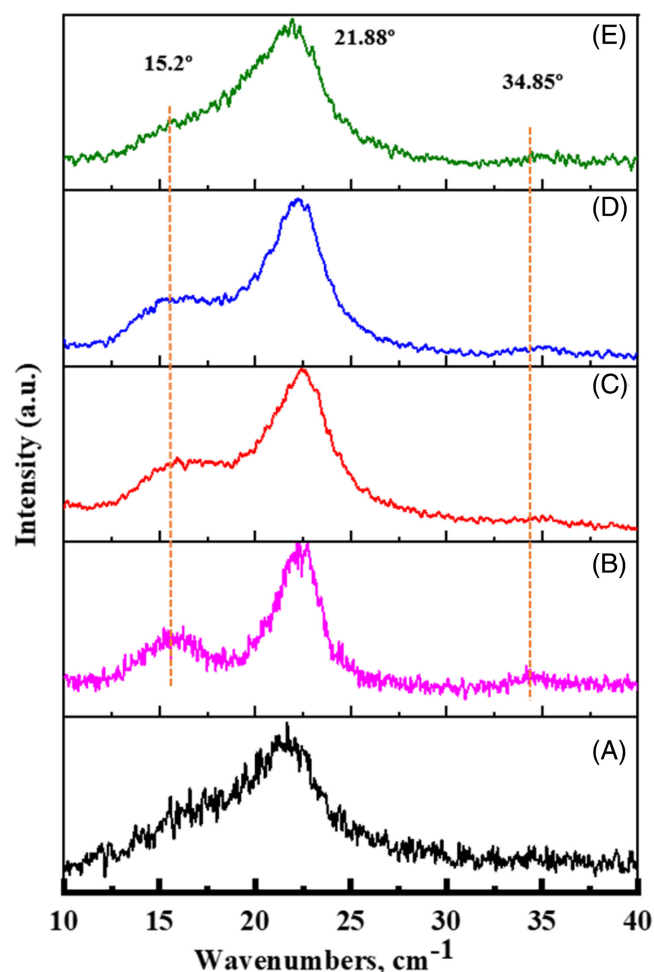


FIGURE 6 | XRD diffractions of: (A) SFH; (B) MCC; (C) CNF_{1/20} film; (D) CNF_{1/30} film and (E) CNF_{1/40} film.

in peak amplitudes. This confirms the structural stability of CNFs formed under different reaction conditions. Therefore, the weight ratio of FA has no great influence on the structural stability of CNFs, at least not within the limits used in the present study.

3.6 | X-Ray Diffraction

Figure 6 shows the comparative diffractograms of raw SFH and MCC samples, along with those of the three processed CNF variants, obtained at ratios of MCC and FA of 1/20, 30 and 1/40.

Figure 6A has a diffraction peak at 2θ 21.71° in the diffractogram of the raw SFH sample. This is a characteristic signal of amorphous carbon [27]. The invisibility of the diffraction peaks of crystalline cellulose in the raw material is due to covering of the surface with fibers that have wax-like substances, such as lignin, hemicellulose and pectin, among others, which is clearly visible in the SEM in Figure 7A,B.

The crystal structure of MCC is characteristic of a two-chain monoclinic unit cell (Figure 6B). In the MCC diffractogram, the typical peaks that are characteristic of microcrystalline cellulose are at 2θ 15.2° (1–10), 21.88° (200) and 34.85° (004), and are, thus, the counterparts to the peaks of the cellulose I β pattern [17]. Furthermore, the diffractograms of the CNF films correspond to the crystal structure of MCC.

The results obtained are comparable with those from FTIR and UV analysis. The weight percentage of a FA did not influence the crystal structure of the CNF films. The preparation of CNFs using FA hydrolysis dissolves most of the amorphous regions in cellulose, which results in the formation of CNFs with increased crystallinity [27]. The crystal index of MCC derived from SFHs is $68\% \pm 4\%$, whereas the crystal indices of CNFs derived from MCC are: $74.9\% \pm 4\%$ for CNF_{1/20}, $70\% \pm 4\%$ for CNF_{1/30} and $71.5\% \pm 4\%$ for CNF_{1/40} (Table 1).

A study by Nehra et al. reported that XRD analysis of nanocellulose exhibited peaks at three angles: 15.5° (1 1 0), though at 15.2° in the present study; 23° (200), at 21.88° in the present study; and, 34° (004), at 34.85° in the present study. Therefore, the results obtained from that research, which used a different source of nanocellulose, are very similar to the present study [25].

In a project by Savadekar et al., synthesis of nanocellulose was performed using short staple cotton, the XRD analysis of which revealed the highly crystalline nature of CNFs, with peaks at 14.7°, 16.3°, 22.6° and 34.7°, which are very similar results to those of the current research [28]. Another study, done by Theivasanthi et al., obtained CNFs from cotton fibers, and reported on their highly crystalline nature, with peaks obtained in similar regions as in the current project, with $2\theta = 14^\circ, 16^\circ, 22^\circ$ and 34° [29].

3.7 | SEM Analysis of CNF Films

Figure 7 shows the comparative surface morphology of CNFs obtained at different ratios of FA to MCC. Figure 7A shows the surface morphology of the raw SFH sample, indicating that the surfaces of the fibers are coated with smooth, wax-like materials, which are pectin, lignin, hemicellulose, and other hydrocarbon compounds. In Figure 7B, the surface morphology of MCC is seen to consist of ribbon-like fibrils with a diameter of about 7 μm . Delignification resulted in the amorphous waxy

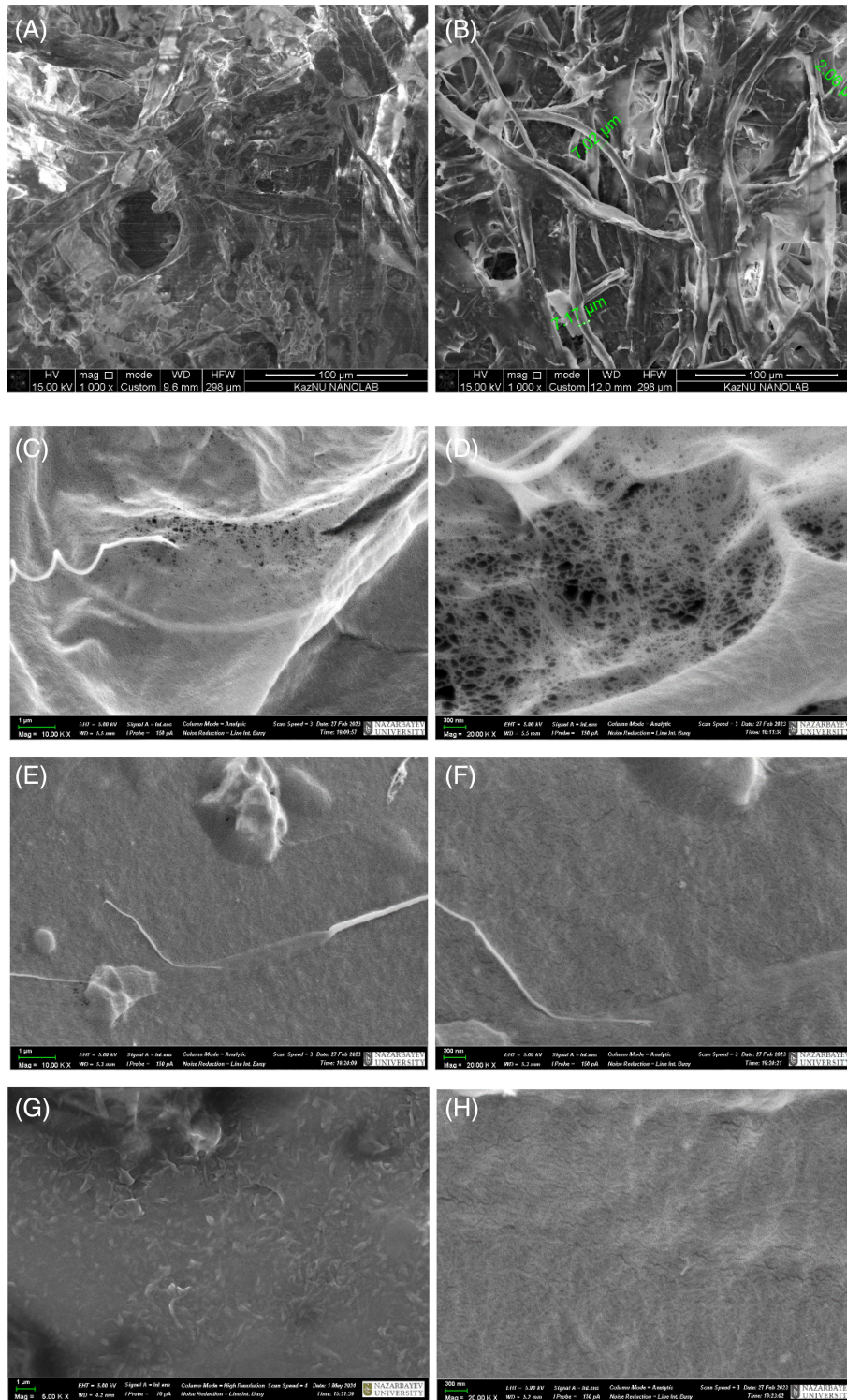


FIGURE 7 | SEM images of: (A) SFH; (B) MCC; (C, D) CNF_{1/20} film; (E, F) CNF_{1/30} film and (G, H) CNF_{1/40} film.

materials being hydrolyzed, along with the release of cellulose crystalline fibers.

The surface morphology of CNFs obtained at different FA ratios is shown in Figure 7C–H. In Figure 7C,D, the surface morphology of CNF_{1/20} is seen to consist of ribbon-like fibers with a diameter of about 35–40 nm. Figure 7E–H show the surface morphology of CNFs prepared at higher FA ratios,

CNF_{1/30} and CNF_{1/40}, in which no fibers or interconnected and fibrillated morphology are observed. The SEM results obtained show the accuracy of the average particle sizes outlined in Table 1.

A study by Nehra et al. reported nanocellulose obtained from wheat straw agricultural waste had a spherical morphology, instead of the ribbon-like structure seen in the present study [25].

Furthermore, Theivasanthi et al. reported CNFs obtained from cotton fiber had a rod shape morphology [26].

3.8 | TEM Analysis of CNF Films

The results of TEM analysis of the CNF films at different ratios of FA are shown in Figure 8. Cellulose nanofibers in CNF_{1/20} are clearly seen individually in Figure 8A. The average diameter of these CNFs was 38 ± 2 nm and they had lengths up to several microns. Figure 8B,C show that the average sizes of fibers obtained in CNF_{1/30} and CNF_{1/40} are larger in comparison to those in CNF_{1/20}, which was found to be consistent with the results in Table 1.

3.9 | Thermogravimetric Analysis

Thermogravimetric analysis was used to analyze the thermal stability of CNFs. Figure 9 shows the curves obtained for CNFs at different ratios of FA. The analysis was done for the weight loss of each sample during continuous heating up to 800°C. Initial weight loss of the samples was observed around 103°C and 108°C, regardless of the treatment conditions, and was due to the vaporization of condensed water molecules in the fibers.

As the temperature increased, sharper drops in weight were seen. Two steps in degradation occurred for all CNFs. In the first stage, the process of thermal decomposition took place in a temperature range of 223°C–580°C, at which all samples lost approximately 80% of their original mass. This degradation of cellulose was due to decomposition of the glycosidic bonds in the cellulose [17, 18].

The second stage took place at a temperature of around 615°C–700°C, and was due to the oxidation and subsequent breakdown of charred residues present in the CNFs. A small degradation observed after reaching 700°C is also attributable to the presence of such charred residues. From the thermogravimetric analysis, the CNF films were seen to be quite stable, regardless of FA content, though CNF_{1/20} was the most stable among the group, particularly at temperatures above 300°C. The difference in thermal stability among the films is quite small, as all of them present nearly identical onset of maximum thermal decomposition at the same temperatures. The determination of thermal stability and thermal properties of CNFs are significant from an application point of view, because most thermoplastics possess a processing temperature of 150°C–250°C. Therefore, the thermal stability of natural fibers above 300°C indicates their potential applications as a bionanocomposite.

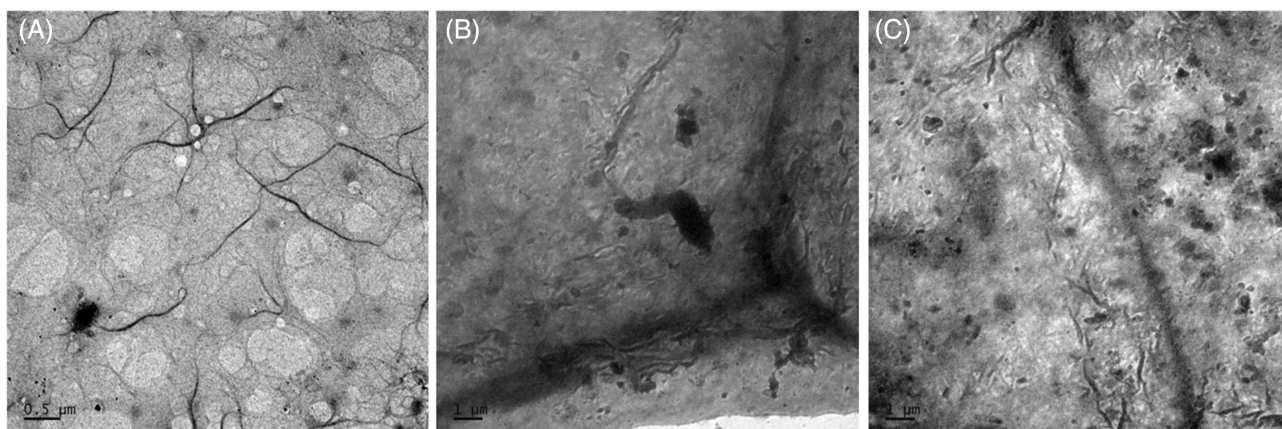


FIGURE 8 | TEM images of the CNF films: (A) CNF_{1/20}; (B) CNF_{1/30} and (C) CNF_{1/40}.

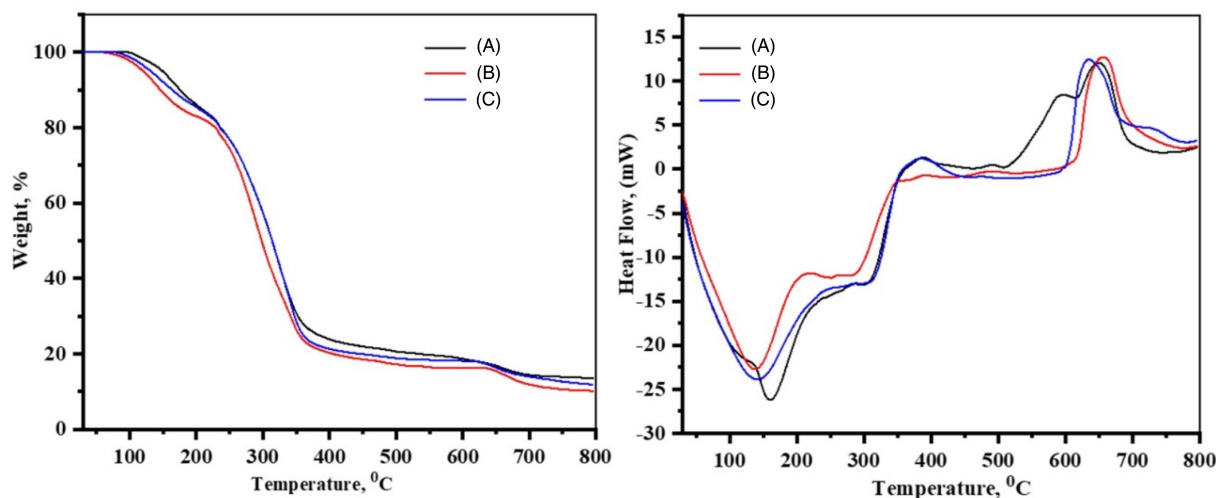


FIGURE 9 | TGA curves of the CNF films: (A) CNF_{1/20}; (B) CNF_{1/30} and (C) CNF_{1/40}.

4 | Conclusion

The present study successfully isolated CNFs from waste sunflower husks SFHs using environmentally benign FA hydrolysis. The extracted CNFs possessed an average diameter of ~ 10 nm and a length over $21.1\ \mu\text{m}$, thus establishing an aspect ratio higher than 1000. The fine CNFs retain excellent crystalline structure and remarkably high decomposition temperatures, even in excess of 300°C , thus indicating their compatibility in thermoplastic processing. Such an environmentally benign process for the isolation of CNFs from agricultural waste, allows for mass recycling, and could potentially result in value-added applications of this abundant resource, such as in the production of bionanocomposites for agriculture, biomedicine and flexible electronics. As stated in the introduction of this work, Kazakhstan already devotes around 5% of all agricultural land to the growth of sunflowers, which form a valuable resource for use both domestically and for export. Sunflower seed oil itself is an excellent value-added product, thus expansion of local processing not only provides an opportunity to export the oil itself, but also the chance to reclaim the husk waste that results. Should there be investment into thermoplastic technology utilizing SFHs for the production of polymers that apply the FA hydrolysis technology developed by this research team, the nation can more fully deepen its economy, and even broaden it if CNFs are then utilized for the domestic production of final goods for export.

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Conflicts of Interest

The authors declare no conflicts of interest.

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